

*Theo Mang, Kirsten Bobzin,
and Thorsten Bartels*

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Preface

The main areas of tribology – friction, wear, and lubrication – include all sciences and technologies relating to interacting surfaces in relative motion. Studies conducted during the 1980s and 1990s have defined the potential savings of tribology as a percentage of the GDP, with between 1.3% and 1.6% being gained by the correct application of actual tribological knowledge. Such benefits are mainly defined as energy savings and the protection of resources. Currently, an increasing number of modern aspects of life cycle assessment are taken in account, with the main targets being economic and environmental performance.

In this book, attention is focused on tribological activities in surface engineering, in lubricants and lubrication as well as in mechanical dynamic tribology and testing methods. The first of these areas includes wear mechanisms, tribological materials with basic principles of the materials sciences, coating developments, surface engineering as converting processes, physical and chemical vapor deposition, sol–gel deposition, electrochemical metal deposition, thermal spraying, deposition welding, brazing, and thermochemical surface treatments. In the area of lubrication, an introduction is provided to the base oils, to the rheology of lubricants, to lubricant additives and the main families of lubricants, to lubricants in the environment, and to the disposal and re-refining of lubricants. For the system analysis, the book presents details of simple tribological test machines and methods, as well as the tribology of the gearbox, transmission and transfer case, of internal combustion engines, and of hydraulic pumps and circuit design.

This book offers all researchers, graduate students and practicing engineers and chemists working in the field of tribology a quick, yet concise, introduction to this area of study.

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Abbreviations

μ-Comb	μ-Comb synchronizer testing machine
AAS	Atomic absorption spectrometry
ABS	Arc bond sputtering
AC	Alternating current
AC6	Reference elastomer (seal material)
ACEA	Association des Constructeurs Européens d'Automobiles (Association of the European Car Manufacturers)
AD	Ashless dispersant (additive)
AES	Auger electron spectroscopy
AFNOR	Association Francaise de Normation (French Association for Normalization)
AGG	Arbeitsgemeinschaft der Deutschen Galvanotechnik (German Society of Galvanotechnics)
AGMA	American Gear Manufacturers' Association (USA)
AIP	Arc ion plating
AO	Antioxidant, oxidation inhibitor
AP	Atmospheric pressure
API	American Petroleum Institute (USA)
APS	Atmospheric plasma spraying; air plasma spraying
ARKL	Axial-Rillenkugellager Adapter (axial thrust ball bearing adapter)
ASTM	American Society of Testing Materials (USA)
ASTME	American Society of Tool and Manufacturing Engineers (USA)
ATC	Additives Technical Committee (Technical Committee of Petroleum Additive Manufacturers in Europe)
ATF	Automatic transmission fluid
ATIEL	Association Technique de L'Industrie Européen des Lubrifiants (Technical Association of the European Lubricant Industry)
AU	Polyurethane-caoutchouc (polyesterurethane-caoutchouc)
AW	Antiwear agent (additive)
AWD	All-wheel drive
AWT	Almen–Wieland test

BAM	Bundesanstalt für Materialprüfung (German Federal Institute for Materials Research and Testing)
bcc	body-centered cubic
B-CVT	Belt-CVT
bf	Basic molecule
BMBF	Bundesministerium für Bildung und Forschung (German Federal Ministry of Research and Education)
BMWi	Bundesministerium für Wirtschaft (German Federal Ministry of Economics)
BOD	Biological oxygen demand
BW6100	Friction plate material (organic paper lamella)
CAFE	Californian Act for Fuel Emission (USA)
CBN	Cubic boron nitride
CC	Cemented carbide
CCEL	China Certification Committee for Environmental Labeling of Products
CCMC	Committee of Common Market Automobile Constructors (EU)
CCS	Cold-cranking simulator
CEC	Coordinating European Council (for the development of performance tests for lubricants and engine fuels)
CETOP	Comité Européen des Transmissions Oleohydrauliques et Pneumatiques - European Oil Hydraulic and Pneumatic (Committee)
CFMS	Closed-field magnetron sputtering
CFT 23	ZF CVT transmission series 23
CFT 30	ZF CVT transmission series 30
CGS	Cold gas spraying
CI	Corrosion inhibitor
COD	Chemical oxygen demand
CONCAWE	The oil companies' European association for environment, health and safety in refining and distribution
cph	Closed-packed hexagonal
CR	Chlorobutadiene-caoutchouc
CRC	Coordinating Research Council (US committee for engineering and interaction between automotive/other mobility equipment and petroleum products)
CSTCC	Continuously slipping torque converter clutch
CVD	Chemical vapor deposition
CVT	Continuously variable transmission
DBTT	Ductile-brittle transition temperature
DC	Direct current
DD	Detergent and dispersant (additive)
DGMK	Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle (German Scientific Society for Mineral Oil - Natural Gas and Coal)

DIN	Deutsches Institut für Normung (German Institute for Normalization)
DKA	Deutscher Koordinierungsausschuß im CEC (German Committee for Coordination in the CEC)
DLC	Diamond-like carbon
DMF	Dual-mass flywheel
DSC	Differential scanning calorimetry
EB-PVD	Electron beam–physical vapor deposition
EBT	Electron beam texturing
ECM	Engine control module
ECP	Environmental choice program (CDN)
ECTCC	Electronically controlled converter clutch
ECU	Engine control unit
EFI	Electronic fuel injector
EHD	Elastohydrodynamic (lubrication regime)
EHEDG	European Hygienic Equipment Design Group
ELGI	European Lubricating Grease Institute
EMCOR	EMCOR Group Inc. (manufacturer of mechanical and electrical construction, energy and facilities services)
EMF	Electromotive force
EN	European norm
EP	Extreme pressure (additive)
EPDM	Ethylene–propylenediene–caoutchouc
ESCA	Electron spectroscopy for chemical analysis (identical to XPS)
ESMA	Elektronenbeam-Microanalysis
EU	European Union
FAG	Schaeffler Technologies GmbH & Co. KG (former FAG Kugelfischer, Germany; manufacturer of bearings and units, seals, mechatronics, and lubrication systems)
FCC	Fuel catalytic cracker
fcc	face-centered cubic
FDA	Food and Drug Administration (USA)
FE8	Roller bearing test apparatus
FE9	Roller bearing test apparatus
FISST	Fuel injector shear-stability test
FM	Friction modifier
FPM	Fluoro-caoutchouc (also named FKM)
FS	Flame spraying
FTMS	Federal Test Methods Standardization (USA)
FVA	Forschungsvereinigung Antriebstechnik (German Research Association for Drive Technology)
FZG	Forschungsstelle für Zahnräder und Getriebebau (German Research Center for Toothed Wheel and Gearing Engineering in Garching)
FZG SSP180	FZG SSP180 synchronizer testing machine

GC	Gas chromatography
GDI	Gasoline direct injection (ICE)
GFKT	Graufle ckentragungsfähigkeitskurzte st (micro-pitting short test)
GfT	Gesellschaft für Tribologie (German Society of Tribology)
GL-4	API GL-4 performance standard of gear oil (application: manual transmission and differential)
GL-5	API GL-5 performance standard of gear oil (application: axel oil)
GNI	Gross National Income
H	Hydraulic fluids type H (also HH), classified in: ISO 6743/4, ISO 11 158 and DIN 51 524
HC	Hydrocracked base oil
HCCI	Homogeneous charge compression ignition
H-CVT	Hydraulic-CVT
HD	Heavy-duty engine oil application (commercial vehicles and trucks)
HDD	Heavy-duty diesel
HDDO	Heavy-duty diesel oil
HEES	Synthetic ester types (non-water-soluble), environmentally friendly, rapidly biodegradable hydraulic fluid according to ISO 15 380 and ISO 6743/4
HEPG	Polyglycol types (water-soluble), environmentally friendly, rapidly biodegradable hydraulic fluid according to ISO 15 380 and ISO 6743/4
HETG	Triglyceride (non-water-soluble, vegetable oil types), environmentally friendly, rapidly biodegradable hydraulic fluid according to ISO 15 380 and ISO 6743/4
HF	High-frequency
HF1	ISO VG 46 monograde fluid (model test fluid 1)
HF2	ISO VG 46 multigrade fluid (model test fluid 2)
HFA	Fire-resistant hydraulic fluid classified according to ISO 6743/4 and DIN 51502 (fluid concentration of HF AE emulsions or synthetic HF AS solutions is between 1% and 5% in water)
HFB	Fire-resistant hydraulic fluid classified according to ISO 6743/4 and DIN 51502 (water-in-oil emulsions with a (flammable) mineral oil content of about 60% mass)
HFC	Fire-resistant hydraulic fluid classified according to ISO 6743/4 and DIN 51502 (mixture of min. 35–50% fully demineralized water and polyglycols – monomers or polymers – as thickeners)
HFD	Fire-resistant hydraulic fluid classified according to ISO 6743/4 and DIN 51502 (synthetic and water-free)
HFRR	High-frequency reciprocating rig
HIP	High-ionization pulsing
HIS	High-ionization sputtering
HL	Hydraulic fluids type HL, classified in: ISO 6743/4, ISO 11 158 and DIN 51 524 Part 1

HLB	Hydrophilic–lyophilic balance
HLP	Hydraulic fluids type HL, classified in: ISO 6743/4, ISO 11 158 and DIN 51 524 Part 2
HLPD	HLP hydraulic fluid plus DD additives, which disperse, suspend and emulsify water, dirt, aging products, and contaminants
HNBR	Hydro-treated acrylonitrile–butadiene–caoutchouc
HPDSC	High-pressure differential scanning calorimetry
HPLC	High-pressure liquid chromatography
HPPMS	High-power pulse magnetron sputtering
HPPS	High-power plasma spraying
HRC	Rockwell hardness (cone measurand)
HSS	High-speed steel
HT	High-temperature
HTBT	High-temperature bearing tester
HT-CVD	High-temperature chemical vapor deposition
HTHS	High-temperature–high-shear fluid measurement
HVAF	High-velocity air-fuel spraying
HVI	High-viscosity index
HVOF	High-velocity oxy-fuel spraying
IAE	Institute of Automotive Engineers
IARC	International Agency for Research on Cancer
IB	Ion-beam sputtering
IBAD	Ion-beam-assisted deposition
ICPS	Inductive coupled radiofrequency plasma spraying
ICE	Internal combustion engine
ICP	Inductively coupled plasma atomic emission
IFP	Institute Française de Petrole (French Institute of Petroleum)
ILMA	Independent Lubricant Manufacturers' Association (USA)
ILSAC	International Lubricant Standardization and Approval Committee
IP	Institute of Petroleum (UK)
IPS	Inert gas plasma spraying
IRM2	Special hydraulic test fluid no. 2, specified by ASTM
IRM3	Special hydraulic test fluid no. 3, specified by ASTM
ISO	International Standard Organization
ISO VG	ISO normed viscosity grade (classification at 40 °C)
JASO	Japanese Automotive Standards Organization
JEA	Japanese Environmental Association
JIS	Japanese Industrial Standard
KpKs	CVT variator efficiency characteristic number
kV	Kinematic viscosity
LDF	Long-drain field test
LIMS	Laboratory information and management system
LOW	CVT variator gear “start-up”
LP	Low-pressure

LPG	Liquid petroleum gas (autogas)
LPPS	Low-pressure plasma spraying
LS	Load stage at the FZG test rig
LT-CVD	Low-temperature chemical vapor deposition
LUK	LuK GmbH & Co. KG (German component supplier for the automotive industry)
LVD	Low-voltage arc discharge
LVFA	Low-velocity friction apparatus
LVI	Low-viscosity index
MAK	Maximale Arbeitsplatzkonzentration (maximum workplace concentration)
MD	Metal deactivator additive
MF	Medium-frequency
MIL	Military Standard (USA)
MLDW	Mobile-lube dewaxing
MMC	Metal matrix composite
MO-CVD	Metal organic chemical vapor deposition
MPR	Micro-pitting test rig
MPS	Micro-plasma spraying
MQL	Minimum-quantity lubrication
MRV	Mini-rotary viscosimeter
MS	Mass spectroscopy
MS	Magnetron sputtering
MSDW	Mobile-selective dewaxing
MSIP	Magnetron sputter ion plating
MT	Metric tonne
MT-CVD	Middle-temperature chemical vapor deposition
MTF	Manual transmission fluid
MTM	Mini-traction machine (manufactured by PCS Instruments Inc., London)
MWM	MWM GmbH (German manufacturer of ICE for energy production)
n-dm	Bearing classification number for bearing kinematic, combining speed and geometry
NAS	National Academy of Sciences, testing chemicals on humans
NBR1	Reference elastomer (seal material)
N-D-M	Analysis using refractive index n, density d and molecular weight m
NFPA	National Fluid Power Association (USA)
NLGI	National Lubricating Grease Institute (USA)
NMMA	American National Marine Manufacturers Association
NMR	Nuclear magnetic resonance
O&K	Orenstein & Koppel OHG (German manufacturer of mobile hydraulic equipment, such as shovels and excavators)
OD	CVT variator gear “overdrive”

ODS	Oxide dispersion-strengthened
OECD	Organization for Economic Cooperation and Development (EU)
OEM	Original equipment manufacturer
PACVD	Plasma-assisted chemical vapor deposition
PAO	Poly-alphaolefin base oil
PC	Passenger car application
PCB	Printed circuit board
PCD	Polycrystalline diamond
PCMO	Passenger car motor oil
PCS	PCS Instruments Inc. (GB manufacturer of test machines for tribological applications)
PD	Pumpe-Düse Kraftstoffeinspritzung (pump-nozzle fuel injection)
PECVD	Plasma-enhanced chemical vapor deposition
PEO	Plasma electrolytic oxidation
PEP	Passive extreme pressure
PLD	Pulsed-laser deposition
PPD	Pour point depressant
PSZ	Partially stabilized zirconia
PTFE	Polytetrafluorethylene (Teflon)
PTWA	Plasma transfer wire arc spraying
PVD	Physical vapor deposition
RAL UZ	Reichsausschuß für Lieferbedingungen und Gütesicherung, Umweltzeichen (German Imperial Committee for Quality Control and Labeling, Environmental Symbol)
RNT	Radionuclide technique
RPS	Reactive plasma spraying
RVT	Reichert-Verschleiß Test (Reichert wear test)
SAE	Society of Automotive Engineers (USA)
SBR	Styrene-butadiene-caoutchouc
SCDSC	Sealed capsule differential scanning calorimetry
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
SHPD	Super high-performance diesel
SKF	SKF Group (Swedish manufacturer of bearings and units, seals, mechatronics, and lubrication systems)
SLPM	Standard liters per minute
SMF	Single-mass flywheel
SNR	SNR Roulements (French bearing manufacturer)
SPS	Shrouded plasma spraying
SRE	Standard reference elastomer
SRV	Schwing-Reibverschleiß Gerät (translatorisches Oszillations-Prüfgerät) (Translatory oscillation apparatus)
STLE	Society of Tribologists and Lubrication Engineers (USA)
STOU	Super tractor oil universal

SUS	Saybolt universal seconds
TAN	Total acid number
TBC	Thermal barrier coating
TBN	Total base number
T-CVT	Traction-drive CVT
TDA	Thermal deasphalting
TDI	Turbo-diesel direct injection (ICE)
TEI	Thailand Environment Institute
TEOS	Tetraethylorthosilicate
TEWL	Transepidermal water loss
TG	Thermogravimetry
TGL	Technische Normen, Gütevorschriften und Lieferbedingungen (former DDR calculation and test standards)
TGO	Thermally growth oxide
TLP	Transient-liquid-phase
TLV	Threshold limit value
TOP	CVT variator gear “highway”
TOST	Turbine oil oxidation stability test
TRIP	Transformation induced plasticity
TRK	Technische Richtkonzentration (German technical guideline concentration)
TSSI	Temporary shear stability index
UEIL	Union Européens des Indépendents en Lubrifiants (European Union of Independent Lubricant Manufacturers)
UHPD	Ultra high-performance diesel (ICE)
UHV	Ultra-high vacuum
UHVI	Ultra-high viscosity index
UNITI	Bundesverband Mittelständischer Mineralöluntemehtmen (Germany) (Federal Association of the Middle-Class Oil Companies)
UPS	Under-water plasma spraying
USDA	United States Department for Agriculture
UTTO	Universal tractor transmission oil
VAMIL	Regeling Willekeurig Afschrijving Milieu-Investeringen (NL) (regulation of discretion deductions for investments into the environment)
VCI	Vapor-phase (volatile) corrosion inhibitor
VDA	Verband der Automobilindustrie (German automobile industry association)
VDEh	Verein Deutscher Eisenhüttenleute (Technical Association for Iron Metallurgy)
VDI	Verein Deutscher Ingenieure (German society of mechanical engineers)
VDMA	Verband Deutscher Maschinen- und Anlagenbau (German engineering federation)

VDS	Volvo oil-drain specification
VDT	Van Doorne Transmission (Belgium) (manufacturer of belt/pulleys for CVT applications)
VGB	Technische Vereinigung der Großkraftwerksbetreiber (Germany) (Technical Association of Large Power Plant Operators)
VGO	Vacuum gas oil
VHVI	Very high-viscosity index
VI	Viscosity index
VIE	Viscosity index extended
VII	Viscosity index improver (additive)
VKA	Vier-Kugel-Apparat (Four-Ball apparatus)
VKIS	Verbraucherkreis Industrieschmierstoffe (association of industrial lubricant consumers)
VOC	Volatile organic compounds
Vp	Viscosity–pressure behavior
VPI	Vapor-phase inhibitor
VPS	Vacuum plasma spraying
VSFT	Variable-speed friction tester
VT	Viscosity–temperature behavior
VTC	Viscosity–temperature coefficient
VW	Volkswagen (OEM; German car manufacturer)
VW-PV	Volkswagen Prüfvorschrift (internal test procedure approved by Volkswagen)
WGK	Wassergefährdungsklasse (Water-hazardous class, water-pollution class)
XHVI	Extra high-viscosity index
XPS	X-ray photoelectron spectroscopy (identical to ESCA)
XRF	X-ray fluorescence spectrometry
YPSZ	Yttria partially stabilized zirconia
ZAF	Zinc and ash-free
ZF	ZF Friedrichshafen AG (OEM; automotive supplier for driveline and chassis technology)

1

Introduction

1.1

The Term Tribology

The term tribology is derived from the Greek *tribos*, which means “rubbing,” and includes all of the sciences and technologies of interacting surfaces in relative motion. The main areas of research and application are friction, wear, and lubrication. The term was first used 1966 in the Jost Report, a study conducted in the United Kingdom which investigated the amount money lost annually due to friction and wear. Tribology is multidisciplinary in nature, and includes mechanical engineering (especially machine elements as journal and roller bearings and gears), materials science, with research into wear resistance, surface technology with surface topography analysis and coatings, and the chemistry of lubricants and additives. The relatively younger disciplines of tribology are: (i) bio-tribology, which includes (among other topics) wear, friction, and the lubrication of total joint replacement; and (ii) nanotribology, where friction and wear are studied on the micro- and nanoscales.

A wide variety of professional bodies or societies have been formed during the second half of the twentieth century, with many institutions of mechanical engineering having incorporated divisions of tribology. Likewise, societies of lubricating engineers or societies of tribology have organized professional meetings on an international scale. For example, in Germany there exists a tribology society – the Gesellschaft für Tribologie (GfT) – which has seven regional subcommittees, and conducts not only an annual international meetings but also numerous regional meetings with professional presentations. The international tribology meetings of the Technische Akademie Esslingen (TAE) have, for many decades, been organized in Germany by W. Bartz as another forum for tribological exchange, and are among the most heavily attended worldwide.

1.2

Importance of Tribology

Over the years, the governments of the most industrialized countries have developed extensive strategies to reduce energy waste. In 1966, the so-called Jost Report [Lubrication (Tribology) – Education and Research; published by Her Majesty's Stationery Office, London, 1966] demonstrated the enormous waste that occurred due to the misrecognition of tribology in the UK. Likewise, in 1977, an American government-financed report suggested that US\$16.25 billion could be saved by the correct use of tribological knowledge. Similar studies have also been conducted in other countries; for example, W. Bartz carried out a study which related to Germany between 1979 and 1983 [1] while in 1990 P. Jost defined the potential savings as a percentage of the GDP, to determine calculated values of 1.3–1.6%. The results obtained for various countries are listed in Table 1.1, taking 1.6% as a basis for the year 2008 (a conservative estimate when taking actual energy prices into account). In this case, the GDP was based on the CIA, List of Fact Book (2008).

Notably, whilst the study of W. Bartz takes into account only lubricated contacts, it categorizes the possibilities of saving into: (i) *primary savings*, due to reductions in mechanical friction; (ii) *secondary savings*, due to a lesser exchange of machine parts owing to wear reduction; and (iii) *tertiary savings*, where a new material is used for the production of new parts, thus raising the energy content of the materials [1].

Currently, the integration of tribology represents a modern aspect in life cycle assessment, with the main targets being environmental and economic performance. In this case, the main roles of tribology are not only to reduce friction in a machine, but also to extend the machine's service life.

1.3

History of Tribology

The history of tribology is as old as the history of humankind, the main driving force being the facilitation of daily activities by reducing friction. This especially the case for weapons, tools, crafts, or construction.

Table 1.1 Potential savings (in US\$ billion) by correct use of tribological knowledge (1.6% of GDP 2008).

European Union	303
United States	186
China	68
Japan	63
Germany	50
France	48
United Kingdom	36

The first man-made *bearings* to be identified date back to the middle Stone Age (Mesolithic period, 11 000–5500 years ago), with the use of stone door sockets, bearings for wheeled vehicles, and bearings for stone potter's wheels. There is also some indication that these 5000-year-old wheel bearings were lubricated with bitumen. Another early use of lubricants (most likely water) is shown in an Egyptian painting from the tomb of Tehuty-Hetep at El Bersheh (1800 BC); this shows a man pouring lubricant onto the ground in front of a sledge, on which a colossal sculpture is being transported. Although this man has often been referred to as the "first tribologist," Dowson [2] has also described an Egyptian tribologist who was 600 years older, and who had applied lubricant in similar fashion to the example of El Bersheh, in front of a sledge when transporting a heavy statue. Clearly, the transportation of heavy statues and building blocks, using wooden rollers beneath the sledges, was seen as a tribological innovation, with the application of early roller bearings being recorded during the first millennium BC [3].

One of the most important innovations from a tribological point of view has been the *wheel*, with the transition from sledges to wheeled vehicles first being seen about 3500 BC. The remains of many wheels dating back to the third millennium have been found in Europe and Asia. When recording the Greek and Roman period (900 BC to AD 400), Dowson [2] made a detailed chronology of tribology, defining political and social events and general technical developments. The description began with the production of bitumen and oils from petroleum and the use of iron bearings in olive mills (500 BC), of bronze rolling bearings in China (200 BC), and also a list of lubricants dating back to Roman times (0 BC). Later, a description was made of bronze journal bearings for wheels and axles (AD 300). Within the western hemisphere, a host of technical knowledge from the Greek and Roman period was lost during the Middle Ages. One of the most interesting examples was the change in materials, as bronze and iron bearings were gradually changed from wood and stone. Further activities in technical development were identified in the Islamic world between the ninth and twelfth centuries, with technical developments more evident in the eastern part of the Roman empire, and in the Byzantine region.

The first scientific developments of tribology began during the Renaissance (1450–1600 AD), with the most important studies of friction and wear being conducted by Leonardo da Vinci (1452–1519), the great painter architect and engineer, whose manuscripts contained over 5000 pages. The most important information regarding friction, bearing materials or roller bearings have been found in the *Codex Atlanticus* and in the *Codex Madrid I* and *II*. Some of Leonardo's studies demonstrated the forces of friction on horizontal and inclined planes, and the influence of the apparent contact area on friction. Another highlight of Leonardo's studies was a description of a low-friction bearing alloy, and of an early form of ball-bearing cage or of ball-and-roller pivot bearings. The most important mathematical result of Leonardo's studies was that the force of friction is not only directly proportional to the applied load, but also independent of the apparent area of contact.

About 50 years before Leonardo's tribological studies, the German Cardinal Nikolaus von Kues (Nikolaus Cusanus, 1401–1464) described the cycloids of gears.

An intensive description of mining technology was provided by Georg Agricola (1494–1555), and published in *De re metallica*. Agricola's tribological interests (mainly in book VI) demonstrated that there had been no development in tribological applications since the Greek and Roman eras when, typically, the bearings on wheel barrows were shown as simple circular holes in wooden side-planks.

During the seventeenth century, the increasing demand for mechanical power served as the main driving force to develop machines for the mining industry, or for windmills or water wheels, in relation to low-friction bearings. Consequently, considerable developments were achieved in the science of tribology during this century, by Hooke, Newton, and Amontons.

Robert Hooke (1635–1703) investigated the processes that occurred during rolling friction that were related, for example, to the hardness of wheels and the deformation of the surface, as well to the adhesion between wheel and ground. Consequently, Hooke presented a series of concepts on bearing design, seals, materials, and lubrication.

In December 1699, in Paris, *Guillaume Amontons* presented the details of his experimental results and interpretations relating to friction, and consequently defined the first and second laws of friction:

- First law. The force of friction is directly proportional to the applied load.
- Second law. The force of friction is independent of the apparent area contact.

But, since Leonardo da Vinci had reported essentially the same findings more than 200 years previously, it might be more honest to speak of da Vinci's laws of friction, and to mention Amontons only briefly!

During the mid-eighteenth century, in Berlin, the famous mathematician *Leonard Euler* (1707–1783) published two famous papers concerning friction. Euler defined, mathematically, the force required to move a weight up a slope of inclination to the horizontal: F (force) $>$ P (weight) $\tan \alpha$, and introduced μ as the coefficient of friction ($\mu = \tan \alpha$). The most important outcome of Euler's studies was his differentiation of kinetic friction from static friction. In Germany, in 1706, *Leibnitz* (1646–1716) was the first to distinguish between rolling and sliding friction. Another highlight of the studies of tribology during the eighteenth century, when lubrication was investigated at only a low level, was the hypothesis of *Isaac Newton* (1642–1727) who, in his law of viscous flow, defined the "*defectus lubricitatis*" that today is known as the internal friction of fluids, or *viscosity*.

It was almost 200 years later that the fluid film lubrication film theory was developed, by *Osborne Reynolds*.

During the first half of the eighteenth century, important progress was seen in the development not only of roller bearings, but also of gears. In this case, the use of animal and vegetable fats as lubricants had been noted for some time, and these included lard oil (in 1699; Amontons, de la Hire), tallow (in 1735), and vegetable oils (Leupold).

1.3.1

The Industrial Revolution

The period between 1750 and 1850 is generally referred to as the “Industrial Revolution,” when rapid technological changes occurred alongside social and economic developments. In the textile industry, for example, the mechanization of spinning and weaving influenced the progress in tribology with regards to the use of effective bearings and lubricants. Similar advances were identified in the development of steam engines for agriculture, and also for the railways. The use of steam power or the intelligent use of machine tools led to improvements in tribological studies. Perhaps the most important investigator during this period was Charles Augustin Coulomb, who defined friction formulas based on his own impressive experiments. These included an apparatus to study rolling friction, as well as studies on inclined planes and rough surfaces, and frictional resistance on sliding. Within the field of lubrication, the basics of fluid mechanics were devised by (among others) Leonhard Euler, Daniel Bernoulli, and M. L. Poiseuille (whose name was given to the unit of dynamic viscosity, the Poise). Claude Navier, a French mathematician (1785–1836) included the viscous terms in Newton’s law for flowing fluids, while the English physicist and mathematician G.G. Stokes defined the basics of viscous flow. Subsequently, the equations developed in this way became known as the Navier–Stokes equations.

Many different vegetable and animal oils were used during this period, including olive oil, rapeseed oil, palm oil, coconut oil, sperm oil, lard oil, or tallow oil. However, the first distillation of mineral oil in Prague (in 1812) led to the use of many more mineral-oil based lubricants, with the first graphite-containing lubricant being patented in the United Kingdom in 1835.

1.3.2

Between 1850 and 1945

The basic tribological studies in this period were characterized by many famous investigators, including:

- studies of rolling friction by Reynolds (in 1875);
- Heinrich Hertz’s analysis of contact between elastic materials (in 1881);
- N.P. Petrov’s studies on unloaded journal bearings (in 1883);
- the development of viscosimeters by Engler, Saybolt and Redwood (between 1884 and 1886);
- the hydrodynamic theory of Tower and Reynolds (1865);
- friction measurements on journal bearings by Richard Stribeck (in 1902);
- the analytical solution of Reynold’s equation by Sommerfeld (in 1904);
- further investigations on Stribeck’s results and defining the major source of dry friction by Ludwig Gümbel (between 1914 and 1925);
- Langmuir’s studies of thin surface films (in 1917);
- continuous improvements of the journal bearing by Tower, Kingsbury, Michell, and Rayleigh (between 1915 and 1925);

- the discovery of the mechanism of polar compounds by Hardy (in 1922);
- the use of extreme pressure and antiwear additives (in 1927); and
- the use of synthetic lubricants in Germany (synthetic esters and synthetic hydrocarbons), VI improvers, antioxidants and corrosion inhibitors (during the 1930s).

Some time later, in 1945, A. Ertel developed the basic formulas for the elastic hydrodynamic lubrication (EHL) (see Chapter 3).

1.3.3

From 1950 to the Present Day

During this period, awareness grew that friction, wear and lubrication represented an important area of technical engineering, notably in relation to the efficiency of operating machines. In 1966, a committee of the Department of Education and Science, headed by Peter Jost, produced the “Jost Report” in which the term tribology was born, together with a worldwide recognition of the importance of wear, lubrication, and friction. In Germany, the energy crisis of the 1970s led to the creation of projects aimed at energy savings via tribological activities [3], while the German Ministry of Research and Technology sponsored major projects in areas of tribology. During the 1980s, a recognition of the economic importance of tribology was complemented by an ecological awareness, with the first biodegradable lubricants produced from harvestable fatty materials being developed during the early part of the decade. In 1997, the University of Aachen (RWTH) began a 12-year interdisciplinary research project for ecological tribo-systems (financed by Deutsche Forschungsgemeinschaft). Globally, this study incorporates important research projects for tribology, including areas of mechanical engineering, materials science, surface technology, ecological aspects, safety at work criteria, and the chemistry of biodegradable lubricants.

During the 1950s, 1960s and 1970s, fluid film lubrication was developed – on both theoretical and experimental bases – into the elastohydrodynamic lubrication. This approach was based on previously acquired knowledge regarding elastic distortion and viscosity pressure characteristics. In 1959, Dowson and Higginson first described a procedure that was seen as a starting point for various later solutions for different lubricated contacts. Today, elastohydrodynamic lubrication has become fully established, and is complemented by methods to characterize surface topography.

Within the twentieth and twenty-first centuries, the details of tribological knowledge relating to the base sciences, to lubricants, and to wear or machine elements, have been published in numerous reports and books, among which are included (listed in chronological order):

Engler, C. and von Höfer, H. (1916) *Das Erdöl IV. Die Prüfung und Verwendung des Erdöls und der Erdölprodukte*, Hirzel-Verlag.
 Gümbel, L. and Everling, E. (1925) *Reibung und Schmierung im Maschinenbau*, Krain.

Vogelpohl, G. (1940) Die geschichtliche Entwicklung unseres Wissens über Reibung und Schmierung. *Öl und Kohle*, 36, 89–93 and 129–134.

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- Hersey, M.D. and Norton, A.E. (1942) *Lubrication*, McGraw-Hill.
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- Bowden F.P. and Tabor, D. (1950) *The Friction and Lubrication of Solids*, McMillan.
- Kühnel, R. (1952) *Werkstoffe für Gleitlager*, Springer-Verlag.
- Boner, C.J. (1954) *Manufacture and Application of Lubricating Greases*, Reinhold, New York.
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- Vogelpohl, G. (1958) *Betriebssichere Gleitlager, Berechnungsverfahren für Konstruktion und Betrieb*, Springer.
- Kuss, E. (1960) Über das Viskositätsdruckverhalten von Mineralölen, *Materialprüfung*, 2 (6), S189–S197.
- Göttner, G.H. (1961) *Einführung in die Schmierungstechnik*, Karl-Marklein-Verlag.
- Kragelski, I.V. and Vinogradova, I.A. (1962) *Coefficient of Friction*, Mashgiz.
- Braithwaite, E.R. (1964) *Solid Lubricants and Surfaces*, Pergamon Press.
- Cameron, A. (1966) *Principles of Lubrication*, Longman.
- Dowson, D. and Higginson, G.R. (1966) *Elastohydrodynamic Lubrication – The Fundamentals of Roller and Gear Lubrication*, Pergamon Press.
- Bartz, W. (1968) *Vergleichende Untersuchung des Seitenflusses von Gleitlagern bei Schmierung mit strukturviskosen und reinviskosen Stoffen*, VDI-Verlag. This was the first of various international congresses to be held over a period of four decades.
- Schey, J.A. (1970) *Metal Deformation Processes – Friction and Lubrication*, Marcel Dekker.
- Neale, M.J. (ed.) (1973) *Tribology Handbook*, Butterworths.
- Sarkar, A.D. (1976) *Wear of Metals*, Pergamon.
- Czichos, H. (1978) *Tribology – a system approach to the science and technology of friction, lubrication and wear*, Elsevier.
- Mang, T. (1981) *Die Schmierung in der Metallbearbeitung*, Vogel-Verlag.
- Klarmann, D. (ed.) (1982) *Schmierstoffe und verwandte Produkte*, Verlag Chemie.
- Czichos, H. and Habig, K.-H. (1992) *Tribologie – Handbuch*, Vieweg-Verlag.
- Mang, T. and Dresel, W. (eds) (2001, 2007), *Lubricants and Lubrication*, John Wiley & Sons.

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- 1 Bartz, J.W. (1988) *Energieeinsparung Durch Tribologische Maßnahmen*, Expert Verlag, Ehningen.
- 2 Dowson, D. (1998) *History of Tribology*, 2nd edn, Professional Engineering Publishing Limited, London, Bury St Edmunds.
- 3 Bartz, J.W. (1988) *Zur Geschichte der Tribologie*, Expert Verlag, Ehningen.

2

The Tribological System

A tribological system has functional character, and performs technical tasks which are either energy-, material-, or signal-oriented (Table 2.1) [1]. The tribological properties of the system depend upon the system function, the complex of loads, and the structure. The complete description of the tribological system (Figure 2.1) is a basic prerequisite for the consideration, evaluation, and design. From the definition of the term *tribology*, it follows that friction and wear are system properties and not material characteristics. If this system is only slightly modified, the properties of friction and wear are changed, in some cases very considerably.

A tribological system describes only a section of an entire system. Thus, for analysis, it is essential that the entire system is defined. Here, a distinction is made between open and closed tribo systems:

- **Closed tribo systems** refers to tribological systems in which the system elements are permanent parts of the system beyond the duration of loading, and constantly participate in the tribological processes. The wear processes of all participating system elements must therefore be taken into consideration in relation to the operability. Examples of these are lifetime-lubricated bearing systems.
- **Open tribo systems** on the other hand, are characterized by having one or more tribo elements which are moved through the system, and are not continuously in tribological contact. This is for example, the case for flowing precursor products or counter-bodies, such as a chain drive. Material processing takes place in open systems, in which new material is constantly fed in for processing. With open tribo systems, only the wear processes of the elements permanently installed in the tribo system, for example the tool for material processing or the conveyor belt of a bulk material system, are considered.

The tribological system describes the frictional and wear contact. Viewed abstractly, this consists of two bodies – the base body and the counter-body – undergoing movement in relation to each other, with or without an intermediate medium

Table 2.1 Functional ranges of tribological systems (after Habig [2]).

Functional range	Examples of tribo systems and tribo-technical components
Guidance	Plane bearings, rolling bearings, linear guidance, running fit
Retardation of motion	Friction brakes, shock absorbers
Power/energy transmission	Gearwheels, belt drives, clutches, piston rings/cylinders, cams/tappets, turbines, articulated joints
Information transfer	Control gears, relays, read heads, printers
Sealing	Linear seals, stuffing boxes, radial shaft seals, piston ring-type sealing, piston seals, abradable coatings
Material transport	Wheel/rail, tire/road, conveyor belt, dredging shovel, chute, pipeline, pump, heart valve
Material separation	Centrifuges, cutting tools for turning, milling, drilling, grinding
Material crushing	Ball-mill, jaw crusher, shredder
Material forming	Forming tools for forging, drawing out, extruding, rolling, bending
Primary material shaping	Primary shaping tools for injection-molding, die-casting, gravity die-casting, sintering

(Figure 2.2); this gives rise to interactions on the surface of the solid. While the base body is always a solid object, the counter-body and also the intermediate material can be either liquid or gaseous. The complex of loads and the structure determine the wear behavior of the tribo system. The analysis of a tribological system is performed

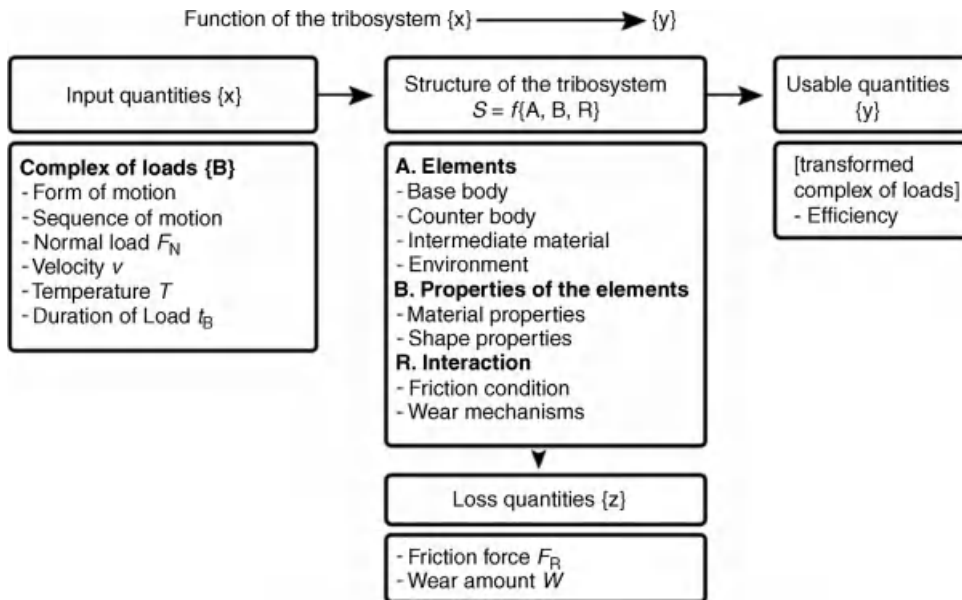


Figure 2.1 Complete description of a tribo system [2].

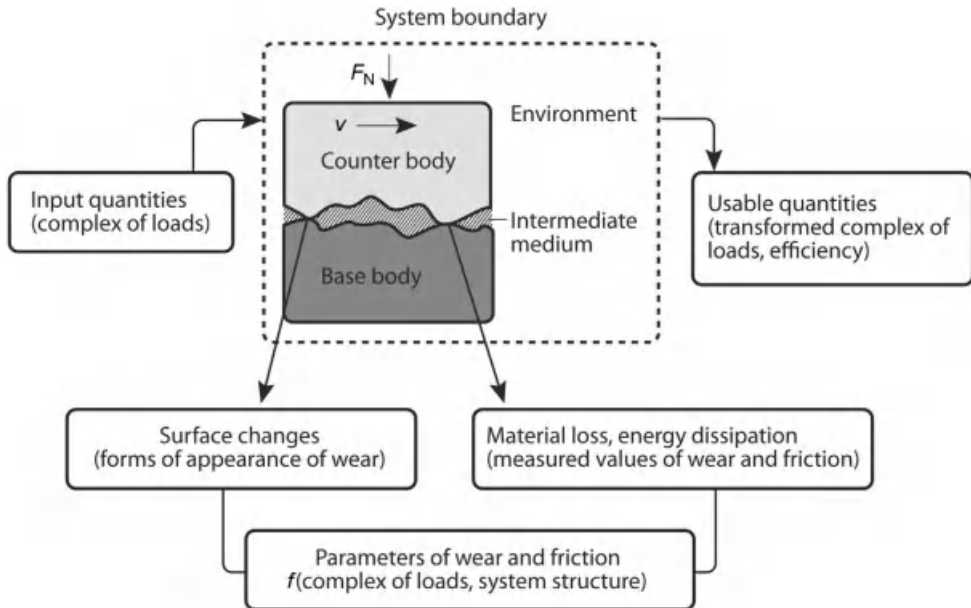


Figure 2.2 Schematic representation of a tribological system.

in four steps [3], and gives indications for optimization potentials in the interest of wear. The system analysis embraces the following points:

- 1) Characterization of the technical functions of the tribo system.
- 2) Definition of the complex of loads.
- 3) Characterization of the structure of the tribo system by:
 - (a) the elements participating in wear processes;
 - (b) the relevant properties of the elements, including the contact-geometrical areas;
 - (c) the interactions between the elements.
- 4) Definition of the frictional and wear parameters.

For the analysis of a tribo system, the interactions occurring between all elements must be considered. The changes to the tribo elements over a period of time in respect of their material and form properties require a time-dependent analysis. The result of this analysis is the operational parameters. The efficiency depends upon the loss parameters (frictional force, amount of wear).

Friction and wear are surface phenomena, and are dependent on the material properties of the participating elements, the tribo contact area, and the chemical and thermal loading. Under technical boundary conditions, a three-dimensional (3-D) surface region with a depth of from a few atomic layers up to several $100\ \mu\text{m}$ is considered. When surface-treated tribo bodies are used, this can include the boundary surface between the base material and the coating material (interface)

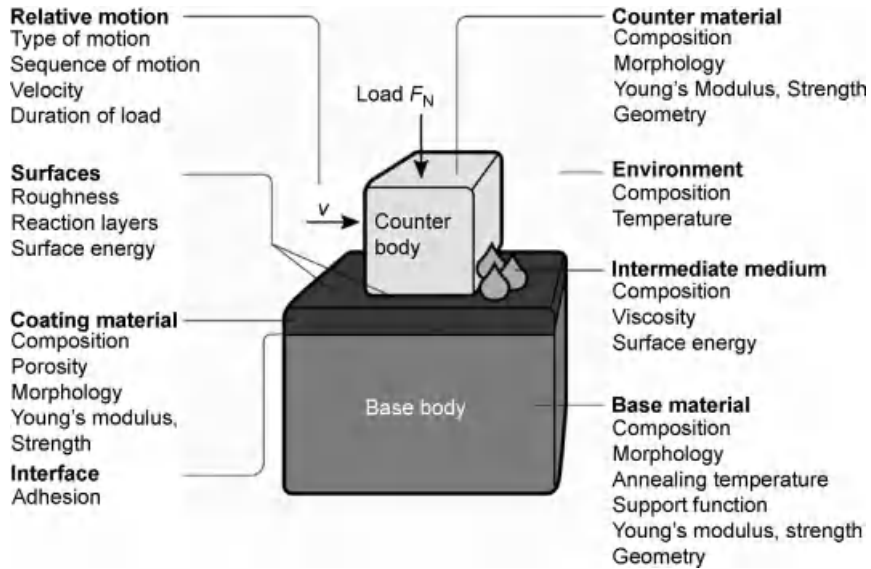


Figure 2.3 Variables governing a tribo system with coated base material.

(Figure 2.3). This view is useful, as most mechanical and thermal loading contributions to tribological loading are of this order of magnitude.

2.1

Tribological Surfaces

The chemical and physical phase boundary reactions on surfaces are based on atomic interactions. Each phase – which can be solid, liquid or gaseous – can be characterized in terms of its chemical composition, the acting bonding forces, and its structure. The cohesion of the individual atoms within a phase is the result of chemical bonding (Figure 2.4). A distinction can be made here between metallic bonding, ionic bonding, and covalent bonding (electron-pair bonding), with increasing bonding energy in this sequence. Much weaker bonding is found in the form of intermolecular bonding, which is responsible for the cohesion of molecules in a crystal lattice (e.g., solid carbon dioxide) or in a liquid (e.g., water) [4].

The aggregated states are solid, liquid or gaseous, depending upon the state variables pressure and temperature. This phenomenon is attributable to the fact that each phase strives to reach a state of thermodynamic equilibrium. Due to material transport, such as by diffusion processes, within a phase the lowest possible level of energy is achieved. The physical and chemical properties within a phase differ from those at the phase boundary, which always extends over a depth of several atomic or molecular diameters. The particles found here are not subject to the uniform forces acting from all sides on the particles within the phases, which results in a minimum

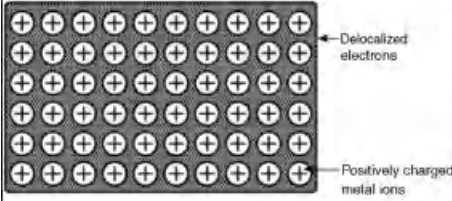
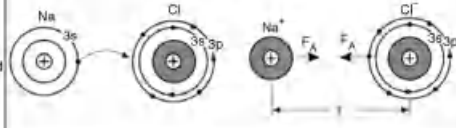
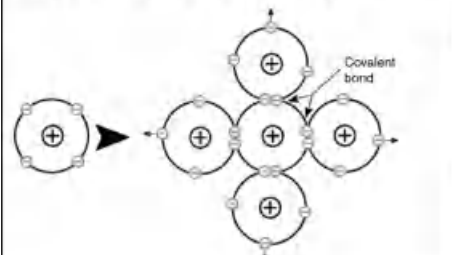
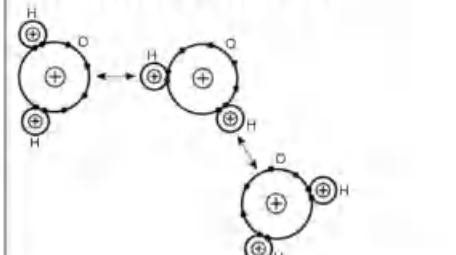
<p>Metallic bonding</p> <p>Metal atoms lose their valence electrons to an electron gas, uniformly surrounding all metallic ions.</p> <p>Examples: All metals and their alloys</p> <ul style="list-style-type: none"> ▪ high electrical conductivity ▪ high thermal conductivity ▪ good plastic and elastic deformability ▪ high thermal expansion coefficient  <p>Labels: Delocalized electrons, Positively charged metal ions</p>	<p>Ionic bonding (heteropolar bonding)</p> <p>An atom loses an electron to another atom, resulting in a noble gas configuration for both atoms. (F_A: Coulomb force)</p> <p>Examples: Oxide ceramics, sulfides, halogenides</p> <ul style="list-style-type: none"> ▪ partly water-soluble (NaCl) <p>Oxide ceramics (Al_2O_3, ZrO_2):</p> <ul style="list-style-type: none"> ▪ no electrical conductivity ▪ poor thermal conductivity ▪ hard, brittle ▪ high chemical stability 
<p>Covalent bonding (electron-pair binding)</p> <p>Two atoms share their electrons, attaining a noble gas configuration. This permits restricted movement of the electrons.</p> <p>Examples: Diamond, silicon, boron carbide</p> <ul style="list-style-type: none"> ▪ very hard, very brittle ▪ low electrical conductivity ▪ good high-temperature behavior  <p>Label: Covalent bond</p>	<p>Vander Waals bonding</p> <p>Overlapping of molecular orbits and electrostatic interactions between permanent or temporary dipole molecules.</p> <p>Examples: Water, polymers, carbon dioxide</p> <ul style="list-style-type: none"> ▪ very low melting point ▪ very soft and elastic ▪ very poor electrical conductors 

Figure 2.4 Structure and properties of atomic bonding types.

potential energy of interaction (Figure 2.5). From this, it follows that phase boundaries are always characterized by greater energy. If the particles of a condensed phase are free to undergo motion, as with liquids, then spherical structures (i.e., the geometric form with the smallest area) are always formed.

The interactions at the phase boundary to the environment can, in practice, frequently not be differentiated from each other. The transitions between physical adsorption, chemisorption, chemical reactions and electrochemical reactions are

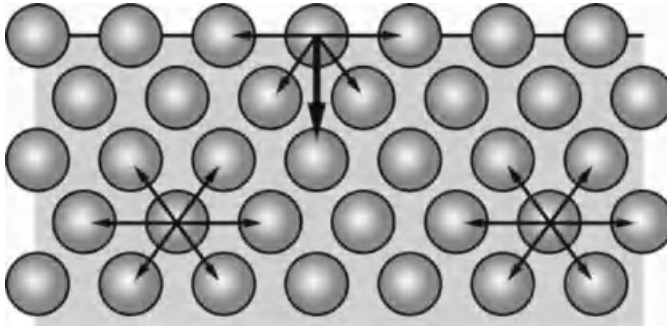


Figure 2.5 Schematic representation of intermolecular interactions within and at the surface of a phase [5].

often not clearly defined. For solid bodies with high-energy surfaces, above all metals and ionic bonding, the adsorption process frequently does not remain at the level of physical adsorption. The effect of strong metal bonding or Coulomb forces on the adsorbate particles leads rather to the strong deformation and partial dissolution of their intermolecular bonds [5]. In the chemisorbed state, the particles of the adsorbate exist in a form approximating that of a surface bonding.

The transition from physisorption to chemisorption requires a higher activation energy E_A^{Chs} , so that this process can be greatly suppressed at low temperatures. At the same time, the strong binding forces in the chemisorption complex cause a significant irreversibility of the process, such that a chemisorptions–desorption equilibrium will set in only at high temperatures, if at all. The energy relationships for the transition of a particle initially to the physisorption state, and from this state to the chemisorption state, is illustrated schematically in Figure 2.6 for the example of the adsorption of oxygen (O_2) on a metallic surface.

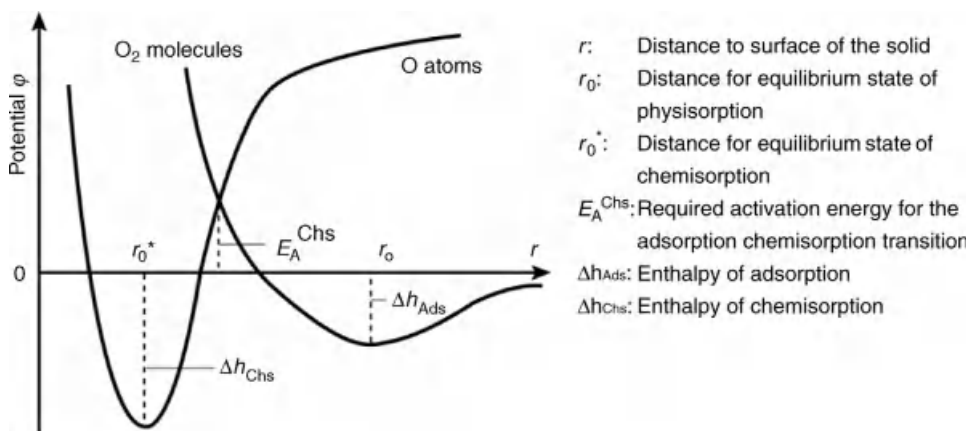


Figure 2.6 Schematic illustration of the potential curves for physisorption and chemisorption of O_2 on a metallic surface [5].

The deformation of the electron shell occurring with the chemisorbed particles during chemisorption enables these to react more easily with other compounds. Pure high-energy solid surfaces (particularly those of metals) can be obtained practically only in high vacuum and with special methods, such as ion-beam technology. Already at low temperatures, the smallest traces of gaseous compounds, including the permanent gases, are adsorbed, whereas at normal temperatures true compound layers are nearly always formed from the closed chemisorption layers, such as oxide or nitride layers.

Besides these atomic interactions, leading to material deviations at the surface of the material, all technical surfaces differ from the ideal geometric form due to their manufacturing processes. In accordance with DIN 4760, a distinction can be made between deviations in form of the first to the sixth order. The form deviations of the first to the fourth order (Figure 2.7) are, as a rule, superimposed to the real surface profile.

The microscopic form deviations of third and fourth order are usually determined using a contact stylus, and described as “roughness values.” The measurement procedures are standardized in accordance with DIN EN ISO 4287. The most frequently cited roughness values are in the form of the mean roughness depth R_z (Figure 2.8) and the mean roughness value R_a (Figure 2.9). These values are usually stated in [μm].

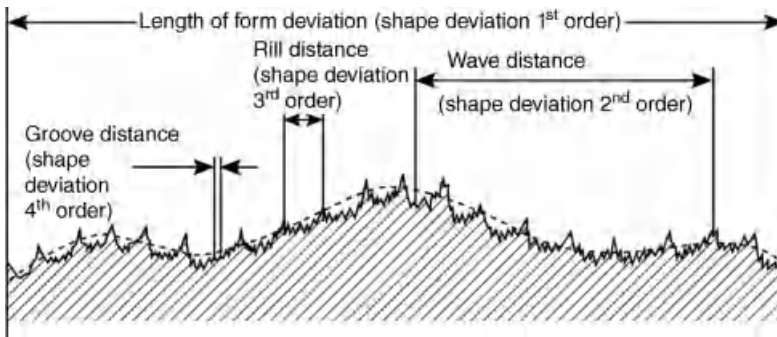


Figure 2.7 Schematic illustration of form deviations of the first to fourth order.

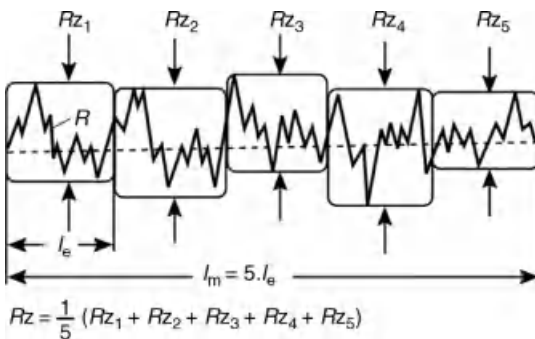


Figure 2.8 Mean roughness depth R_z : Mean value of the individual roughness depths ($R_{z_1} \dots R_{z_5}$) of five successive individual measurement segments l_e .

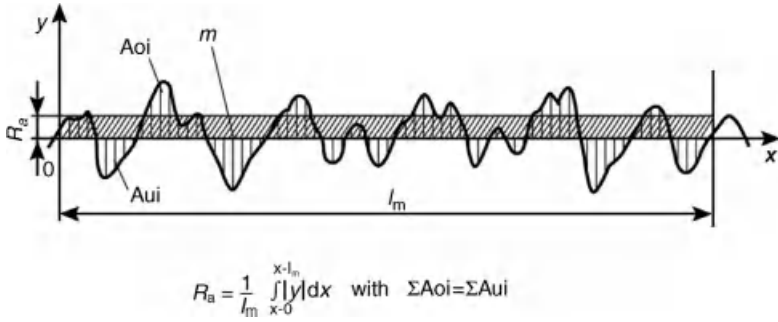


Figure 2.9 Mean roughness value R_a : Arithmetic mean of all deviations of the roughness profile R for the central reference line within the measurement segment l_m .

The form deviations of fifth and sixth order refer to deviations in the microstructure and lattice structure of materials. In particular, due to the manufacturing process, the microstructure of material surfaces nearly always differs from that within the material. For materials manufactured by the melting metallurgical process, the grain size in the edge zone of the component is frequently smaller. Mechanical loading during material processing results in plastic deformation of the boundary zones. As a result of strain hardening, the edge zone possesses a higher degree of hardness, as well as a greater yield strength and greater tensile strength. Due to thermal loading, diffusion processes in the edge zone can lead to changes in the chemical composition, solidification effects, and/or re-crystallization effects. The internal stress situation in the edge zone, particularly with metallic substances, can in part considerably deviate from the value within the material. In summary, it can be said that the edge zone of tribological surfaces is built up of several boundary layers (Figure 2.10). The strength properties, residual stress situation and chemical composition of these boundary layers will decisively influence the tribological properties of a solid body.

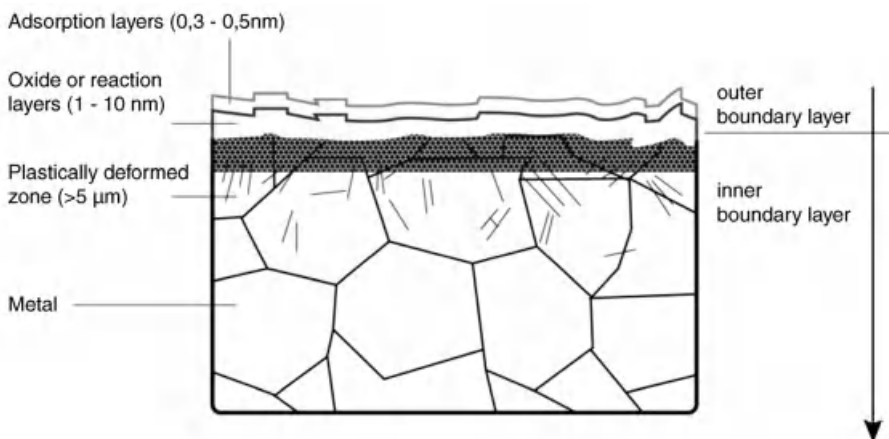


Figure 2.10 Structure of a metallic surface (after Schmalz).

2.2 Wetting of Solid Surfaces

When two condensed phases come into contact, the interactions between the two phases reaching into the boundary layers determine the geometric form of the phase boundary [6]. This becomes particularly apparent for contact between a liquid and a solid. Here, a liquid droplet is initially subjected only to external gravitational effects and deformed, according to the prevailing intermolecular forces of adhesion (Van der Waals forces) in the solid body. The size of the boundary surface and the geometric form of the liquid surface are determined by the condition that the free energy of the entire system must be a minimum. From the form of a liquid droplet, conclusions can therefore be drawn concerning the type and magnitude of forces of adhesion acting over the boundary surface.

The first and best known description of a state of wetting was given by T. Young, in the year 1805 [7]. Young's equation describes the equilibrium of forces between the interfacial tensions σ_{ij} at the three-phase boundary (Figure 2.11). This determines the contact angle β , as a measure of wetting, from the material properties of the participating phases [8].

$$\text{Young's equation : } \sigma_{sv} = \sigma_{sl} + \sigma_{lv} \cdot \cos \beta$$

β : contact angle

σ_{sv} : solid–vapor surface tension

σ_{sl} : solid–liquid interfacial tension

σ_{lv} : liquid–vapor surface tension.

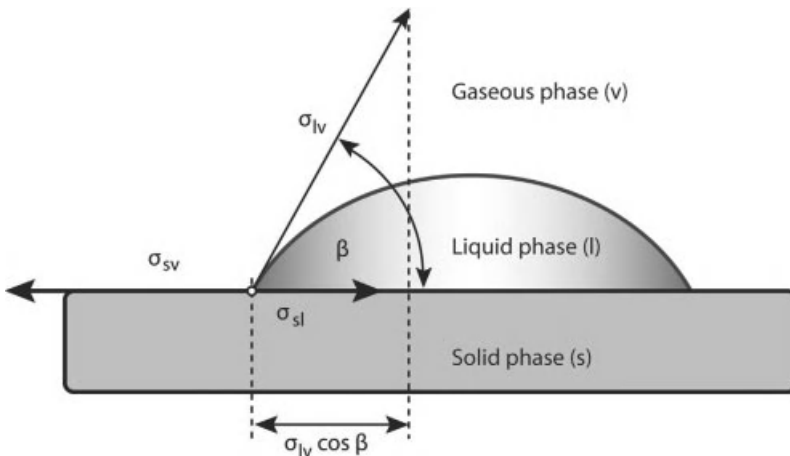


Figure 2.11 Tension relationships at the three-phase boundary acting on a liquid droplet (after Young).

While the contact angle β and the surface energy σ_{lv} are measurable parameters, σ_{sv} and σ_{sl} can only be determined as the difference ($\sigma_{sv} - \sigma_{sl}$). The term ($\sigma_{sv} - \sigma_{sl}$) is referred to as “adhesion tension,” or also “wetting tension.” Some sixty years after Young, Duprè formulated the relationship between the interfacial tension and the adhesion energy, W_A , as [9]:

$$W_A = \sigma_{lv} + \sigma_{sv} - \sigma_{sl}$$

Thermodynamically, this expression can be descriptively explained: when a liquid is separated reversibly from a solid surface, the common boundary surface A_{sl} and the interfacial tension σ_{sl} vanish. However, two new boundary surfaces A_{lv} and A_{sv} then emerge, for which the interfacial σ_{lv} and σ_{sv} must exist. Starting with Young’s equation, the Young–Duprè equation is then obtained:

$$\text{Young–Duprè equation} \quad W_A = \sigma_{lv} + \sigma_{lv} \cdot \cos \beta = \sigma_{lv} \cdot (1 + \cos \beta)$$

Analogously, the work of cohesion, W_K , can be calculated. In this case, a homogeneous substance is torn apart.

$$W_K = \sigma_{lv} + \sigma_{lv} - \sigma_{ll} = 2 \cdot \sigma_{lv}$$

as $\sigma_{ll} = 0$

Both, the complete lack of wetting ($W_A = 0$, i.e., $\beta = 180^\circ$) and partial wetting ($W_A \leq W_K$, i.e., $0 < \beta < 180^\circ$), are states of equilibrium. However, the formal limiting case $W_A = 0$ does not occur in Nature, as otherwise no interactions would take place beyond a boundary surface. Due to the fraction of dispersion forces in the Van der Waals interaction, however, even different particles always feel the presence of other particles. Consequently, even on ceramics or glasses in contact with metals, wetting angles of less than 180° are observed [10]. Complete wetting ($W_A > W_K$), on the other hand, represents a nonequilibrium state. The liquid flow rises unimpeded on a partially immersed platelet – that is, it “spreads.” The spreading parameter is the spreading tension S (also referred to as the spreading coefficient):

$$\begin{aligned} S &= W_A - W_K \\ S &= \sigma_{sv} - (\sigma_{sl} + \sigma_{lv}) \end{aligned}$$

In accordance with the spreading condition $S > 0$, spreading is expected when a liquid with a low surface tension is applied to a solid body with a greater surface tension. Spreading then occurs when the interactions between the particles of the liquid and the solid body (adhesion energy W_A) are stronger than the interactions of the liquid particles (cohesion energy W_K) among each other. Whereas, σ_{lv} and σ_{sv} are always positive, σ_{sl} can also be negative, exactly when the interaction between the atoms of the solid body and the molecules of the liquid is greater than the interactions of the atoms of the solid body among each other. In chemical equilibrium, the energy of the system is reduced by the expansion of the boundary surface between the solid body and the liquid. In chemical nonequilibrium, a low or even negative interfacial tension σ_{sl} is an indication that not only an increase in the size of the boundary

surface, but also an exchange of substances, is taking place between the solid body and the liquid. For the interaction of metals with solder, this can be attributed to the formation of intermetallic phases, and also to dissolution processes or the diffusion-induced flow of solder or metal components beyond the boundary surface, without the involvement of chemical reactions [10].

2.3

Tribo Contact Surfaces

The tribo contact surface describes the contact area between bodies in contact, in which the tribological loading is effective [2]. The surface pressure, p , is given by the ratio of the normal force F_N to the tribo contact area A :

$$p = \frac{F_N}{A}$$

Due to the microgeometry of technical surfaces, the contact between two tribo bodies is restricted to discrete microcontacts, which deform under the influence of the normal force. In accordance with Figure 2.12, it is therefore necessary to distinguish between the geometric and nominal contact area A_0 and the (usually vastly smaller) real contact area A_r – that is, the area given by the sum of the microcontact surfaces. The true contact area is of central importance for all tribo-technical systems, as the frictional and wear processes take place primarily here [11].

The macroscopic contact between the tribo bodies is determined by the construction. Here, it is possible to distinguish between conform contact forms, leading to surface contact, and contra-form contact forms, which are in turn further divided into linear and punctiform contacts. The most important forms of contact for closed tribo systems are summarized in Figure 2.13.

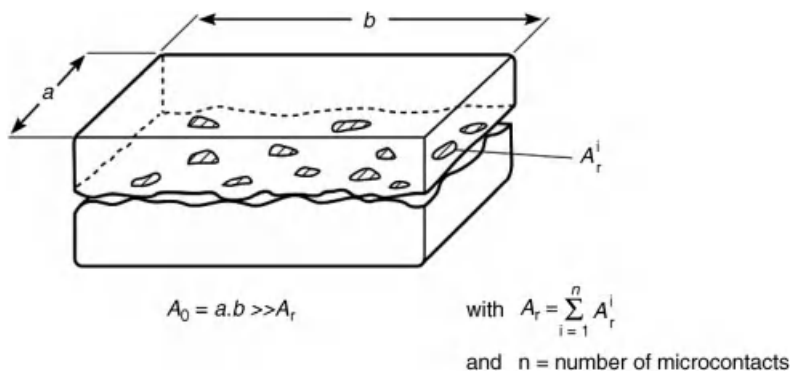


Figure 2.12 Geometric contact area A_0 and real contact area A_r at roughness peaks [11].

Contact shape		Area of Base body I	Counter-body II	Sketch	Application examples
Conform	Surface contact	Plane	Plane		Straight-line motion
		Hollow cylinder	Full cylinder		Plain bearing, cylindrical fits, cylinder slight ways
		Hollow cone	Full cone $d_I \approx d_{II}$		Bearing, conical fits
Contra- conform	Line contact	Plane	Cylinder		Roller guides
		Hollow cylinder	Full cylinder $d_I \gg d_{II}$		Needle bearings
		Full cylinder	Full cylinder $d_I \leq d_{II}$		Roller mills, roller bearings
		Full cone	Full cone		Conical friction wheel gearing
		Hollow cone	Ball calotte		Toe bearing
		Full prism	V-prism		Knife-edge bearing
		Involute surface	Involute surface		Gearwheel
	Point contact	Plane	Ball		Ball guides
		Hollow cylinder	Ball		Ball guides
		Full cylinder	Ball		Ball guides
		Inner ring surface	Ball		Rolling bearings
Outer ring surface		Ball			

Figure 2.13 Construction-conditioned contact geometries of tribological systems. (after Weingarber and Abou-Aly, 1989) [11].

2.4 Tribological Loading

The relative motion of two bodies with surface contact leads to friction. Besides the relative motion, physical and chemical interactions between the surfaces induced by the presence of forces characterize the tribological loading [3] (Figure 2.14). Over the duration of loading, and as a result of these interactions, the tribo system continuously changes. The rate of the ongoing reactions on the surface of the material depends strongly upon the pressures (pressing) and temperatures arising. Mechanical material failure depends, furthermore, on the form of motion and the loading over time (dynamic or static) and the related application of forces.

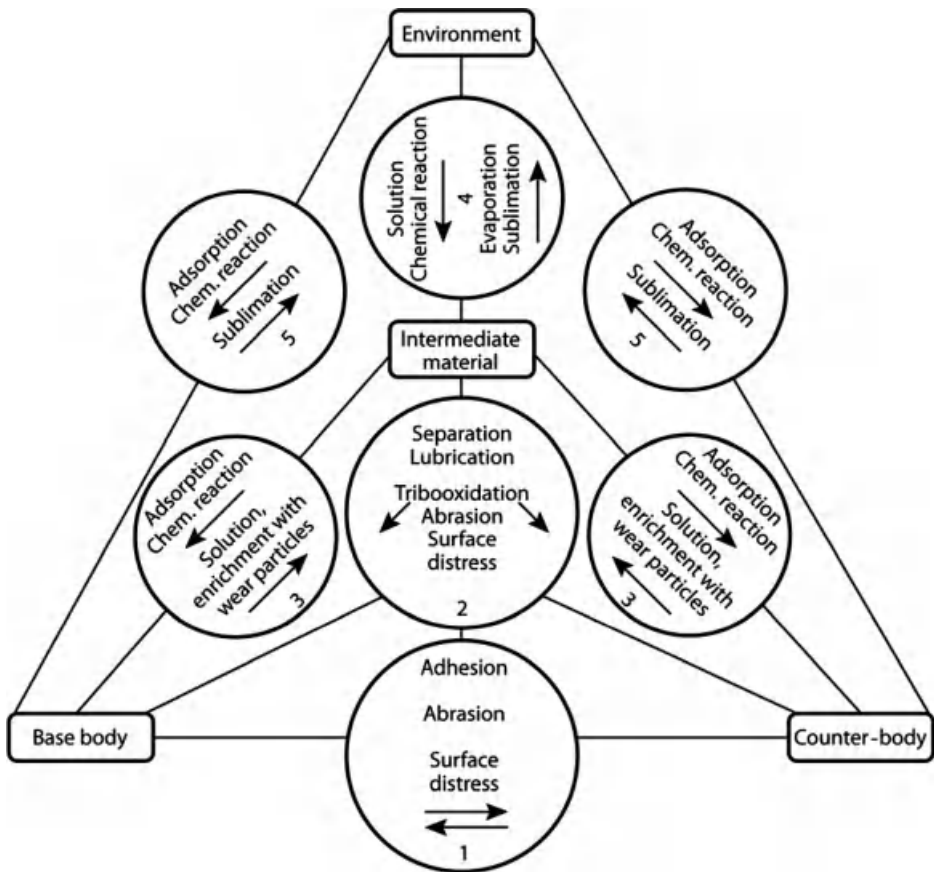


Figure 2.14 Possible interactions between the elements of a tribo system [1].

In accordance with the Society for Tribology (GfT) worksheet 7 [3], the complex of loads is comprised of:

- **The form of motion** which includes the four “elementary forms of motion,” as well as the superposition of these:
 - (1) Gliding: including the form of motion “drilling,” in which the surface elements move in the contact area with different relative velocities
 - (2) “Rolling without slip”: this always refers to the microscopic sliding part (micro-slippage). When macroscopic sliding parts (macro-slippage) simultaneously occur, we speak of “rolling with slip.”
 - (3) Impact: as a synonym for the term “impact,” the term “collision” is frequently used.
 - (4) Flowing: the term “flowing” corresponds to the term “gliding” for the case that the counter-body is a grained, liquid, or gaseous material.
- **The behavior over time**
 - (1) Continuous
 - (2) Oscillating
 - (3) Intermittent.
- **The physical-technical loading parameters** which include:
 - (1) The normal force F_N : on the basis of the normal force F_N , knowledge of the size of the geometric contact area allows us to calculate the mean surface pressure $p = F_N/A_0$. In addition, knowledge of the geometric dimensions of the components, the Young’s modulus of the materials used, and the coefficients of friction allow us to determine the material strain.
 - (2) Velocity v : the decisive velocity v for wear processes is the “relative velocity” between the two wear partners.
 - (3) Temperature T : this refers to the respective state of thermal equilibrium of the entire tribo system. For states of thermal nonequilibrium, for example, with different temperatures of the base material and counter-body, the introduction of several temperatures or temperature functions may be necessary.
 - (4) Load duration t_B : this describes the length of time during which the tribological loading causing wear remains in effect. From knowledge of the load duration t_B and the velocity v , the loading path can be calculated.

Besides this complex of loads, required for the technical function of the tribo system, other disturbance variables, such as mechanical oscillations or radiation effects, can influence the wear process [3]. In all tribo-technical systems, force or energy transmission loads the components in the tribo contact surfaces; this is referred to as “material strain” [11]. In the general theory of strength of materials, for the assessment of material strain on the basis of failure theories, equivalent stresses σ_v are calculated, such as the

Shear stress according to Tresca:

$$\text{Equivalent stress } \sigma_v : \quad \sigma_v = 2 \cdot \tau_{\max} = \sigma_1 - \sigma_2$$

σ_1 : largest normal stress

σ_2 : smallest normal stress

τ_{\max} : maximum shear stress.

Form change energy hypothesis according to Huber and von Mises:

$$\text{Equivalent stress } \sigma_v : \quad \sigma_v = 1/2^{1/2}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]^{1/2}$$

$\sigma_1, \sigma_2, \sigma_3$: Normal stresses

For the area of tribology, these general hypotheses for material strain must be applied to contact processes. Material failure can occur when σ_v is greater than the respective material parameter for the given type of loading, for example [11]:

- yield strength R_p for the onset of flow;
- tensile strength R_m for rupture;
- fatigue strength σ_w for continuous alternating loading.

Within the scope of tribological investigations, wear phenomena and causes have been increasingly investigated since the 1950s. The tasks of the scientific examination of tribological effects consist primarily of optimizing the system properties friction and wear for different tribological systems [12]. Here, the goal is the reduction of material (wear) and energetic (frictional) losses, in order that the function of the tribological contact partners remains intact over a sufficiently long period of time. Tribo research distinguishes here between qualitative and quantitative research:

- Qualitative research deals with the type (of tribological loading), form (perceptible processes) and cause (mechanisms).
- Quantitative research, also referred to as *tribometry*, deals with load collectives, energy losses (frictional forces, heat of friction, acoustic emission), wear (change in form, detached particles), geometrical relationships in the contact zone (contact areas), and changes to the materials and lubricants.

Although in recent decades there has been an enormous growth in the knowledge for the area of tribology, the complex processes are to this day not entirely understood nor representable. Thus, until today it is not possible to predict the coefficients of friction for an arbitrary tribological system, let alone the rate of wear. Tribological testing therefore has special meaning in connection with the design of tribological systems.

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3

Friction

Friction is the mechanical force which resists movement (dynamic or kinetic friction) or hinders movement (static friction) between sliding or rolling surfaces. This force of friction is also called “external friction.” The work done by friction can translate into deformation, wear, and heat.

Internal friction as part of external friction when lubricants are used results from the friction between lubricant molecules; this is described as *viscosity* (see Chapter 7) (The meaning of internal friction in material science is the force resisting motion between the elements making up a solid material while it undergoes deformation).

The causes of external friction are, above all, the microscopic contact points between two sliding surfaces; these cause adhesion, material deformation, and grooving. Energy which is lost as friction can be measured as heat and/or mechanical vibration. Lubricants should reduce or avoid the microcontact which causes the greatest part of external friction.

3.1

Kinetic and Static Friction

Different from static friction, kinetic friction occurs under conditions of relative motion. The American Society for Testing and Materials (ASTM) defines the kinetic coefficient of friction as the coefficient under conditions of macroscopic relative motion of two bodies. The *kinetic coefficient of friction*, which sometimes is called the “dynamic coefficient of friction,” is usually somewhat smaller than the static coefficient of friction.

The *static coefficient of friction* is defined as the coefficient of friction corresponding to the maximum force that must be overcome to initiate macroscopic motion between two bodies (ASTM). The maximum value of static friction is sometimes referred to as “limiting friction.”

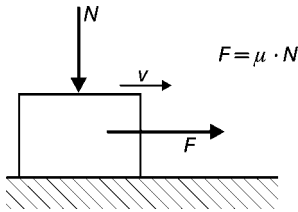


Figure 3.1 Coefficient of friction.

3.2

Coefficient of Friction

Figure 3.1 defines the coefficient of friction as the dimensionless ratio of the friction force F and the normal force N . The proportionality between normal force and friction force is often given in dry and boundary friction, but not in fluid film lubrication.

The coefficient of friction is also known as the frictional coefficient or friction coefficient, and is symbolized by the Greek letter μ (or sometimes by f).

The coefficient of friction is not a material property, but is better described as a system property. It cannot be deduced by calculations, but must be determined by empirical measurements. For several combinations of material in a dry and clean state, and under same test procedure, the static coefficient of friction for steel against the most metals is found between 0.4 and 0.6. (The kinetic coefficient of friction relating to the various friction regimes is shown in Figure 3.7.)

On occasion, the static coefficient of friction is defined in terms of the maximum angle before which one of the items will begin to slide. This is the “angle of friction,” $\tan \alpha = \mu_{st}$, where α is the angle from horizontal and μ_{st} is the coefficient of static friction (Figure 3.2).

3.3

Stick-Slip

Stick-slip is a special form of friction which often results from very slow sliding movements when the friction partners are connected to a system which can vibrate.

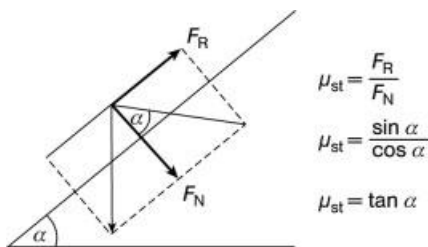


Figure 3.2 The static coefficient of friction in terms of the maximum angle before which one of the items will begin sliding.

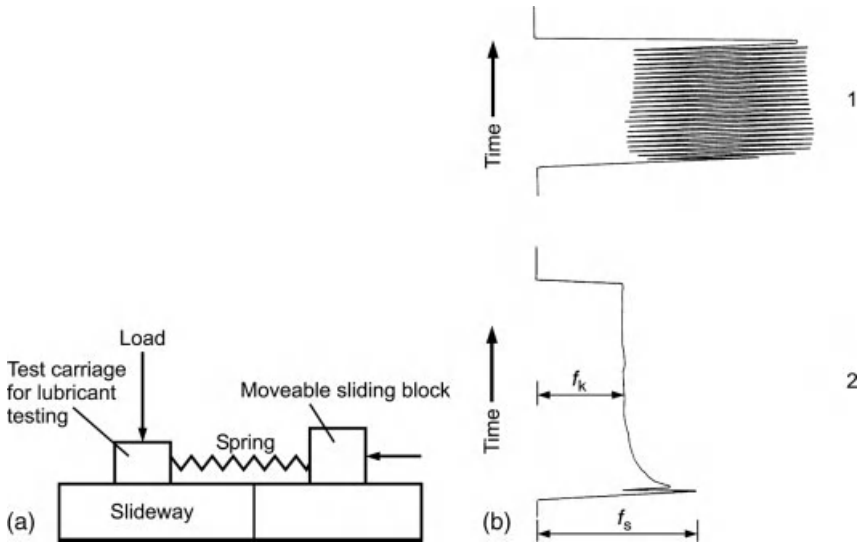


Figure 3.3 Stick-slip. (a) Test equipment for stick-slip; (b) Results of stick-slip behavior of two oils. 1, Oil with bad stick-slip behavior; 2, Oil with good stick-slip behavior; f_k , relative kinetic coefficient of friction; f_s relative static coefficient of friction.

The process is influenced by the dependence of the coefficient of sliding friction on speed. This generally occurs when the static coefficient of friction is larger than the kinetic coefficient of friction. Stick-slip is normally encountered with machine tools which operate with slow feeds, and can cause chatter marks on components. The inclusion of special additives in lubricants, or special surface treatment of the bodies, can lead to stick-slip being reduced or even avoided (Figure 3.3).

3.4

Sliding and Rolling Friction

Sliding friction is friction in a pure sliding motion with no rolling and no spin (Figure 3.4).

Rolling friction is the friction generated by rolling contact. In roller bearings, rolling friction mainly occurs between the rolling elements and the raceways, whereas sliding friction occurs between the rolling elements and the cage. The main cause of friction in roller bearings is sliding in the contact zones between the rolling elements and raceways. It is also influenced by the geometry of the contacting surfaces and the deformation of the contacting elements. Although the existing slip velocities are small (normally <1%), they may produce a major part of the total resisting in rolling. In addition, sliding also occurs between the cage pockets and the rolling elements.

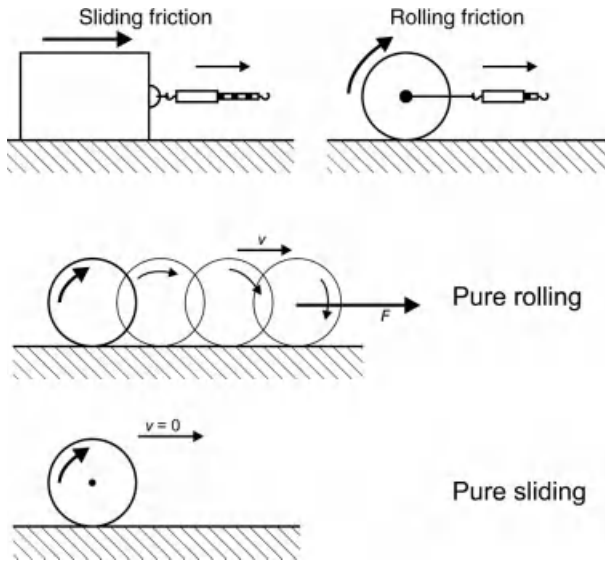


Figure 3.4 Sliding and rolling.

In the case when rolling motion and sliding motion combine to any significant extent, as for gear tooth meshing, a special terminology has been created. The term “Wälzreibung,” which is derived from “Wälzen” (rolling, e.g., steel rolling), is used in Germany. Situations in which a high sliding/rolling ratio occur require totally different lubrication than does pure sliding. Figure 3.5 shows this “rolling friction” during rolling and during gear meshing. A special form of sliding friction is called *spin*, or *spin friction*; this can be illustrated by a drilling operation or a rotating cone on a plate. In ball bearings, this type of friction can be seen when analyzing the rotating movement of the balls round various axes.

3.5

Friction Regimes: Friction and Lubrication Conditions

In tribological systems, different forms of contact can exist between contacting partners, and this results in different friction and lubrication conditions.

3.5.1

Solid Friction (Dry Friction)

This occurs when two solids have direct contact with each other, without a separating layer. If conventional materials are involved, the coefficients of friction and wear rates are high; lubrication technology attempts to eliminate this condition.

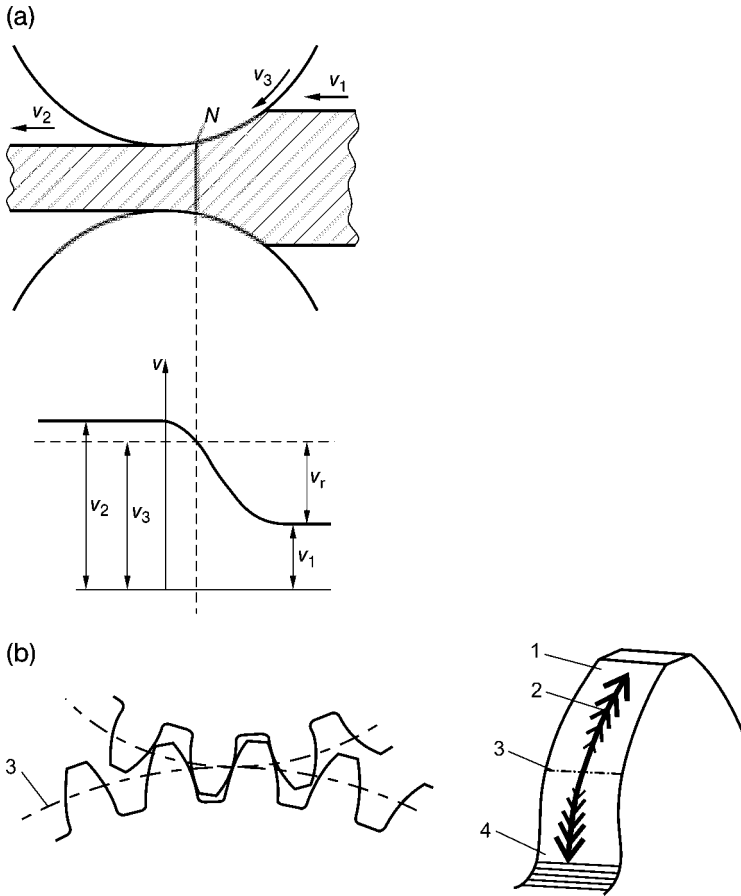


Figure 3.5 “Wälzreibung,” the mixing of rolling and sliding motions. (a) Rolling in metal forming, v_1 = initial speed of the sheet metal, v_2 = final speed of the sheet metal, v_3 = speed of the roller, v_r = speed difference in the roll gap

(sliding part), N = neutral point (nonslip point, pure rolling); (b) Engagement of gear teeth. Points 1, 2, 4 = high sliding/rolling ratio, point 3 = pitch circle (pure rolling, no slip).

3.5.2

Boundary Friction

The contacting surfaces are covered with a molecular layer of a substance, the specific properties of which can significantly influence the friction and wear characteristics. One of the most important objectives of lubricant development is to create such boundary friction layers in a variety of dynamic, geometric, and thermal conditions. These layers are of major importance in practical applications when thick, longlasting lubricant films to separate two surfaces are technically impossible to achieve. Boundary lubricating films are created from surface-active substances and their

chemical reaction products. Adsorption, chemisorption, and tribochemical reactions also play significant roles.

Although boundary friction is often allocated to solid friction, the difference is of major significance to lubricant development and the understanding of lubrication and wear processes, especially when the boundary friction layers are formed by the lubricants.

3.5.3

Fluid Film Friction

In this form of friction, both surfaces are fully separated by a fluid lubricant film (full-film lubrication) which is formed either hydrostatically or, more commonly, hydrodynamically. From a lubricants point of view, this is known as hydrodynamic or hydrostatic lubrication (Figure 3.6). Liquid or fluid friction is caused by the frictional resistance, owing to the rheological properties of fluids. If both surfaces are separated by a gas film, this is known as “gas lubrication.”

3.5.4

Mixed Friction

This occurs when boundary friction combines with fluid friction. From a lubricants technology standpoint, this form of friction requires sufficient load-bearing boundary layers to form. Machine elements which are normally hydrodynamically lubricated experience mixed friction when starting and stopping. For roller bearings – which represent one of the most important machine elements – it has been shown that the reference viscosity either of lubricating oils or of the base oils of greases is not sufficient to ensure the formation of protecting lubricant layers and the required minimum lifetime. Under mixed friction conditions it is important to choose the appropriate lubricant; that is, the one which enables the formation of tribolayers by anti-wear and extreme pressure additives [1] and/or a specific surface treatment (as described in Chapter 6).

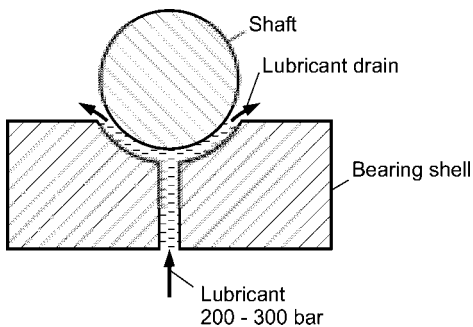


Figure 3.6 Hydrostatic lubrication as a form of fluid friction.

In 2004, Schwarze and Wiersch described a means of calculating mixed lubrication contacts over a wide range of operating conditions and applications. The performance of the mixed friction model was demonstrated using the example of a cam tappet contact [2, 3].

3.5.5

Stribeck Curve

The friction or lubrication conditions between boundary mixed and fluid friction are graphically illustrated by using the Stribeck diagram/curve, first developed in 1902 (Figure 3.7) [4]. These curves are based on the starting-up of a plain bearing, the shaft and bearing shells of which are, when stationary, separated only by a molecular lubricant layer. As the speed of revolution of the shaft increases (peripheral speed), a thicker hydrodynamic lubricant film is created; initially this causes a sporadic mixed friction which, nevertheless, causes a significant reduction in the coefficient of friction. Then, as the speed continues to increase, a full, uninterrupted film is formed over the entire bearing faces, causing a sharp reduction in the coefficient of friction. As the speed increases further, internal friction in the lubricating film adds to the external friction such that the curve passes a minimum coefficient of friction value and then increases, solely as a result of internal friction.

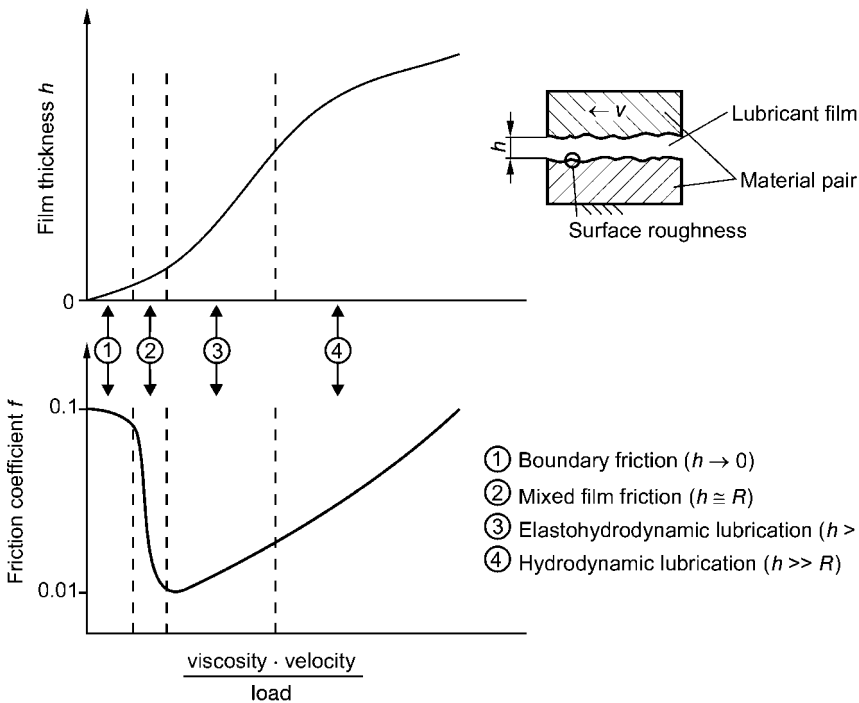


Figure 3.7 The Stribeck graph, according to H. Czichos and K.-H. Habig.

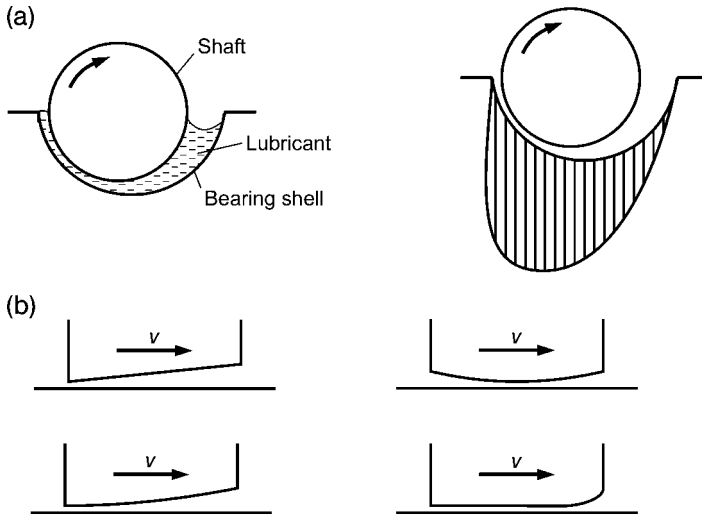


Figure 3.8 Formation of a hydrodynamic liquid lubricant film. (a) Rolling development of pressure in the hydrodynamic film; (b) Sliding, preferred geometry.

The lubricant film thickness shown in Figure 3.7 depends on the friction and lubrication conditions including the surface roughness,

3.6

Hydrodynamic and Elastohydrodynamic Lubrication

The formation of a hydrodynamic fluid film is shown in Figure 3.8. Here, the lubricant is pulled into the conical converging clearance by the rotation of the shaft. The created dynamic pressure then carries the shaft.

Based on the Navier–Stokes theory of fluid mechanics, Reynolds created the basic formula for hydrodynamic lubrication in 1886. Several criteria remained excluded, however, especially the influence of pressure and temperature on viscosity. Application of the Reynolds' formula led to theoretical calculations on plain bearings, where the only lubricant value was viscosity.

3.6.1

Elastohydrodynamic Lubrication (EHL) Regime

Hydrodynamic calculations on lubricant films were extended to include the elastic deformation of contact faces (Hertzian contacts, Hertz's equations of elastic deformation) and the influence of pressure on viscosity (see Chapter 7). This enables the application of these elastohydrodynamic (EHD) calculations to contact geometries other than that of plain bearings – for example, those of roller bearings and gear teeth.

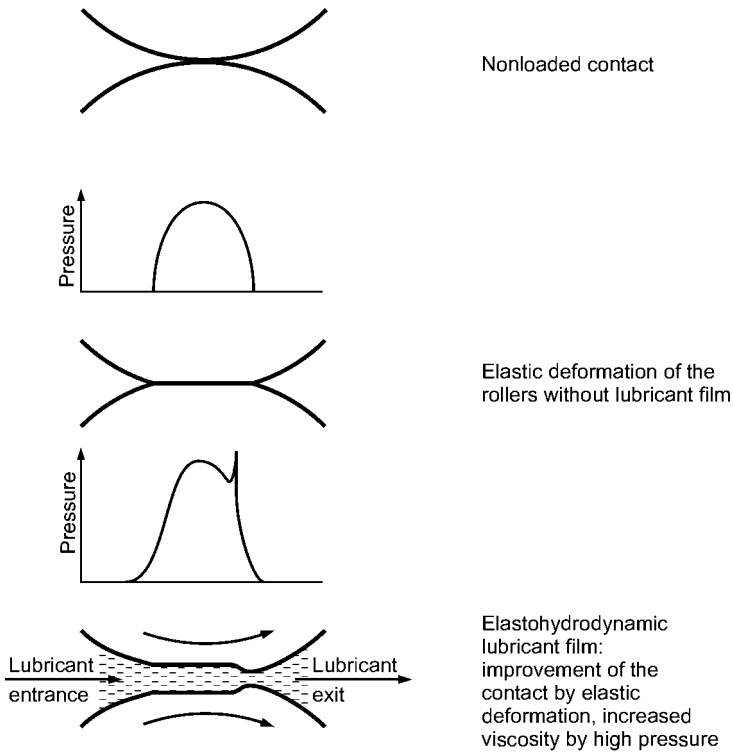


Figure 3.9 Improvement of hydrodynamic lubrication clearance between two rollers by Hertzian deformation [elastohydrodynamic (EHD) contact], pressure distribution in the Hertzian contact.

Figure 3.9 shows the elastic deformation of the ball and raceway of a ball bearing, while Figure 3.10 shows an example of Hertzian contacts for various pairs with nonconverging lubricant clearance.

In 2006, H. H. Spikes produced an article which defined the history of EHL over a sixty-year period [5], thus providing a very competent understanding of one of the most complex areas of friction and lubrication.

The EHL regime is relevant in lubricated nonconforming contacts, as are found in rolling element bearings, gears, and cam-tapped systems. The fluid behavior caused by motion of the surface can be calculated by using the Reynolds equation, similar to conforming contacts. In nonconforming contacts with a high elastic modulus, solids such as metals develops a very high pressure, so that the load is concentrated in a line or a point. However, this has effects on the lubrication behavior: typically, the high pressure causes the contacting surfaces to be elastically deformed, which in turn causes a large increase in the viscosity of the lubricant in the contact zone. This combined effect is known as “piezoviscous-elastic lubrication.”

In 1945, in order to solve the mathematical description of EHL, Hertel [6] combined the solution of the three equations for fluid flow, elastic deformation of

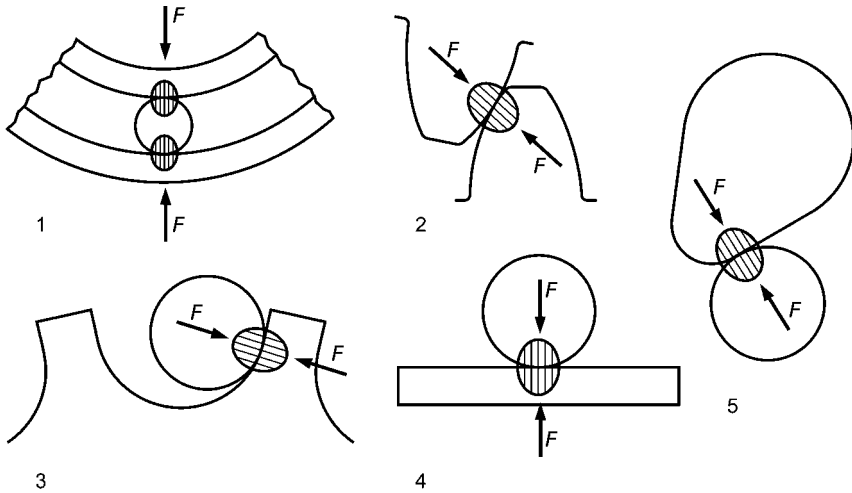


Figure 3.10 Hertzian contact for different pairs with nonconverging lubricant clearance. 1 = roller bearing, 2 = gear wheels, 3 = chain wheels, 4 = roller on flat path, 5 = cam lifter.

the contacting solids, and of the dependence of fluid viscosity on pressure. In this way, he obtained the following equation for the fluid film thickness in line contact (parallel cylinders in contact):

$$h_0 = 1.93 \frac{(\eta U \alpha)^{0.727} R'^{0.364} E'^{0.091}}{W_L^{0.091}} \quad (3.1)$$

where W_L is the applied load per unit length, U is the mean rolling speed, and R' is the reduced radius:

$$\frac{1}{R'} = \frac{1}{R_1} + \frac{1}{R_2}$$

and E' is the reduced elastic modulus:

$$\frac{2}{E'} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}$$

where η is the viscosity of fluid at atmospheric pressure, and α is the pressure-viscosity coefficient of the fluid.

Later calculations of film thickness for EHL contacts were reported by Dowson and Higginson. For the ratio of the minimum film thickness and the normal film thickness, an approximate value of 0.75 was obtained. Figure 3.11 demonstrates the calculations of film thickness of Dowson and Higginson, according to G. Knoll, for two contacting balls [7]. Based on different approaches, various research groups identified variant values of the exponents, with e_2 -values ranging from 1.00 to 0.73.

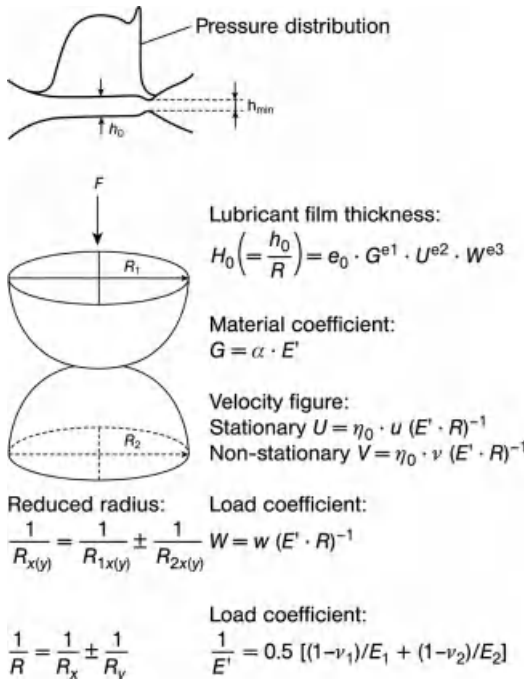


Figure 3.11 Calculation of film thickness of Dowson and Higginson (according to G. Knoll for two contacting balls).

Numerous studies have been conducted during the past years to predict the EHL conditions, by combining the Reynolds equation with the elasticity and 3-D energy equations, so as to obtain the pressure, film thickness, and temperature distribution within the lubricant film. In addition, computer-controlled instruments have been developed for measuring the film thickness down to 1 nm and defining the conditions of EHL.

Yet, despite a more than 60-year history of EHL applications, further improvements in the regime have been demonstrated during recent years [7, 8].

3.6.2

Thermoelastohydrodynamic Lubrication (TEHL)

TEHL theory solves the Reynolds equation, including the energy equation of the lubricant film. Calculation of the energy takes into consideration heat convection in all directions, heat conduction in the radial direction, compression, and heating caused by viscous and asperity friction.

TEHL theory has been applied, for example, in important areas of automotive engines, by using a model that includes a shear rate-dependent viscosity (see Chapter 7), and also in the simulation of lubrication conditions for the main crankshaft bearing of commercial automotive engines [9].

3.6.3

Plastohydrodynamic Lubrication

In metal-working processes – and especially in metal forming - the lubricant film thickness is formed by wedging before the workpiece enters the plastically deformed working zone. Although the geometric and pressure conditions of this zone are important parameters, in many processes a reasonable lubricant film can be generated hydrodynamically. This special lubrication condition, occurring under plastic deformation, is termed “plastohydrodynamic lubrication.”

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4

Wear

The term “wear” is defined as the progressive loss of material from the surface of a solid object due to mechanical causes – that is, the contact with and frictional motion against a solid, liquid, or gaseous counter-body [1]. The occurrence of wear is undesirable, and is related to a deterioration of functional capability and a depreciation of value. Only in exceptional cases, such as run-in procedures, is wear desirable from a technical standpoint. “Wear damage” occurs when the function of the tribo system is no longer ensured. Therefore, based on the definition of value depreciation, all production processes such as lapping, polishing, and so on that lead to a value increase are not considered as wear processes but rather as machining processes, even though the functional principle is identical.

Whilst wear processes are the result of mechanical loading, chemical processes may be interfacially superimposed on them, and can also influence such loading. Wear processes cause a number of material, and also geometric, alterations in the tribological system. Material alterations are understood here to mean the formation of tribological reaction layers and metallurgical compounds between the materials of the tribo elements in the tribo contact. Geometrical alterations arise by the abrasion of material on the surface of the object. The causes are to be found in the four “wear mechanisms,” which will be described below. Alterations to the surface, as well as the type and form of particles that arise due to wear, are described as “wear phenomena forms.” In real tribo systems, there is nearly always a superposition of several wear mechanisms. Hence, in order to simplify the analysis, for the most important basis tribological systems “wear types” have been defined from the superposition of the possible wear mechanisms. The alteration in the form or mass of a body due to wear is designated by parameters which are standardized as “wear parameters” in the Society for Tribology (GfT) worksheet 7 [2], the successor to the (in the meantime withdrawn) DIN 50 321 standard.

4.1

Wear Mechanisms

Wear is the result of the four wear mechanisms: surface fatigue; abrasion; tribochemical reaction; and adhesion. These mechanisms lead to material and form alterations, and also to the formation of wear particles, and occur in the form of characteristic wear phenomena (Figure 4.1) [1–3]. The four wear mechanisms are described in the following subsections.

Although each wear mechanism can occur alone, the examination of wear damage indicates that there is nearly always a superposition of several wear mechanisms, which complicates any wear analysis and wear prevention. Figure 4.2 shows, schematically, how such a superposition might appear; frequently, the individual wear mechanisms will mutually reinforce each other.

4.1.1

Adhesion

Adhesion is a material interaction of tribo pairs. Due to the contact of two solid surfaces under high pressure, atomic bonds arise. Subsequently, with the renewed separation of the tribo elements, material will be detached from one surface and remain adhering to the opposite surface. For metallic contact partners, adhesion is also described as “cold welding” [4]. The required energy for the reaction is made available by high pressures and frictional heat.

Every surface possesses a certain degree of roughness. When two surfaces come into contact, only the roughness peaks of the two bodies are directly in tribo contact, which means that the actual contact area is considerably smaller than the geometric area of the bodies in contact (see also Section 2.3). Very high mechanical stresses occur in these micro-contacts, but these may be further increased by the relative movement of the bodies. Both, elastic and elasto-plastic deformation of the roughness peaks may then take place, with the result that the adhering adsorption layers and reaction layers are destroyed. Simultaneously, frictional energy is transformed to heat at the micro-contacts, giving rise locally to very high short-term temperatures (flash temperature theory). The interplay of high temperatures, high normal and tangential forces, and exposed high-energy surfaces enables the formation of atomic bonding between the base material and the counter-body, which may have greater strength than the bonding between the two contact partners. The separation of the two surfaces then no longer takes place in the original contact zone, but below the surface of the contact partner having the weaker cohesion (cohesive failure). This leads to the formation of material fragments, which are then transferred from object A to object B, or *vice versa*. This process can reverse itself, and loose particles can then arise [2].

As a counter-measure, chemically inert materials should be chosen for the tribo-body surface. Materials with high fractions of ionic bonding offer very high chemical stability. As these materials (e.g., Al_2O_3) are also typically very hard, a relationship is frequently seen, for example, between the material hardness and the adhesion

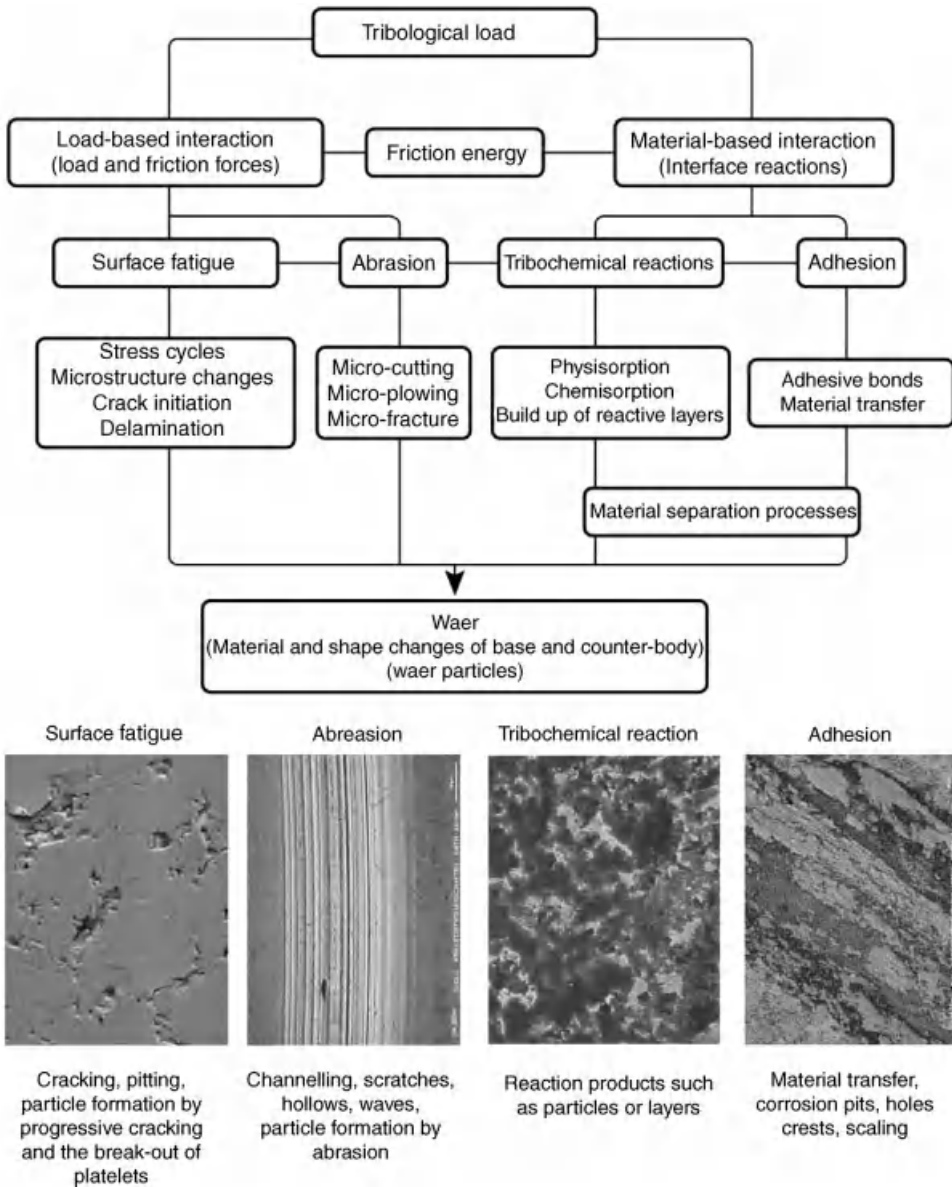


Figure 4.1 Wear mechanisms. An overview of material and form alteration processes due to tribological loading [4], and the forms of wear that result.

resistance. However, this theory is contradicted by the fact that many polymers [e.g., polytetrafluoroethylene (PTFE, Teflon)] possess excellent adhesion resistance. Material pairs with different types of atomic bond have also proved to be favorable, as interactions take place preferentially between materials having the same type of

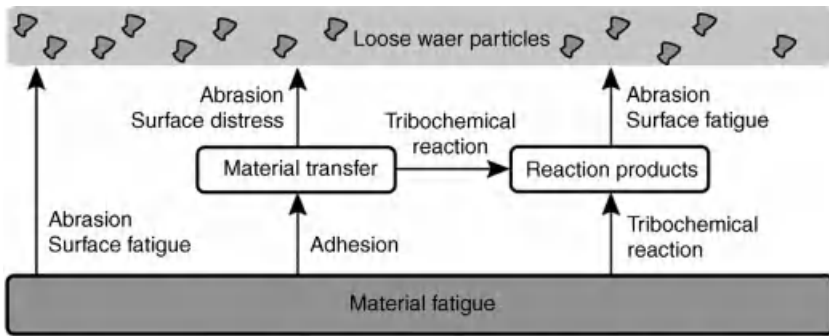


Figure 4.2 Possible superposition of wear mechanisms on the surface of a material.

bonding. With the combination of metallic materials, it is necessary to ensure the low solubility of the alloy components in the material of the counter-body. The most common method of protecting against adhesion is to separate the tribo-bodies at the contact surface, by using suitable intermediate materials.

4.1.2

Tribochemical Reactions

Tribochemical reactions cause material alterations in the surface of tribo-bodies. In contrast to adhesion, in this case a chemical reaction takes place on the surface with the ambient medium and/or the intermediate material, and not with the counter-body material. This differs from corrosion, in that tribochemical reactions take place only on the contact surface, during simultaneous relative motion. The reaction products of the tribochemical reactions actively influence the course of the wear process.

The frictional processes brought about by the relative motion may result in frictional losses, such as frictional heat. At the same time, the naturally occurring reaction layers on the material surfaces are destroyed by mechanical loading, so that high-energy surface regions become exposed. The enhanced capacity of the surfaces to enter into chemical reactions leads to tribochemical reactions, such as tribo-oxidation. The altered chemical composition of the surface in turn influences its properties in respect of strength and frictional values. The reaction products – both those arising from the natural reaction layers and those arising from tribochemical reactions – can be very hard and brittle (e.g., metal oxides). If these break away due to mechanical loading, they contribute additionally to progressive wear (abrasion), thus sustaining the ongoing tribochemical reactions. A typical example of tribochemical wear is the formation of fretting corrosion, which can develop on stainless steels when the protective passive layers are continuously destroyed. In order to prevent tribochemical reactions from occurring, materials should be chosen which are chemically inert relative to the ambient medium and intermediate material. A suitable additive in the lubricant can prevent tribochemical reactions from occurring, via the formation of a protective layer on the surface of the material.

4.1.3

Abrasion

Abrasion occurs predominantly in tribo systems in which the tribo elements possess widely different hardness values. The harder material acts abrasively, in that harder roughness peaks of or harder particles in the object penetrate the surface of the softer object. As a result of the relative motion, channeling and scratches are formed, and for the case of stronger attack the material breaks away from the surface, causing an extensive amount of wear. The process of material abrasion consists of the following diverse processes, which usually occur simultaneously (Figure 4.3) [5]:

- **Micro-plowing:** Pronounced plastic deformation of the material by the abrasive counter-body gives rise to pile-up at the edge of the channel, so that material abrasion is not compelled to occur. (ideal: $f_{ab} = 0$)
- **Micro-cutting:** Hard roughness peaks or abrasive particles cut the surface, with the formation of micro-shavings. (ideal: $f_{ab} = 1$)
- **Micro-fracture:** The supercritical loading of a brittle material by an abrasive particle leads to the formation and spreading of cracks, and ultimately to material break-away. ($f_{ab} > 1$)
- **Micro-fatigue:** Repeated micro-plowing results in local material fatigue, causing material abrasion. This partial process is, strictly speaking, part of the process of surface fatigue.

The so-called f_{ab} value describes the relative fractions of the partial processes micro-cutting and micro-plowing. The ratio of the two partial processes is influenced by the angle of attack α of the abrasive material which, in this regard, represents the “cutting angle” (Figure 4.4) [5].

The preferred measure for protection against abrasion is the use of harder materials. The greatest hardness is achieved with highly covalent bonding fractions (e.g., diamond, CBN, or B_4C). Here, it is necessary to consider that very hard materials are often also very brittle. Under supercritical loading, these materials

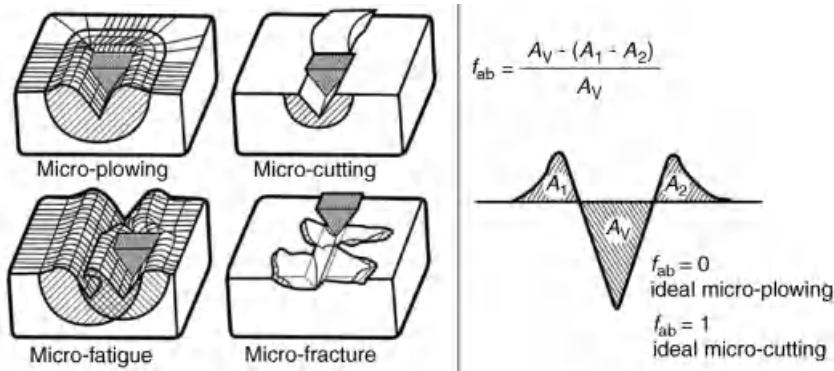


Figure 4.3 Abrasion processes [5]. A_V = cross-section of the wear furrow; A_1, A_2 = cross-sections of the material pile-up due to micro-plowing.

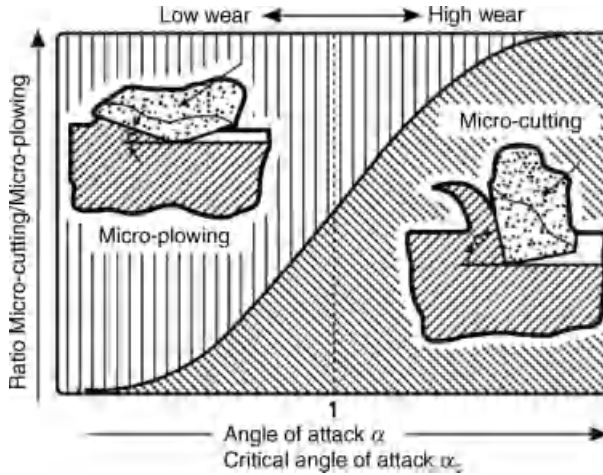


Figure 4.4 Influence of the cutting angle of the abrasive material on the abrasion process [5].

tend to fail due to the presence of micro-fracturing, so that sufficient fracture toughness is required in addition to hardness. Compound systems comprised of a tough metal matrix with embedded hard materials (MMC = metal–matrix composite) exhibit good properties in respect of abrasive wear. In order that hard material particles are not torn away by the abrasive material, the mean free path of the hard phase must be less than the mean diameter of the abrasive particles.

4.1.4

Surface Fatigue

Besides static loading, alternating mechanical loads can also occur in tribological systems, and may be described as a “periodic oscillation” (Figure 4.5). Dynamic loading in the surface regions of materials can cause material fatigue in the edge zone, leading ultimately to the formation of cracks and their subsequent spreading.

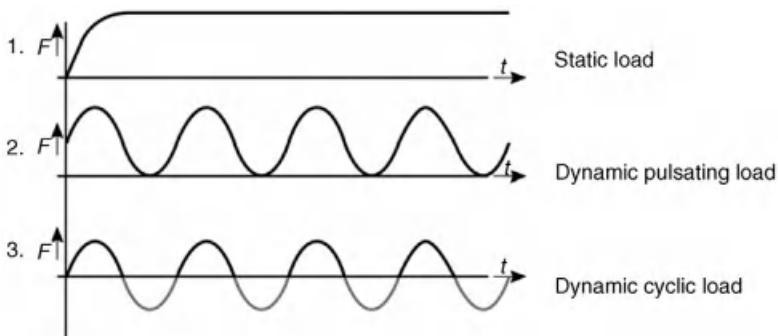


Figure 4.5 Time behavior of cases of mechanical loading.

Surface fatigue exhibits certain similarities with the volume-based fatigue of massive materials. The difference lies in the smaller penetration depth of the loads acting, which in surface destruction act only in the edge zone of a material. Material fatigue can also result in fracture for load amplitudes below the static yield strength. Cracks are formed on the surface, especially at faulty positions with stress concentration. These grow further step-wise, and the residual cross-section ultimately fails due to forced rupture [6]. Likewise, with cyclically loaded sliding contacts, forms of wear phenomena are observed similar to those known from volume-based fatigue fracture in the manner of “lines of oscillation” and “lines of rest” [4].

Well before the formation of cracks, material fatigue already becomes apparent in the micro-structure. The prerequisite for fatigue is the plastic deformation of the material; when the applied load exceeds the elastic limit, the crystal begins to undergo *plastic deformation*, which may be attributed to the migration of displacements (linear lattice defects) along the slip planes (Figure 4.6). With *progressive deformation*, the dislocations that arise and migrate during deformation pile up with an increasing degree of deformation, mutually block each other, and are finally no longer capable of gliding (termed Lomer–Cottrell dislocations). Other dislocations migrate up to the grain boundary, where they are stopped. Such a pile-up of dislocations at obstructions results in the strain hardening of the material.

The dislocation lines, when driven back and forth by the alternating loads, will band together to form distinct persistent slip bands (PSBs). These bands then propagate along the primary slip plane, when the amplitude of plastic deformation lies within a certain range. Characteristic for the morphology of PSB dislocation structures are ladder-like dislocation structures (Figure 4.7) [7]. In this case, the break-through of slip bands on the surface results in the formation of pushed-out and drawn-in slip-off zones (shear lips) [6], which – due to their stress concentration – represent potential regions for the formation of cracks. As a result of the dislocation motion, defects form in the crystal lattice which, under progressively greater mechanical loading, grow to form microscopic holes (voids), thus weakening the mechanical stability of the structure in the edge zone of the part. Typical of surface fatigue is cracking that runs parallel to the surface, joining the voids and breaking platelet-shaped particles out of the surface. The surface then appears to be “destroyed” due to the cracking and the pitting left behind by the delaminating particles.

The formation of wear particles therefore assumes a certain incubation time, during which no measurable wear takes place. As compression stresses of varying magnitude are transferred by a lubricating film, surface fatigue may occur in

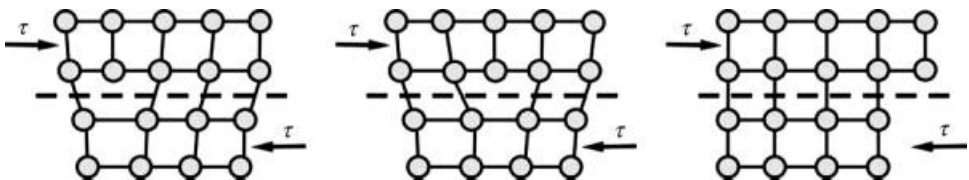


Figure 4.6 Dislocation for an edge dislocation along a slip plane (τ = shear stress).

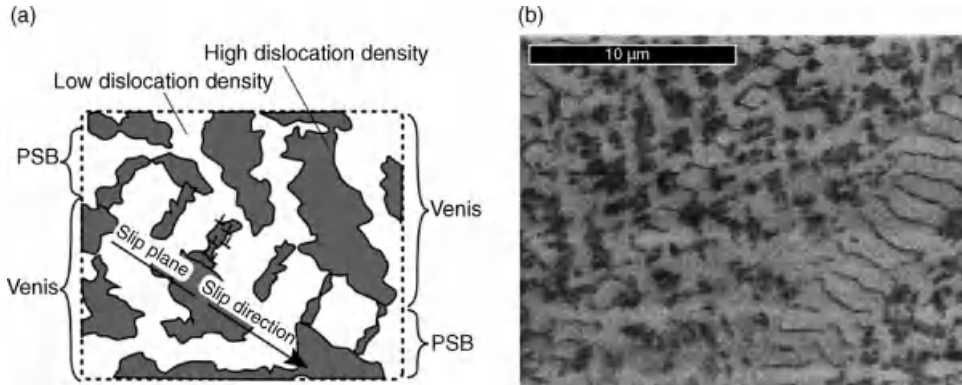


Figure 4.7 (a) Ladder-like structures of persistent slip bands (PSBs) along the primary slip planes. After Ref. [7]; (b) Transmission electron microscopy image of a Ni polycrystal following fatigue testing with distinct PSBs. Illustration courtesy of H. Vehoff *et al.*, WWM, Universität Saarland.

dynamically loaded plain bearings, and also in elasto-hydrodynamically lubricated gearwheel pairings [8]. Protection against surface fatigue is offered by the same measures as for volumetric material fatigue and, above all, the application of compressive stresses to the edge zone of the component surface has proven to be of value. Mechanical surface treatment processes (such as shot-blasting) or thermochemical diffusion processes (such as nitriding or carbonization) can be employed in this case. Polished surfaces show a better stability against surface fatigue, as they exhibit fewer notches that would represent potential regions for the formation of cracks.

4.2

Types of Wear






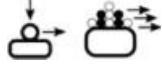




Wear processes are classified according to their type of motion, tribological loading, and system structure (in particular of the materials concerned) into different types of wear [1], in which the different mechanisms of wear usually occur simultaneously (Table 4.1). Based on an analysis of the different forms of wear (type and form of the wear particles, alterations to the surface), it is possible to determine which wear mechanisms are involved.

4.3

Wear Parameters




The analysis of wear allows the determination of direct, normalized, or indirect wear parameters [1]. Direct wear parameters describe alterations in the form or mass of a system component, whereas normalized parameters are derived from direct

Table 4.1 Types of wear and frequently occurring wear mechanisms [1].

Elements of system structure	Tribological load (symbols)	Wear type	Effective mechanisms			
			Adhesion	Abrasion	Surface fatigue	Tribochemical reaction
Body (1) Intermediate material (3) (hydrodynamic) Body (2)	Gliding rolling (no slip) Rolling (slip) Impact 	—			X	X
Body (1) Body (2) (Solid friction, boundary friction, mixed friction)	Sliding 	Sliding wear	X	X	X	X
	Rolling (no slip) Rolling (slip) 	Rolling wear (no slip) Rolling wear (slip)	X	X	X	X
	Impact 	Impact wear	X	X	X	X
	Oscillating 	Fretting wear	X	X	X	X
Body (1) Solid particle (2)	Sliding 	Scoring abrasion, Erosion		X		X
Body (1) Body (2)	Sliding 	Particle sliding wear, three-body-wear		X	X	X
Solid particle (3)	Rolling (slip) Grinding 	Particle rolling wear (slip) Grinding wear		X	X	X
Body (1) Fluid with particles (2)	Streaming 	Flush wear (erosion wear)		X	X	X
Body (1) Gas with particles (2)	Streaming 	Sliding jet wear (erosion wear)		X	X	X

(Continued)

Table 4.1 (Continued)

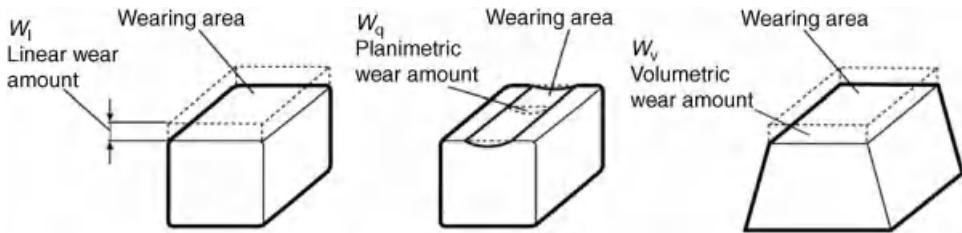
Elements of system structure	Tribological load (symbols)	Wear type	Effective mechanisms			
			Adhesion	Abrasion	Surface fatigue	Tribochemical reaction
	Impact 	Impact jet wear, Inclined jet wear		X	X	X
Body (1) Fluid or Gas (2)	Streaming Vibrating 	Material cavitation, Cavitation erosion			X	X
	Impact 	Droplet erosion			X	X

parameters. These represent a normalized value, in relation to a reference value, such as length and/or time, and are also referred to as “wear rates.” These parameters are used preferentially in connection with tribological systems, as their information value in respect of the tribological system is greater than that of direct parameter values.

To arrive at a well-defined loss of functionality in advance is based on the measurement of indirect parameters, where the information refers to a component or to the entire system in respect of required time or throughput. The parameters that can be measured are listed in Figure 4.8. Recommendations for the use and selection of wear parameters are also offered [1] which are helpful when designing the methods of testing. A detailed overview of the development and principles of the different calculation models for characteristic wear values is provided in Ref. [9].

Wear parameters:

Direct:	Alterations to the form or mass of a tribological component
Normalized:	Direct measurement, normalized to a reference value
Indirect:	Statement of loss of functionality of a tribo element or system, in respect of required time or throughput



Amount of waer Reference value	Linear	Planimetric	Volumetric	Mass-like	Designation
	W_l m	W_q m^2	W_v m^3	W_m kg	
Load duration t [h]	$W_{l/t}$	$W_{q/t}$	$W_{v/t}$	$W_{m/t}$	Wear velocity
Load duration s [m]	$W_{l/s}$	$W_{q/s}$	$W_{v/s}$	$W_{m/s}$	Wear distance ratio
Throughput z [m^3 ; kg; pieces]	$W_{l/z}$	$W_{q/z}$	$W_{v/z}$	$W_{m/z}$	Wear throughput ratio

Figure 4.8 Definition of direct wear parameters and an overview of normalized wear parameter measurements [1].

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5

Tribological Materials

Today, a choice of some 40 000–80 000 materials is available to the design engineer. Over the historical development of materials engineering, a shift in the preferably used materials can be observed, which is taking place at an increasing rate (Figure 5.1). This chapter provides only a very brief overview, in the form of material groups that have gained importance in tribological systems, the aim being to explain the most important terms and definitions from the point of view of tribology.

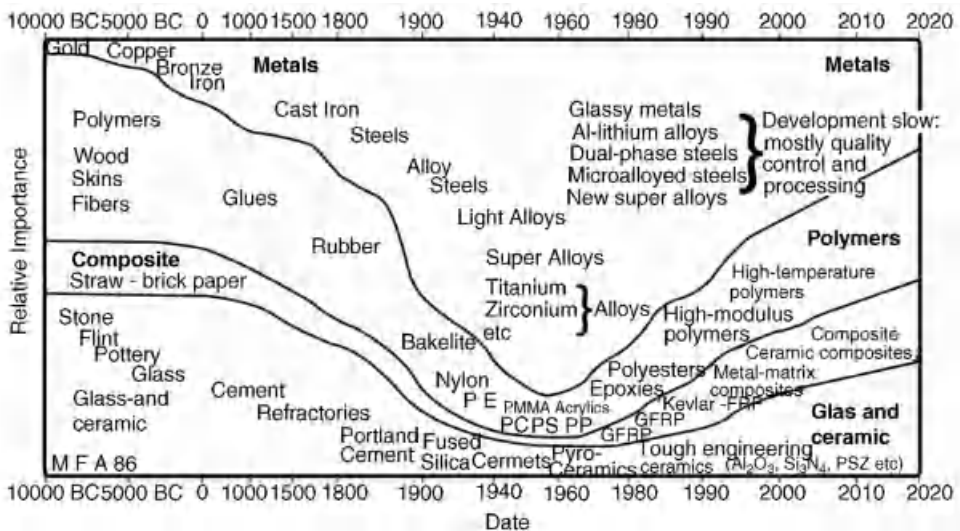


Figure 5.1 The evolution of engineering materials with time. “Relative Importance” in the stone and bronze ages is based on assessments of archaeologists; that in 1960 is based on allocated teaching hours in UK and US

universities; and that in 2020 on predictions of material usage in automobiles by manufacturers. The time scale is nonlinear. The rate of change is far faster today than at any previous time in history [1].

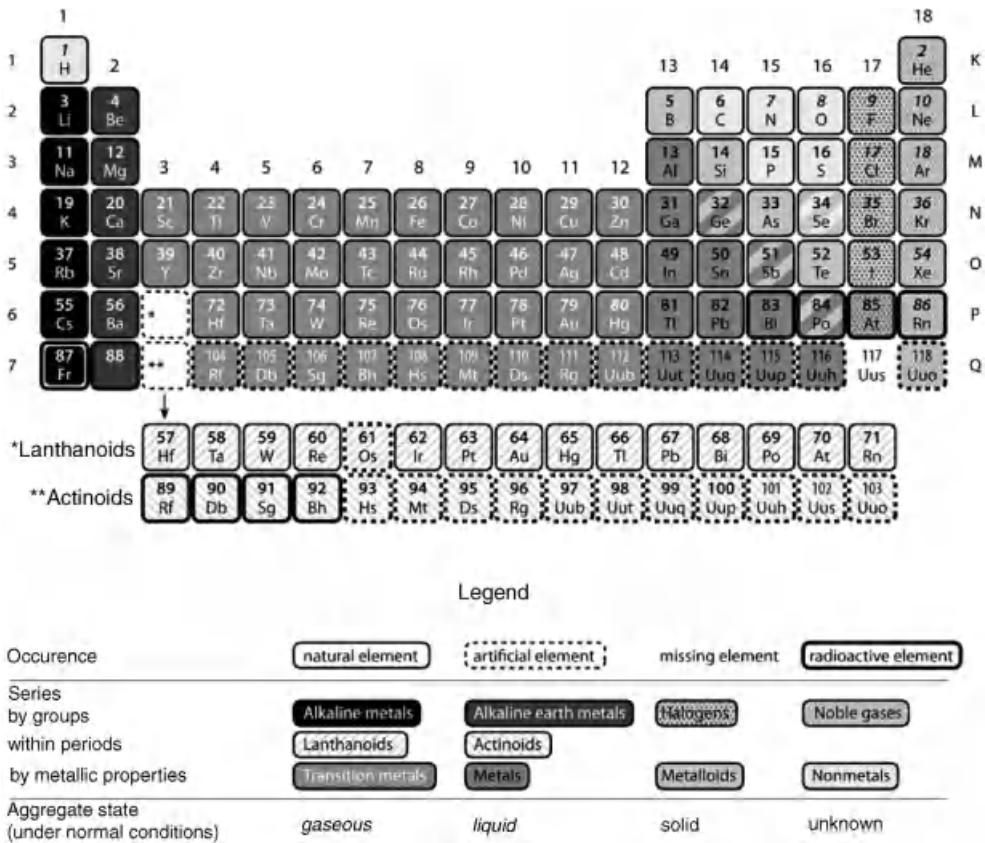


Figure 5.2 The Periodic System of the elements.

Beginning with the basic chemical element (Figure 5.2), the chapter deals with important material properties, such as the lattice structure, the melting point, and the modulus of elasticity, as these parameters decisively influence the tribological properties such as strength, hardness, and material behavior at high temperatures. In consideration of environmental and resource protection, the use of lightweight materials is becoming increasingly important for the design of moving parts; thus, the materials' densities are also of interest. The most important alloy concepts will also be discussed.

Comprehensive data collections for the selection of materials have been compiled above all by Michael F. Ashby (e.g., "Materials Selection in Mechanical Design" [1, 2]), on the basis of which he has developed material identification cards, for example, for the ratio of the modulus of elasticity to the density (Figure 5.3) or of the fracture toughness to the strength (Figure 5.4).

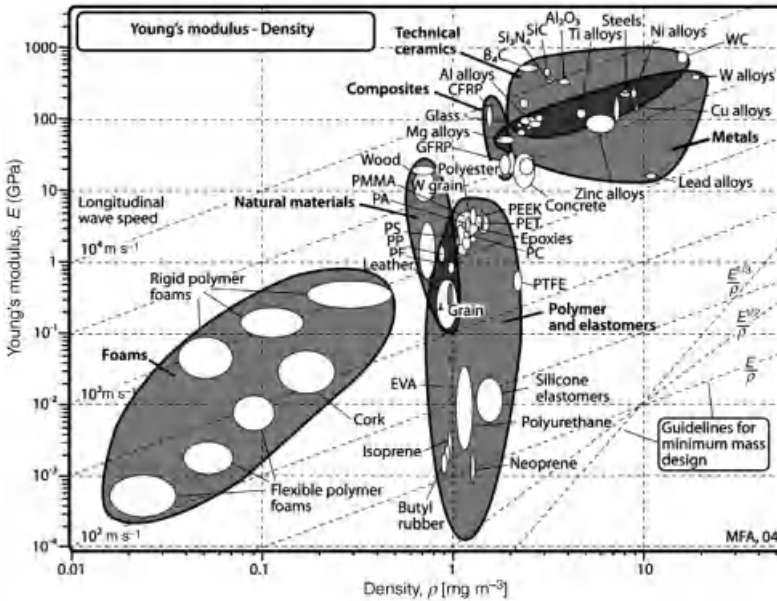


Figure 5.3 Young's modulus E , plotted against the density ρ . The lines of constant E/ρ , $E^{1/2}/\rho$ and $E^{1/3}/\rho$ allow selection of materials for minimum weight, deflection-limited, design [2].

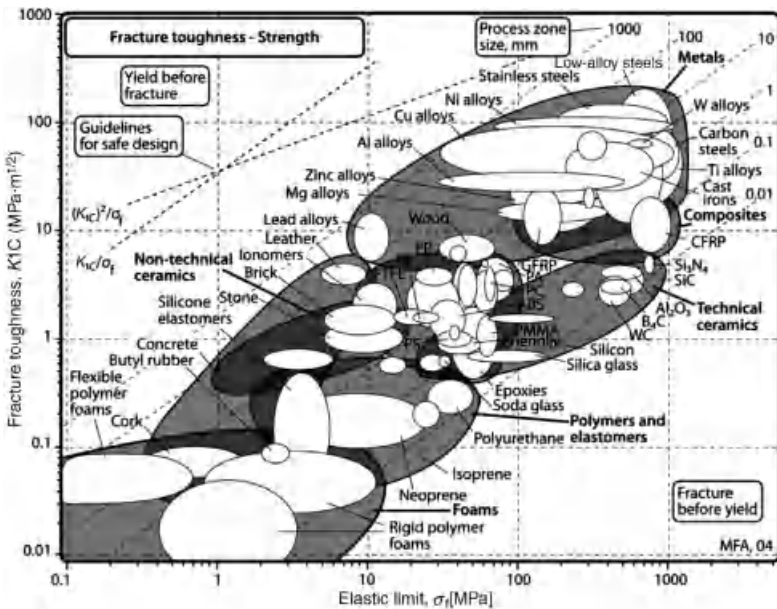


Figure 5.4 Fracture toughness K_{IC} plotted against the failure strength σ_f . The contours show the value of K_{IC}^2/σ_f – roughly, the diameter of the process zones at a crack tip. The design guidelines are used in selecting materials for damage-tolerant design [2].

5.1

Basic Principles of Materials Science

Compared with metallurgy, the materials science treatment of ceramics and polymers is relatively new. In their basic relationships, however, metals, ceramics and polymers can be largely described within a single framework, which can essentially be derived from the basic principles of metallurgy [3]. For the design of tribological components, above all, the strength properties and the behavior of the material at higher temperatures are of importance, and these will be discussed here in general terms.

5.1.1

Influencing the Strength Properties

The term “strength” refers to the resistance of a material to a change in shape, arising from its atomic structure and micro-structure. The mechanical loading which can cause a change in shape may be in the form of radial and axial stresses, shear stresses and tangential stresses, as well as torques and bending moments. Pressure applied to all sides can also cause deformation. A distinction can be made between elastic deformation (which is completely reversible when the loading is removed, allows only very limited deformation, and follows Hooke’s law), and plastic deformation, which is irreversible. There is no linear relationship between the change in shape and deformation. The mechanical properties of materials are influenced not only by their composition, but also to a large extent by the state of their microstructure – that is, the crystal structure, grain size, grain form, and type and density of lattice defects (Table 5.1).

According to loading requirements, strength properties are demanded of technical materials which concern both the entire cross-section of the component and only certain zones, for example, the surface. According to the composition of the material, in addition to its state, temperature, form of loading and loading velocity, several different strengths can be achieved. The technically relevant static strength parameters are determined from the stress–strain diagram (Figure 5.5), which is compiled from tensile tests with standard samples (DIN 50 125). The tensile test

Table 5.1 Lattice defects according to their spatial extent.

Point defects (0-D)	Line defects (1-D)	Planar defects (2-D)	Bulk defects (3-D)
<ul style="list-style-type: none"> • Vacancies • Interstitial atoms • Interstitial impurity atoms • Substitutional impurity atoms 	<ul style="list-style-type: none"> • Screw dislocations • Edge dislocations 	<ul style="list-style-type: none"> • High-angle boundaries • Low-angle boundaries • Twin boundaries • Phase boundaries 	<ul style="list-style-type: none"> • Voids • Clusters

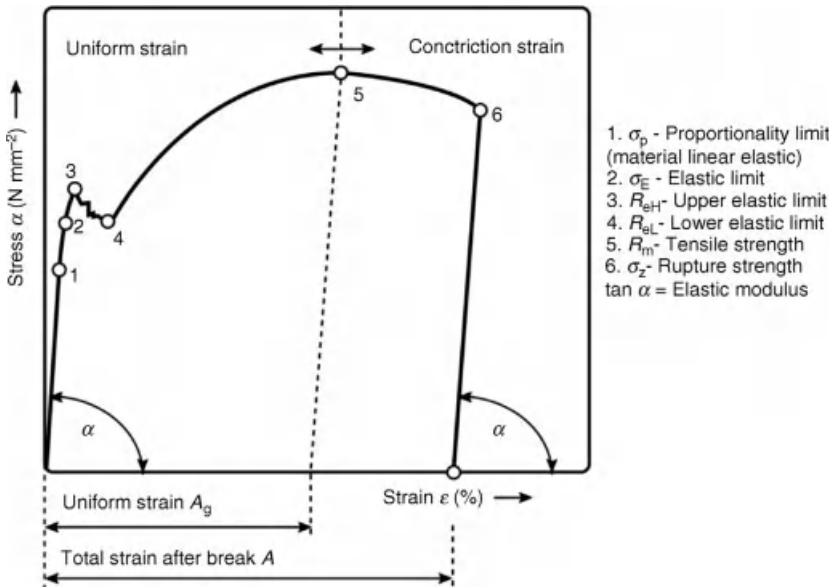


Figure 5.5 Schematic representation of a stress–strain diagram (e.g., for soft steel).

itself is used predominantly for metallic materials and polymers, and is standardized in DIN EN 10 002. For brittle materials, such as glass and ceramics, as well as cast iron, the bending test or compression test is preferentially employed. Important terms are:

Elasticity:	Linear relationship between stress and strain, reversible
Modulus of elasticity E :	Constant of proportionality between normal stress σ and strain ϵ
Shear modulus G :	Constant of proportionality between shear stress τ and shear strain γ
Hooke's law:	$\sigma = E \epsilon$ or $\tau = G \gamma$
Poisson number ν :	(also Poisson's ratio) – Ratio of cross-section diminution to elongation under tensile stress. Here: $E = 2 \cdot (1 + \nu) G$ (approximate values: metals $\nu \approx 0.3$; ceramics $\nu \approx 0.25$; thermoplastics $\nu \approx 0.35$)
Yield point:	Stress above which plastic deformation occurs, that is: yield strength for tensile loading compressive yield point for compressive loading torsion limit for torsional loading
Strength:	Resistance to plastic deformation
Ductility:	Capability for undergoing plastic deformation
Toughness:	Resistance to the propagation of cracks or fracture

In contrast to an ideal crystal, for a real crystal the critical shear stresses are two orders of magnitude lower. Whereas, an ideal iron crystal has a strength of 28 000 MPa, real technical pure iron has a strength of only 240 MPa. The reason for this is to be found in the lattice defects of a real crystal, above all screw dislocations and edge dislocations. Notably, real crystals grow with dislocations, which further propagate during plastic deformation (Frank–Read sources); assuming that the plastic deformation takes place primarily due to the migration of dislocations along the slip planes of a crystal lattice, then in principle two methods are available for improving the strength in a real component:

- 1) Reducing the dislocation density, and thus approximating the ideal crystal. Technically, this is realized with fibers and whiskers, which must have a diameter of $D \leq 1 \mu\text{m}$, because dislocation-free zones occur for this order of magnitude. Normally, per μm^2 there exists one penetration point of a dislocation line. Fibers and whiskers are used in composite materials as reinforcement (see below, point 2 b).
- 2) Inhibiting the migration of dislocations by incorporating obstacles. Here, there are two possibilities for actually existing polycrystalline materials:
 - (a) Inhibiting translation, that is, slippage, for example, by:
 - (i) **Cold forming.** The dislocations that occur and migrate during forming are seen to pile up with increasing deformation level as forming progresses; as a consequence, they block each other and ultimately are no longer capable of slippage (Lomer–Cottrell dislocations). The probability of work hardening increases with the number of slip planes in the crystal lattice. Other dislocations migrate to the grain boundary, where they are stopped and cause subsequent dislocations to pile up. This means that the probability of work hardening increases as the grain size of the material is decreased.
 - (ii) **Mixed crystal formation.** One type of atom dissolves in the matrix of the other and, depending upon the relative radii of the atoms, forms either an interstitial crystal or a substitution mixed crystal. Such lattice distortions result in a substantial increase in strength.
 - (iii) **Transformation hardening (e.g., martensitic transformation).** Prerequisite for a martensitic transformation is an allotropic phase transformation, which the material passes through while cooling. Furthermore, the high-temperature modification must have a greater solubility for alloying elements than the low-temperature modification. During rapid cooling, the excess alloying element is forced to remain dissolved, leading to a pronounced lattice distortion which improves the strength and hardness.
 - (b) Incorporation of multidimensional obstacles, such as:
 - (i) **Grain boundaries (fine-grain hardening).** Slip planes end at grain boundaries, which is why grain boundaries represent an insurmountable obstacle for the migration of dislocations. The pile-up

of dislocations at grain boundaries results in the build-up of a strong counter-stress for the further migration of dislocations. The contribution of the grain boundaries to the hardening of the material increases as the grains of the material become finer (more boundary layers per unit volume) and the dislocation density falls off. The yield point (which is dependent on the dislocation density) is more strongly influenced by the grain size than by the tensile strength (Hall–Petch relationship).

- (ii) **Precipitation (precipitation hardening).** This can be regarded as a continuation of mixed crystal formation. Here again, the different solubilities of atoms in host lattices at high and low temperatures are exploited. At high temperatures, alloys capable of precipitation hardening must consist entirely of mixed crystals. During slow cooling, due to the decreasing solubility with a drop in temperature for one type of atom or component, segregates precipitate out of the mixed crystal.
- (iii) **Foreign particles by dispersion and fiber reinforcement.** The improvement in strength derives from the dispersed distribution of foreign particles or the incorporation of fibers in the material. The difference compared with precipitation hardening lies in the fact that the impurity particles do not dissolve in the matrix at high temperatures.

Until now, the strength properties discussed have referred to static loading. For dynamic loading (oscillatory or tumescent), as a result of material fatigue (see also Section 4.1.4), the materials show a fundamentally different behavior. Material fatigue can also result in rupture at load amplitudes below the static yield point. Due to the alternating tensile and compressive loading, dislocations already begin to migrate back and forth at low stress amplitudes. With prolonged cyclical loading, dislocations accumulate along the slip planes to slip bands, which become visible on the surface as intrusion or extrusion (Figure 5.6). The grooves arising from intrusion form crack nuclei – that is, starting points for the formation of cracks [4]. The incipient cracks continue to grow step-wise, and the residual cross-section ultimately fails as an overload breakage [5]. The introduction of compressive residual stresses in the regions of the material close to the surface can suppress the danger of crack formation and propagation.

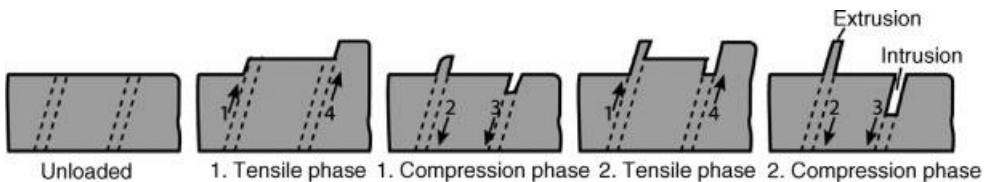


Figure 5.6 Formation of extrusions and intrusions (1..4: active slip planes) [4].

5.1.2

Influencing the Material Behavior at Higher Temperatures

The materials used in the construction of tools, machines, and systems are subjected to increasingly greater mechanical and thermal loadings. Whereas, purely mechanical loading can be taken into consideration via structural measures (by enlarging the load-bearing cross-section), at higher temperatures problems arise which can be solved only with the use of suitable materials. The general requirements for heat-resistant and high-temperature materials can be expressed in terms of the parameters high-temperature strength from the mechanical viewpoint, and high-temperature corrosion resistance from the chemical viewpoint. Decisive for the values of these parameters is the metallurgical load capacity of the material – that is, the extent to which a material suffers deterioration of the micro-structural properties over the specified service life at the given operating temperature. Here, above all it must be noted that thermally activated processes can destroy the micro-structural alterations introduced for the improvement of the strength (see Section 5.1.1). The thermally activated processes include:

- Diffusion
- Recovery, recrystallization and grain growth
- Creep and stress relaxation
- Thermo-mechanical fatigue.

5.1.2.1 Diffusion

Diffusion refers to material transport within solid, liquid, and gaseous matter, which occurs by the atomic exchange of positions of individual atoms. Diffusion is characterized by a macroscopic mass transport, which takes place as a result of the migration of individual atoms (in steps greater than one atom distance). Diffusion arises due to the presence of differences in concentration, giving rise to different enthalpies in the different regions of the system. Whilst the system strives to attain a thermodynamically more stable state, this requires an activation energy, in order for the atom to change its position. As a rule, this energy is introduced in the form of thermal energy, which causes the atoms to oscillate about their given positions. The lowest energy is required for diffusion via vacancies, so that here the highest probability exists. Moreover, the vacancy concentration c_L in the crystal lattice increases with temperature, because – due to the work of expansion with the introduction of heat – atoms are transported out of the volume to the surface, leaving vacancies behind. A detailed thermodynamic description of the formation of vacancies is provided in Ref. [3]. While the vacancy concentration at room temperature is approximately 10^{-12} (i.e., about one vacancy per mm^2), at the melting point the vacancy concentration rises to 10^{-4} (i.e., 100×10^6 vacancies per mm^2) [4]. The number of vacancies is calculated according to:

$$\text{Vacancy concentration } c_L : \quad c_L = e^{-\frac{\Delta G_B^c}{R \cdot T}}$$

where

G_B^L = enthalpy of formation for vacancies

R = general gas constant (= 8.314 472 J K mol⁻¹)

T = absolute temperature (K)

Here, it is possible to distinguish between three types of diffusion: volume diffusion (see also Section 6.1.4); grain boundary diffusion; and surface diffusion. As the packing density at grain boundaries is much lower than within the grains and the vacancy concentration and the degree of disorder are at the same time also greater, grain boundaries are always the preferred diffusion paths. Surface atoms have fewer neighboring atoms than atoms within the grain, so that surfaces possess higher energy potentials (surface energy); this favors the diffusion of atoms on the surface so as to obtain an energetically favorable position, with the goal of dissipating the maximum possible energy.

5.1.2.2 Recovery, Recrystallization, and Grain Growth

With the introduction of thermal energy, the alterations to the properties of plastically deformed materials take place in three stages: (i) recovery (ii) recrystallization; and (iii) grain growth. Due to plastic deformation, the energy content of the material is noticeably increased. Thermodynamically, this means that the micro-structural state is displaced in the direction of increasing nonequilibrium (higher potential). The stored energy is primarily comprised of the elastic distortion energy of the piled-up dislocations, the concentration of which rises from 10^{5...6} mm mm⁻³ to 10^{8...10} mm mm⁻³ during deformation. With sufficient activation energy (temperature rise), energy is dissipated by the healing and rearrangement of the lattice defects (recovery) or grain re-formation as a result of nucleation and grain growth (recrystallization). The number of energy-rich dislocations again falls off to the value of the nondeformed material, and at the same time the strength and hardness decrease [4]. The temperature at which the onset of recrystallization occurs depends upon the material; the higher the melting point T_S of the material, the higher the temperature for the onset of recrystallization. For many metals, the recrystallization temperature can be given as $T_R \approx 0.4 \times T_S$ (in K).

5.1.2.3 Creep and Stress Relaxation

At increased temperatures ($\sim 0.4 \times T_S$), in metallic materials under constant loading, a plastic deformation – described as “creep” – can occur below the yield strength R_e . The creep resistance is determined in an endurance test, in which a sample held at a constant temperature is subjected to a constant stress σ (mostly at constant loading, as this is easier to realize technically). The resulting change in shape ε is measured as a function of time and plotted in an $\varepsilon = f(t)$, ($\sigma, T = \text{constant}$) diagram (Figure 5.7). Creep takes place at different rates, allowing the division of the creep curve into three regions:

- I. Transient creep (primary region): Deformation at a decreasing rate, due to the pile-up of dislocations blocking each other. Recovery processes simultaneously take place.

The information obtained from creep investigations does not always yield reliable guide values for the material behavior in practice. For example, it is often found that an applied load will change over time so that, if materials subject to creep loading are joined to materials which are only elastically deformed, stress relaxation will reduce the stress in both materials. Numerous examples of stress relaxation have been applied in engineering, including screw connections and pre-stressed concrete.

5.1.2.4 High Temperature Strength

High-temperature strength is the strength of a material at higher temperatures. To determine the heat strength of a material, it is not sufficient to determine the relevant parameters in tensile tests conducted at higher temperatures, and to use these as a basis for calculation. At higher temperatures, the specific strength properties of every material show a pronounced time dependence. The temperature limit, above which a noticeable time dependence is observed, roughly coincides with the recrystallization temperature. Moreover, the cyclic thermal stressing and mechanical stressing can cause fatigue. Due to thermal expansion, the crystal lattice grows and shrinks with cyclic thermal stressing, resulting in cyclic mechanical tensile and compressive stressing of the microstructure, and giving rise to the same phenomena as for isothermal cyclical mechanical loading. Whereas, for temperatures below the recrystallization temperature, the yield point at elevated temperatures is altogether sufficient, at higher operating temperatures the observation of the influence of time on the material behavior is indispensable. This includes all parameters determined in short-term and long-term testing, including:

- high-temperature yield strength and high-temperature tensile strength in tensile testing at elevated temperatures (short-term testing: thermal, static)
- creep strength in creep–rupture testing: creep resistance, creep limit, creep–rupture strength (long-term testing: thermal, static)
- high-temperature fatigue strength (thermal shock resistance) (short-term or long-term testing: thermal, dynamic).

The material behavior at elevated temperatures furnishes the basis for different methods of improving the high-temperature strength:

- **Increasing the melting point:** Alloying with metals having a high melting point and therefore a high recrystallization temperature (e.g., W, Mo, Ta, Nb), yielding mixed crystals which also have a high recrystallization limit.
- **Avoiding phase changes of allotropic materials:** From the standpoint of alloys, the high-temperature modification of different allotropic materials can be stabilized. A typical example of this is steel. Alloying with Ni, C, Co, Mn, and N stabilizes the austenitic face-centered cubic phase at room temperature. The lattice rearrangement in the ferritic body-centered cubic phase is suppressed, and the resultant lacking plasticity due to position exchange increases the creep stability. Furthermore, the face-centered cubic lattice possesses a higher packing density than the body-centered cubic lattice, inhibiting diffusion by the exchange of atomic positions.

- **Precipitation hardening:** The high-temperature strength can be influenced with alloys, by inducing highly temperature-stable precipitations. A typical example is the special carbides in steel, formed from alloying elements with a high affinity for carbon. This includes such refractory metals as Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, and W, as well as Co, Mn, and Ni, having high melting points. The stability of the phases increases with their complexity. Besides hard phases, intermetallic precipitations, such as the γ' phase Ni_3Al in super-alloys, are also utilized. With precipitation hardening for the improvement of high-temperature strength, three rules must be observed:
 - The type and distribution of the precipitation influence the magnitude of the creep resistance.
 - Due to the danger of embrittlement and inter-crystalline corrosion, precipitations at grain boundaries are to be avoided.
 - The hardening temperature must lie above the operating temperature, as otherwise over aging can set in.
- **Dispersion hardening:** This method of improving high-temperature strength is identical with the methods described for improving resistance at temperatures below the recrystallization temperature (Section 5.1.1)
- **Hot-cold forming:** Hot-cold forming (also referred to as semi-hot forming) takes place at higher temperatures, though below the recrystallization temperature in the recovery region. The operating temperature must lie below the forming temperature, in order that no softening occurs due to recovery. The degree of deformation must be carefully calculated, as the recrystallization temperature falls off with increasing deformation.
- **Diminishing the grain boundary:** A different behavior in terms of strength as a function of temperature is observed at the grain boundaries compared to inside the grains. While the strength of the grain boundary is greater at lower temperatures, at high temperatures the strength inside the grain is greater. For this reason, at lower temperatures the materials preferentially undergo trans-crystalline fracture within the grain, and at higher temperatures inter-crystalline fracture at the grain boundaries. The temperature at which the strength inside the grain and the strength of the grain boundary are identical is referred to as the “equicohesive temperature,” attained in relation to the beginning of recrystallization. In order to avoid material failure at grain boundaries when used at high temperatures, directionally solidified alloys or single crystal alloys are employed.

5.2

Metallic Materials

The majority of the chemical elements are metallic in character. Due to the state of their atomic binding, metals possess good electrical conductivity, which decreases with increasing temperature, and a high thermal conductivity. For technical applications, alloys consisting of two or more elements are preferentially used, so as to allow the selective definition of physical, chemical, and mechanical

properties. With a current increasing demand for the weight reduction of materials, the proportion of lightweight metals used – especially of aluminum alloys, but also of magnesium and titanium alloys – is increasing. In tribological applications, copper materials are also important. Although, in the machinery sector, iron-based materials such as steel and cast iron still occupy the largest proportion of metallic materials, for highly stressed tribological components, specialized hard alloys and super-alloys have been developed which, in addition to the basic iron materials, include cobalt- and nickel-based alloys. Here, particular importance is attached to the refractory metals, which – due to their high affinity for B, C, N and O and their high melting points – represent important alloying elements. Finally, intermetallics which can selectively contribute to improving the strength of alloys should also be mentioned. Because of their complex crystal structures, intermetallics possess special properties which make them increasingly interesting as structural materials.

5.2.1

Lightweight Metals

Lightweight metals are the group of nonferrous metals and their alloys with a density $\rho \leq 4.51 \text{ kg dm}^{-3}$ for the pure metal. Of technical interest here are aluminum, magnesium, titanium, and their alloys (see Table 5.2). Besides high-strength steels and compound materials, lightweight metals represent the most important group of materials for lightweight construction. Their applications occur principally in the area of transportation engineering (aviation/aerospace, automotive industries), although with the current increased interest in preserving resources, lightweight constructions are becoming increasingly important in all areas of machine and system engineering (Figure 5.8).

5.2.1.1 Aluminum and Aluminum Alloys

After steel, aluminum is today the most widely used metal and, in the group of lightweight metals, the most important [7]. Aluminum comprises approximately 8% of the Earth's crust and, after oxygen (ca. 49%) and silicon (ca. 23.5%), is the third most common element; it is, therefore, the most widely represented metal, before

Table 5.2 Physical and mechanical properties of lightweight metals and iron.

	Symbol	Crystal structure	Density ρ (g cm^{-3})	Melting point T_S ($^{\circ}\text{C}$)	Youngs modulus (MPa)
Aluminum	Al	fcc	2.70	660.5	70 000
Magnesium	Mg	hcp	1.74	648.8	44 100
Titanium	Ti	hcp > 882 $^{\circ}\text{C}$ bcc	4.51	1660	110 000
Iron	Fe	bcc; > 911 $^{\circ}\text{C}$ fcc > 1392 $^{\circ}\text{C}$ bcc	7.87	1535	210 000

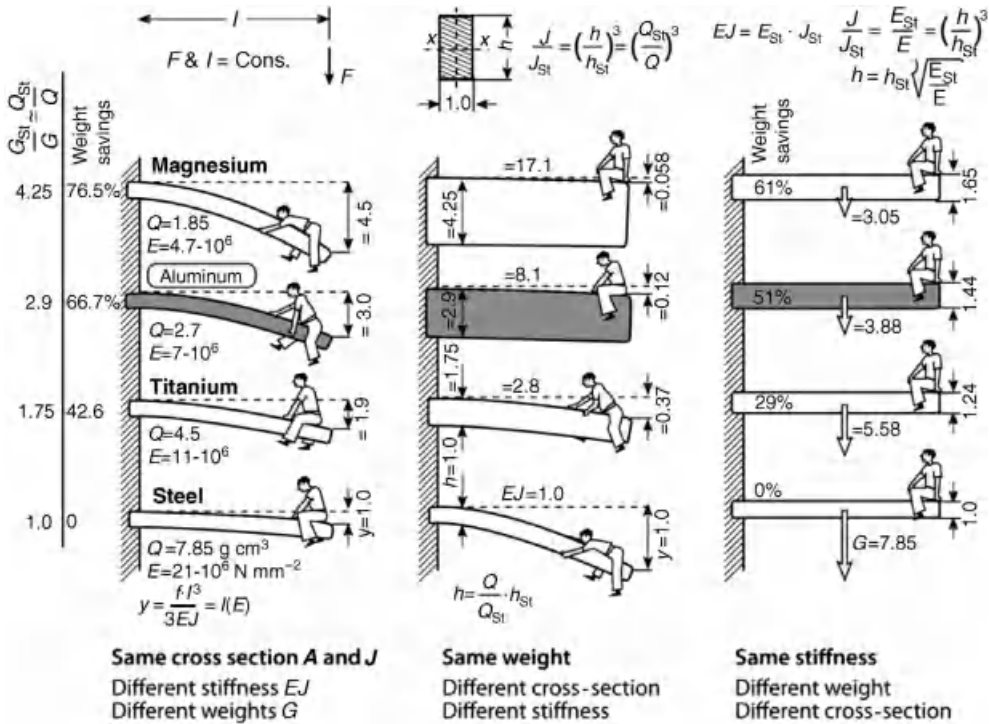


Figure 5.8 Comparison of the mechanical properties of aluminum, magnesium and titanium with those of steel [6].

iron (ca. 5%), magnesium (ca. 2%) and copper (ca. 0.01%). Due to its high affinity for other elements (particularly oxygen), aluminum is not found in pure form in nature. Primary aluminum is extracted as an intermediate product largely from bauxite, by way of $\gamma\text{-Al}_2\text{O}_3$ (clay). Al_2O_3 belongs to the most stable chemical compounds, and its reduction to metal requires a very high expenditure of energy [4]. Only with the development of dynamos (Werner von Siemens, in 1867) was sufficient electrical energy made available for the production of aluminum by electrolysis. Once extracted, aluminum can be recycled without problem; for the extraction of secondary aluminum, only 5% of this energy is required, permitting high recycling rates of 75–95% in Germany.

Conversely, however, the high affinity for oxygen also means that immediately stable protective oxide layers form (passivation) on metallic aluminum when it is exposed to the atmosphere. The oxide layers of aluminum are very dense, and therefore serve as good diffusion barriers; moreover, as the layers are not electrically conductive, this enhances their resistance to corrosion. Indeed, these layers are responsible for the very high corrosion resistance of aluminum in the atmosphere and in weak acids, although they rapidly dissolve in basic media. An additional improvement of the protective effect is achieved through the converting process (see

also Section 6.2.1). From a technical point of view, the most important properties of aluminum are its [8]:

- favorable ratio of strength to density;
- corrosion resistance in relation to the atmosphere and weak acids;
- favorable ratio of electrical and thermal conductivity to density; and
- good formability, due to its face-centered cubic structure.

The properties of aluminum can be influenced over a wide range by alloying with other elements. The following description of the influence of the main alloying elements Mg, Si, Cu, Zn and Mn is taken from Ref. [9]. Aluminum alloys can be divided into “wrought alloys” and “cast alloys,” as well as hardenable and nonhardenable naturally hard alloys. The improvement in strength is the result of mixed crystal formation and strain hardening. For hardened Al alloys, a greater strength can be obtained by the precipitation of intermetallic phases (Al_2Cu , Mg_2Si , MgZn_2). Typical particle diameters for hardenable Al alloys are approximately 1 nm, while typical particle spacings are 10–20 nm; consequently, in a 1 mm^3 sample of alloy there are between 10^{10} and 10^{20} such particles [4]. Hardening takes place by solution annealing (e.g., $520\text{ }^\circ\text{C}$ for AlMgSi), quenching and, finally, by natural aging or hot aging (e.g., $125\text{--}175\text{ }^\circ\text{C}$ for AlMgSi).

Magnesium: With an increasing magnesium content, the elastic limit σ_p and the tensile strength R_m increase, while the elongation at fracture decreases by around 3 wt% Mg, but then increases again slightly. AlMg alloys are not brittle at low temperatures; only a few weight-percent of Mg renders aluminum stable against seawater and thus suitable for shipbuilding. Magnesium is also used for both wrought alloys and cast alloys.

Silicon: Silicon increases the flowability of the melts and lowers the melting point of aluminum cast alloys, causing a decisive improvement in both castability and mold-filling capacity. Silicon also helps to prevent shrinkage during solidification.

Copper: Copper improves the strength of aluminum, but also lowers the corrosion resistance due to its large electrochemical potential difference from aluminum. Copper is used for both wrought alloys and cast alloys; in the latter case it helps to reduce shrinkage during solidification.

Zinc: As an alloying element, zinc alone has virtually no influence on the strength properties. However, when combined with other elements, such as magnesium and copper, zinc achieves the highest strength properties compared with other alloy systems. The danger of a lack of corrosion resistance can be compensated by heat treatment. In cast alloys, zinc improves both the flowability and mold-filling capacity.

Manganese: Manganese improves the shaping behavior and, within limits, also the strength. The addition of manganese is limited to 1.5 wt% for wrought alloys, as brittle Al_6Mn phases would otherwise cause problems with further processing.

5.2.1.1.1 Aluminum Wrought Alloys Al wrought alloys are processed by rollers, extruding machines, pulling and forging to semi-finished products. Delivery is in the form of strand casting formats to finishing plants [7] for further processing, to profiles, films, sheets, and tubes. Identification is standardized in accordance with

Table 5.3 Classification of aluminum wrought alloys according to alloy series after DIN EN 573, identified with the specification EN AW.

	Series	Alloying elements	Groups	Applications	
Naturally hard	1xxx	>99% Al	Al	Films, packaging, electronics	
	3xxx	Mn	Mg, Cu	AlMn	Tubing, containers, heat exchangers
	4xxx	Si	Mg, Bi, Fe, CuNi	AlSi	Forge pistons, welding filler materials
	5xxx	Mg	Mn, Cr, Zr	AlMg(Mn)	Preformed car body parts, vessels
	8xxx		Fe, FeSi, FeSiCu	Special alloy	
Hardenable	2xxx	Cu	Mg, Mn, Bi, Pb, Si	AlCuMg	Screws, injection molds, gearwheels
	6xxx	MgSi	Mn, Cu, Pb	AlMgSi	Profiles, tubing, forged vehicle parts
	7xxx	Zn	Mg, Cu, Ag, Zr	AlZnMg(Cu)	Vehicle construction (steering/braking parts)

DIN EN 573, with the specification EN AW (W = wrought alloys) and a four-digit code number, divided into eight alloy series corresponding to the most frequently used alloying elements (Table 5.3). The alloys of the 6000 series are the most frequently used hardenable aluminum alloys [7]. Because of their comparatively high melting points, together with their high strengths, aluminum wrought alloys are particularly favored for aviation and automotive constructions and also in general machine construction, as they are comparatively well-suited for welding (see Figure 5.9).

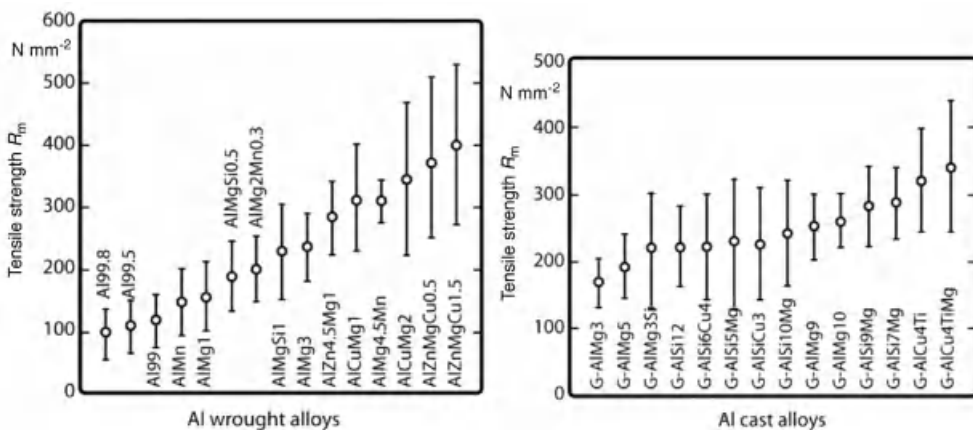
**Figure 5.9** Comparison of the tensile strength ranges for important aluminum alloys.

Table 5.4 Classification of aluminum cast alloys with silicon as main alloying element in accordance with DIN EN 1706, identified with the specification EN AC.

Series	Alloying elements		Examples	Applications
	>99% Al		Al	
41xxx	Si	Mg, Ti		
42xxx	7% Si	Mg	AlSi7Mg	Engine housings, gearbox covers, wheel rims
43xxx	10% Si	Mg	AlSi10Mg	Engine and machine construction
44xxx	Si		AlSi	Complex thin-walled cast parts
45xxx	5% Si	Cu	AlSi5Cu	Engine blocks
46xxx	9% Si	Cu	AlSi9Cu	Motor and gearbox housings
47xxx	Si	Cu	AlSiCu	Cylinder heads
48xxx	Si	Cu, Ni, Mg	AlSiCuMgNi	Pistons for combustion engines

5.2.1.1.2 Aluminum Cast Alloys Al cast alloys are processed by sand casting, ingot mold casting and die casting, with 50% allocated to diecasting. Typical areas of application are engine blocks and other components for the automotive industry (see Figure 5.9) [7]. Cast alloys are identified by the specification EN AC (C = cast alloy), in accordance with DIN 1706, followed by a five-digit code. By far the greatest part of Al cast alloys are based on the binary system Al–Si with 2–20 w% Si. A detailed listing of the second digit is provided in Table 5.4.

5.2.1.2 Magnesium and Magnesium Alloys

Magnesium is not found in pure form in nature, but as compounds with other elements. The most important ore minerals for the extraction of magnesium are magnesite (MgCO_3) and dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$). Magnesium also occurs in large amounts in seawater, to the extent of 1.3 kg m^{-3} . Although a small amount of pure magnesium was produced as early as 1808 by Sir Humphrey Davy, its industrial production did not begin until 1886, with the electrolysis of molten carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6 \text{ H}_2\text{O}$). Today, there are two main processes for the production of magnesium:

Electrolysis of molten magnesium chloride (75%) : $\text{MgCl}_2 \rightarrow \text{Mg} + \text{Cl}_2$

Silico-thermal process (25%) : $2 \text{ MgO} + \text{Si} \rightarrow 2 \text{ Mg} + \text{SiO}_2$

Magnesium is a good example of how materials and their applications can be influenced over the course of time by the re-evaluation and re-valuation of its properties and how these, in turn, have “compelled” further technological developments. In the aviation and automotive industries, magnesium was used as early as the 1930s. In the case of the Volkswagen “Beetle,” the serial production of which began in 1939 and continued until 1962, more than 17 kg of magnesium alloys were processed per car when producing the gearbox and crankcase housings, generator arm, camshaft timing gear, bearing pedestals, and various covers. This amounted to a saving in weight of more than 50 kg compared to the use of steel [10]. Unfortunately, magnesium was subsequently driven from the market due to several disadvantages

which included poor strength, inadequate heat resistance, insufficient corrosion resistance, poor forging and cold-forming capabilities, higher costs and, allegedly, the danger of fire in its molten form and with the machining of aluminum. Nevertheless, lightweight construction technologies are today in great demand with regards to reducing the fuel consumption of automobiles. The corrosion resistance of magnesium alloys has been considerably improved with the use of so-called “high-purity” (HP) alloys, while environmental aspects have also been considered with modern production technologies utilizing water as a clean source of energy and permitting a good recycling capability. Another area worthy of mention here is the electronics industry, with the rapidly increasing demand for mobile telephones, laptops and digital cameras, all of which require lightweight housings (mostly made from magnesium alloys) [11].

Magnesium is a relatively soft, very non-noble metal, the glossy silver surface of which quickly oxidizes in air to create a dull finish. At temperatures up to 225 °C the shaping of magnesium is very difficult, as the metal – with its hexagonal, close-packed structure – crystallizes out, and deformation is possible only by base slipping and pyramidal twinning. The suitability for forming is improved enormously at temperatures above 225 °C, since above this temperature other slippage systems are activated. The major advantage of magnesium alloys is that they have the lowest density of all metallic construction materials, of the order of 1.74 g cm⁻³, together with a high specific strength. The good castability, low energy requirements for melting, and the possibility of using steel forms leads to a reduction in the costs of manufacture. Unfortunately, the pronounced tendency of magnesium to oxidize requires the alloys to be cast under a shrouded gas atmosphere, which must be maintained throughout the entire casting process.

Magnesium alloys are distinguished by their, in part, outstanding processability and machinability. They are also suited to the manufacture of complex die-casting parts, and can also be machined and welded, albeit under a shroud gas.

Besides its poor cold-forming capability, other negative properties of pure magnesium which must be mentioned are its poor corrosion resistance, low strength, and pronounced shrinkage of 4% during solidification. To these can be added the relatively high thermal expansion coefficient, which is approximately 10% greater than that of aluminum. Consequently, there is a need to improve the properties of magnesium by alloying with different elements (Table 5.5). The most important alloying element is aluminum, which increases the tensile strength and hardness of the magnesium alloy, whereby the improvement in hardness is attributable to mixed crystal formation and the precipitation of intermetallic phases. The improvement in strength is, however, stable only up to a maximum temperature of 120 °C, as the mixed crystals again dissolve at higher temperatures. Aluminum improves not only the mechanical properties, but also to a large extent, the castability. For this reason, all magnesium alloys utilized on a large scale contain a not-insignificant amount of aluminum (3–9 wt%). A disadvantage here, however, is the increased tendency to micro-porosity.

The worldwide nomenclature for magnesium and magnesium alloys is in accordance with the ASTM (B 275) system. In this case, the first two letters describe the most

Table 5.5 Properties of certain alloying elements [12].

Properties	Alloying element
Strength	Al, Li, Mn, rare earths, Th, Zn
Hardness	Al, Si
High-temperature strength	Ag (with addition of rare earths), Ag (with additional Th, without Al, Mn), Ce
Elongation, ductility, shaping capability	Li, Zr, In
Creep strength	Ag (only with addition of rare earths), Ca, rare earths, Si, Th, also Y with Zr
Grain refinement, finer microstructures	Ca, Mn, Zn Zr, Ce, Y, Nd, Si, Zr, rare earths
Suitability for welding	Mn
Modulus of elasticity	Si, Be
Castability	Al, Zn
Reducing oxidation of the melt	Be
Reducing shrinkage during solidification	Sr
Corrosion resistance	
- Surface passivation	Al, Be, Si, Ge, Ga, P, Th
- Volume	Mn, Ga, Zn, Ca, V, Ti, Zr

frequently employed alloying element, in decreasing sequence; this is followed by numbers specifying the (rounded) percentage contents of the two alloying elements:

A	Aluminum	E	Rare earths
H	Thorium	K	Zirconium
M	Manganese	Q	Silver
S	Silicon	T	Tin
Z	Zinc	L	Lithium

An example of a commonly found magnesium alloy is AZ91; that is, a magnesium alloy with ca. 9% aluminum and ca. 1% zinc, with the DIN designation MgAl9Zn1. Other additional elements for MgAl alloys are principally zinc and manganese. Aluminum-free alloys are special alloys, mostly for use at higher temperatures, above 200 °C, and contain alloying elements such as zirconium, rare earths, thorium, and silver. Newly developed high-purity and corrosion-resistant magnesium alloys are identified with the additional specification, HP.

As with aluminum alloys, a distinction can be made between wrought alloys and cast alloys.

5.2.1.2.1 Magnesium Cast Alloys Magnesium cast alloys are predominantly processed in die casting. Important alloy groups are:

- magnesium–aluminum–zinc alloys: AZ91
- magnesium–aluminum–manganese alloys: AM20, AM50, AM60
- magnesium–aluminum–silicon alloys: AS21, AS41

- magnesium–aluminum–rare earth alloys: AE42
- magnesium–rare earth–silver–zirconium alloys: EQ21.

5.2.1.2.2 Magnesium Wrought Alloys The processing of magnesium wrought alloys takes place largely by forging and rolling. Due to the hexagonal close-packed structure, forming is made difficult. Cold forming leads to cracking, so that hot forming at temperatures above 350 °C is employed. Important alloy groups for wrought alloys include:

- magnesium–aluminum–zinc alloys: AZ31, AZ61, AZ80
- magnesium–zinc–zirconium alloys: ZK30, ZK40, ZK 60.

5.2.1.3 Titanium and Titanium Alloys

The fraction of titanium in the Earth's crust is around 0.6%, with the metal occurring in almost all minerals, soils and stones, in small amounts. Ilmenite (FeTiO_3) and rutile (TiO_2) are important for the extraction of titanium. The normal technical production processes for metallic titanium begin with liquid titanium halogenides (normally TiCl_4), as until now no economically feasible process for the direct reduction of titanium dioxide has been determined. The two most important production processes for titanium are the Kroll process (reduction with magnesium), and reduction with sodium. When these (relatively common) processes are used to produce high-purity titanium, the metal will be present as so-called "sponge titanium." Since even very small amounts of impurities, such as oxygen (>2%), iron (>0.3%), hydrogen, nitrogen and carbon can have a negative influence on the metal's properties (notably toughness and strength), the sponge titanium is re-melted in a high-vacuum furnace. Due to requirements in respect of purity, the method used involves the melting of consumable titanium electrodes, during which the titanium electrodes from the first re-melting process are consumed. Currently, all common titanium alloys are produced via melt-metallurgical processes.

In air, titanium forms an extremely stable protective oxide layer (passivation), rendering it corrosion-resistant in aqueous media over virtually the entire pH range, from 0 to 14. One remarkable property of titanium is its high strength with a relatively low density. Because of the high melting point ($T_{S, \text{Titanium}} = 1660 \text{ }^\circ\text{C}$), titanium can also be used at higher temperatures, although above a temperature of 400 °C the strength properties fall off dramatically. As a result of the absorption of oxygen, nitrogen and hydrogen at higher temperatures, with titanium there is also the danger of embrittlement. Nonetheless, a strength comparable to that of high-tensile steels, a weight of only 60% of the steels, and an excellent corrosion resistance to many widely differing materials, have led to titanium materials becoming a permanent part of transport technology. A good example is that of aerospace technology; typically, 7% of the Airbus A330/A340 aircraft is produced from this class of materials, while in the aircraft engine the fraction is still higher, with about one-third of the materials used composed of titanium and its alloys. The landing gear of a present-day Boeing 777 is comprised almost entirely of titanium, with a saving in weight of 270 kg per aircraft compared to the steel that is normally used. Titanium is also well known for its outstanding *biocompatibility*, and is frequently used as an implant material, for

example in hip or knee joints. In the latter situation, the favorable ratio of weight to strength is also very beneficial.

Titanium and its alloys possess two micro-structural modifications. At room temperature, the hexagonal α -modification exists, which has only moderate cold-forming capability. However, at 882 °C a phase change to the high-temperature body-centered cubic structure (β -modification) occurs. The alloying of pure titanium with α - or β -stabilizing elements allows the displacement of this micro-structural transformation temperature in both directions. Sn and Zr show good solubility in both phases.

α -Stabilizers: As α -stabilizers, aluminum, oxygen, nitrogen and carbon extend the α -phase region to higher temperatures. In addition, a two-phase α - β -region forms [13]. The most important alloying element is aluminum, which in α -titanium alloys is limited to 6 wt% in order to prevent the precipitation of brittle intermetallic α_2 -phases (Ti_3Al). Due to its hexagonal closed-pack structure, the α -titanium alloys are less ductile, and therefore have a poorer forming behavior. At the same time, however, the diffusion coefficient of the α -phase is two orders of magnitude lower than that of the β -phase, as a result of which the resistance to creep and oxidation is greatly increased. α -Titanium alloys are therefore preferentially employed for high-temperature applications, such as in jet engines. While Si, Sn, Zr and interstitially dissolved oxygen harden the α -phase, the Si atoms tend to cause segregations at dislocations and thus effectively prevent climbing, which leads to an improved creep behavior [13]. The 9 wt% limit for the aluminum equivalent applies also to the composition of α -titanium alloys:

$$\begin{aligned} \text{Al equivalent} = & \text{weight\% Al} + 1/3 \text{ weight\% Sn} + 1/6 \text{ weight\% Zr} \\ & + 10 \text{ weight\% O} < 9 \text{ weight\%} \end{aligned}$$

β -Stabilizers: Vanadium, iron, chromium, molybdenum and niobium, amongst others, stabilize the β -phase down to room temperature. The most important example of this group of materials is the alloy TiV15Cr3Al3Sn3 . β -Titanium materials possess good hardening and cold-forming properties, although when compared with α -titanium materials they have a lower heat resistance and a greater tendency towards creep at higher working temperatures. The good cold-forming behavior can be attributed to the body-centered cubic crystal structure.

The alloying of pure titanium with simultaneously α - and β -stabilizing elements led to the production of titanium materials having both micro-structural modifications at room temperature, while combining the advantageous physical properties of both modifications, such as the outstanding combination of strength and ductility, in a single material (Table 5.6). The most important example of these so-called α - β -alloys is the alloy TiAl6V4 , which – with approximately 50% of the market share – is also the most widely used titanium material. Due to the decreasing solubility of vanadium in the α -mixed crystal with falling temperature, TiAl6V4 can be hardened. Its broad spectrum of applications lies in the areas of aviation and aerospace technology, as well as in components subjected to heavy loading. The values of strength and toughness locate between those of steels and aluminum alloys, while the α - β transformation temperature of this material is 960–980 °C.

Table 5.6 Properties of selected titanium alloys.

Lattice structure	α -Ti alloys hcp	α - β -Ti alloys hcp + bcc	β -Ti alloys bcc
Properties	<ul style="list-style-type: none"> • Stable up to $\sim 550^\circ\text{C}$ • Limited hardening capability • Poor cold-forming behavior • Low strength • High high-temperature strength • Low creep tendency • High oxidation resistance 	<ul style="list-style-type: none"> • Stable up to $\sim 430^\circ\text{C}$ • Good hardening capability • Good cold-forming behavior • Moderate strength • Moderate high-temperature strength • Moderate creep tendency • Good oxidation resistance 	<ul style="list-style-type: none"> • Stable up to $\sim 320^\circ\text{C}$ • Very good hardening capability • Very good cold-forming behavior • High strength • Low high-temperature strength • High creep tendency • Moderate oxidation resistance
Examples	<ul style="list-style-type: none"> • TiAl5Sn2,5 • TiAl7Zr12 • TiAl6Sn2Zr4Mo2Si0,1 • TiAl6Zr5Mo0,5Si0,2 	<ul style="list-style-type: none"> • TiAl6V4 • TiAl6V6Sn2 • TiAl4Mo3V1 • TiAl6Sn2Zr4Mo6 	<ul style="list-style-type: none"> • TiV15Cr3Al3Sn3 • TiV10Fe2Al3 • TiMo11,5Zr6Sn4,5 • TiAl3V8Cr6Mo4Zr4

A number of technical possibilities are employed for the hardening of titanium alloys:

- Intermetallic phases can be precipitated from the β -phase by quenching, followed by annealing. Here, the cubic body-centered β -mixed crystal is transformed to an hexagonal close-packed α -mixed crystal. The lattice shearing results in improved hardening, similar to the hardening of steel by martensite formation. Follow-on annealing causes a precipitation of the coherent β -phase from the newly formed α -phase, further improving the strength. The formation of a brittle transitional phase, the so-called ω -phase, must be avoided by the selection of a suitable annealing temperature.
- For alloys having β -stabilizing additives, with solution annealing and quenching, followed by aging, besides the α -phase the super-cooled metastable β -phase can also form, which during aging then passes through a metastable intermediate ω -phase to the α -phase and is transformed to a β -phase by enriching with additives.

5.2.2

Copper and Copper Alloys

Copper was the first metal to be exploited by mankind. Due to its face-centered cubic structure, copper possesses favorable prerequisites for plastic deformation [4]. The most important technical properties of copper include its high thermal and electrical conductivity, good castability behavior, and good chemical stability. Copper is principally extracted from its sulfide ores (chalcopyrite CuFeS_2 , digenite CuS_2);

Table 5.7 Comparison of the physical and mechanical properties of copper and iron.

	Symbol	Crystal structure	Density ρ (g cm ⁻³)	Melting point T_s (°C)	Modulus of elasticity (MPa)
Copper	Cu	fcc	8.92	1083	125 000
Iron	Fe	bcc; > 911 °C fcc > 1392 °C bcc	7.87	1535	210 000

indeed, its noble character allows a simple extraction by oxidation of the sulfur in atmospheric oxygen, followed by cleaning in an air furnace or by aqueous electrolysis, with comparatively low energy requirements [14]. In spite of this easy extraction the price of copper is high, due mainly to its low natural occurrence (ca. 0.01%) in comparison with aluminum (ca. 8%) and iron (ca. 5%) (Table 5.7). Consequently, the recycling of copper materials is of major importance. The poor strength of copper led to its use as bronze for the manufacture of utensils as early as 2500 BC.

The strength of copper can be considerably enhanced by cold forming ($R_{m,annealed} = 180\text{--}230 \text{ N mm}^{-2}$ to $R_{m,hard-rolled} = 440 \text{ N mm}^{-2}$), although at the expense of a significant worsening of the ductility ($A_{annealed} = 40\%$ to $A_{hard-rolled} = 2\%$) [14]. With small amounts of alloying additives, mixed crystal hardening (Ag, As) or precipitation hardening (Cr, Zr, Cd, Fe, P, Be) can be achieved [4]. Because of copper's high thermal conductivity (the second highest of all metals after silver, and before aluminum), it is used as an ingot mold material in foundries. The thermal conductivity depends to a large extent on the purity of the copper. Hence, in order to reach a compromise between a high thermal conductivity and a moderate high-temperature strength, low-alloy copper materials with silver (e.g., CuAg0,1) or Be (e.g., CuBe2) as the alloying element are employed as ingot mold materials. The most technically interesting in this respect are the high-alloy binary copper alloys bronze (Cu with Sn, Al or Ni) and brass (Cu–Zn), along with the ternary alloys German silver (Cu–Zn–Ni), lead bronze (Cu–Pb–Sn), and red bronze (Cu–Sn–Zn) (Table 5.8).

5.2.3

Iron and Iron Alloys

Approximately 90% of the metallic materials used in machine construction are ferrous materials [14]. Iron, which comprises 5% of the structure of the Earth's crust, is extracted as iron ore (e.g., magnetite Fe_3O_4 , hematite Fe_2O_3 , or siderite FeCO_3), and reduced with carbon in a blast furnace to pig iron:

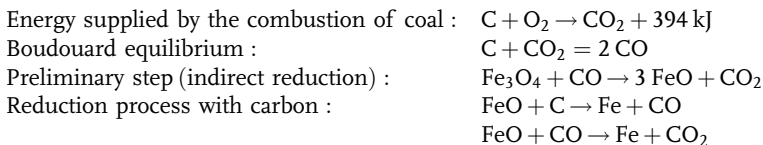


Table 5.8 Classification of copper alloys, properties and examples of their applications (all in wt%, summary taken from Refs [4, 8, 14]).

	Alloying element	Examples of applications
Sn bronze (Cu–Sn)	1.5% Sn	Wear and chemical resistance increase with Sn content
	6–8% Sn	Wrought alloy: “post bronze”, overhead telephone lines
	10–14% Sn	Wrought alloy: “bronze wire”, contact springs
	20–25% Sn	Cast alloy: worm gears, gearwheels, plain bearings, impellers Cast alloy: bells
Al bronze (Cu–Al)	3–10% Al	Hot steam fixtures, plain bearings, guides, rollers Resistant to seawater, sulfuric acid, saline solutions
	+ Fe, Mn, Ni, Si	For improvement of strength by precipitation hardening
Ni bronze (Cu–Ni)	1–45% Ni	Heat-resistant pipes, coins, thermo-elements (CuNi44) Very good corrosion resistance and high-temperature strength
	+ 1.5% Fe, 2% Mn	Improves corrosion resistance
	+ 0.15–1% Si	Improves heat resistance by precipitation of Ni ₂ Si
Brass (Cu–Zn)	Up to 20% Zn	Red brass, very ductile, imitation gold leaf
	20–37% Zn	Yellow brass, deep-drawing parts such as sleeves, musical instruments
	37–44% Zn + 1–2% Pb	Hard brass ($\alpha + \beta'$)-alloy for screws, metal fittings Improves machining capability of hard brass
Special brass (Cu–Zn + X)	0.1–10% additives	Ship propellers, control elements, bearings, munition shells
	Al	Improves strength and resistance to corrosion and oxidation
	As, P	Improves corrosion resistance, suppresses elution of zinc
	P	Improves castability
	Mn, Fe	Improves sliding properties, serves for grain refining
	Ni	Improves corrosion resistance and high-temperature strength
German silver (Cu–Zn–Ni)	11–46% Zn	Eating utensils, medical instruments, keys
	11–28% Ni	Good shaping behavior, corrosion-resistant
Pb bronze (Cu–Pb–Sn)	5–18% Pb	High-stress plain bearing materials, e.g. for Diesel motors
	4–10% Sn	Very high thermal conductivity, good dry-running properties
	+ Ni, Zn, Fe, Sb	Good resistance to dynamic and impact loading
Red bronze (Cu–Sn–Zn)	3–10% Sn	Bearing sleeves, paper roll sleeves, fittings
	2–7% Zn	Good corrosion resistance, good rollability

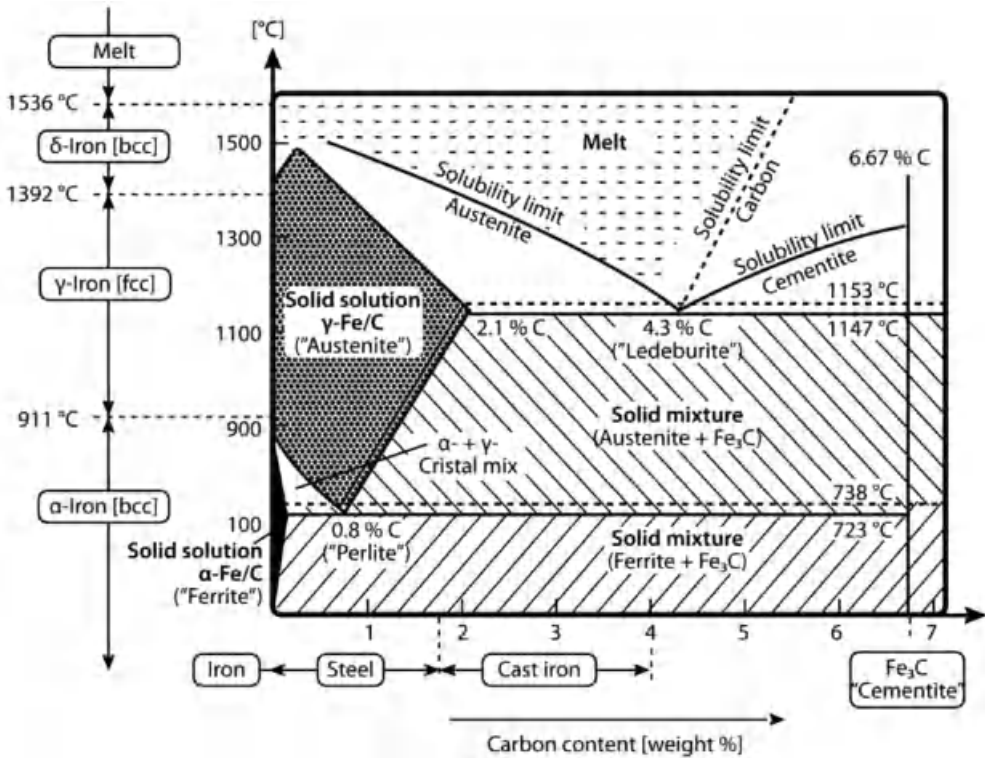


Figure 5.10 Fe–Fe₃C phase diagram.

The production costs and availability of iron are therefore relatively favorable today. The cubic crystal structure imparts a good plastic deformability with a high rigidity [15]. The superiority of iron-based alloys compared with other materials derives from their strength and toughness at low cost, while the high solubility of iron for many elements furnishes the basis for wide-ranging alloy concepts. The most important alloying constituent is the cost-effective element, carbon. The most technically important of these alloys is the meta-stable iron–cementite (Fe–Fe₃C) (see the phase diagram in Figure 5.10). Iron materials are classified as either *pure iron*, which contains only traces of other elements, *steel* (containing < 2.1 wt% C), and *cast iron* (containing 2.1 < wt% C < 4) (Table 5.9).

Table 5.9 Physical and mechanical properties of iron.

	Symbol	Crystal structure	Density ρ (g cm ⁻³)	Melting point T_S (°C)	Modulus of elasticity (MPa)
Iron	Fe	bcc; > 911 °C fcc > 1392 °C bcc	7.87	1535	210 000

The properties of iron materials are determined by the microstructure, which can be influenced by alloying, the manufacturing process employed, and heat treatment. Since, in Europe alone, more than 2000 types of steel are registered, only a general overview of the classification of iron materials can be provided here, though particular emphasis is applied to the alloying concepts.

5.2.3.1 Cast Iron

Cast iron refers to cast iron–carbon alloys incorporating 2.1–4 wt% C and, according to intended purpose, 0.5–3 wt% Si (Table 5.10). Cast iron possesses good corrosion resistance in relation to atmospheric air. Following solidification, it is possible to distinguish – according to the color of the fracture structure – between *white cast iron*, for which solidification takes place in accordance with the meta-stable system Fe–Fe₃C; and *gray cast iron*, for which solidification takes place in accordance with the stable iron–graphite system. In the case of white cast iron, the high fraction of cementite (Fe₃C) results in a high hardness and brittleness; white cast iron also demonstrates a low tensile strength, and a high compressive strength and wear

Table 5.10 Classification of cast iron.

White cast iron	Gray cast iron with lamellar graphite GJL (formerly GG)	Gray cast iron with spheroidal graphite GJS (formerly GGG)	Special cast iron GLY
Composition			
2.4–3.3% C 0.5–1.4% Si	3.0–3.5% C 1.5–2.5% Si	3.5–3.8% C <0.01% S slight addition of Mg	1.5–3.5% C High-alloy with Si, Mn, Cr, Ni, Al
C as Fe ₃ C (cementite)	C primarily as graphite	(a) pearlitic base mass with C as graphite and Fe ₃ C (b) ferritic base mass with C as graphite	
Identification			
White fracture structure	Gray fracture structure	Gray fracture structure	High-alloy
Hard cast GJN (formerly GH)	Malleable iron GJM (formerly GT)		
	white (GTW) ¹	black (GTS) ²	

¹GTW: Annealing in an oxidizing atmosphere decarburizes the peripheral zone → white fracture structure

²GTS: Annealing in a neutral atmosphere

resistance. Notably, hard cast iron (GJN) is used as the balls in ball-mills, as the crusher jaws in milling machines, and as mandrels for drawing pipes, drawing plates or rolling. It is also used as clear chilled casting with a white cast structure of the peripheral zone, with a gray cast structure as the core, for example, in a camshaft. With subsequent long-term annealing, the malleable iron (GJM) causes disintegration of the cementite. The relatively low Si content prevents the formation of lamellar graphite, while the temper carbon coagulates in the form of flakes. A large part of the carbon is incorporated into the microstructure of the gray cast iron as graphite. Although gray cast iron is brittle, due to the graphite inclusions it has a high damping capacity; the lubricating effect of the graphite also results in a good machining behavior of cast iron. At this point, it is possible to differentiate between gray cast iron with lamellar graphite (GJL) and spheroidal graphite (GJS), according to the form of graphite precipitation. Among the different types of cast iron available, gray cast iron with spheroidal graphite most closely approximates the steel construction material since, with its hot-shaping capabilities, it offers certain advantages over steel and malleable iron. For example, with suitable heat treatment and alloying, the base material can be hardened or quenched and tempered, which in turn provides an improvement of the mechanical parameters. With high contents of nickel, chromium and other alloying elements, specific properties such as high-temperature strength, sufficient toughness at low temperatures, high corrosion resistance to sulfuric and nitric acids, or scaling resistance can be adjusted (special cast iron). Hardness values of up to 65 HRC, with an elastic modulus comparable to that of steel, can be achieved. Consequently, special cast iron is suited for use in motor or aircraft engine construction, for example, in crankshafts, crankcases, connecting rods, or camshafts.

5.2.3.2 Steel

Steel is an iron–carbon alloy with up to 2.1 wt% C, and with hot-shaping capability. Above 2.1 wt% C, brittle cementite (Fe_3C) increasingly forms, leading to a loss of the forming capability. In addition to the carbon content, the rate of cooling during solidification from the melt has a very important influence on the resultant microstructure, which can be read from time–temperature transformation diagrams for given compositions. With slow cooling, the stable system corresponding to the iron–carbon diagram is formed, whereas with very slow cooling a complete martensite formation will occur.

Besides carbon, other alloying elements play an important role in the formation of the microstructure. These include (mainly) nickel and chromium and their equivalent alloying elements which stabilize the austenitic γ -phase (“Nicomann”) and ferritic α -phase (“Craltitasimovv”). The relationship between the composition of the alloy and the formation of the microstructure is given by the Schaeffler diagram (Figure 5.11). High-alloy steels having both an austenitic and a ferritic phase are described as duplex steels. In contrast to austenite, the ferrite is ferromagnetic (up to 769 °C). Austenite also has a much greater tendency towards strain hardening and, overall, is far tougher than ferrite.

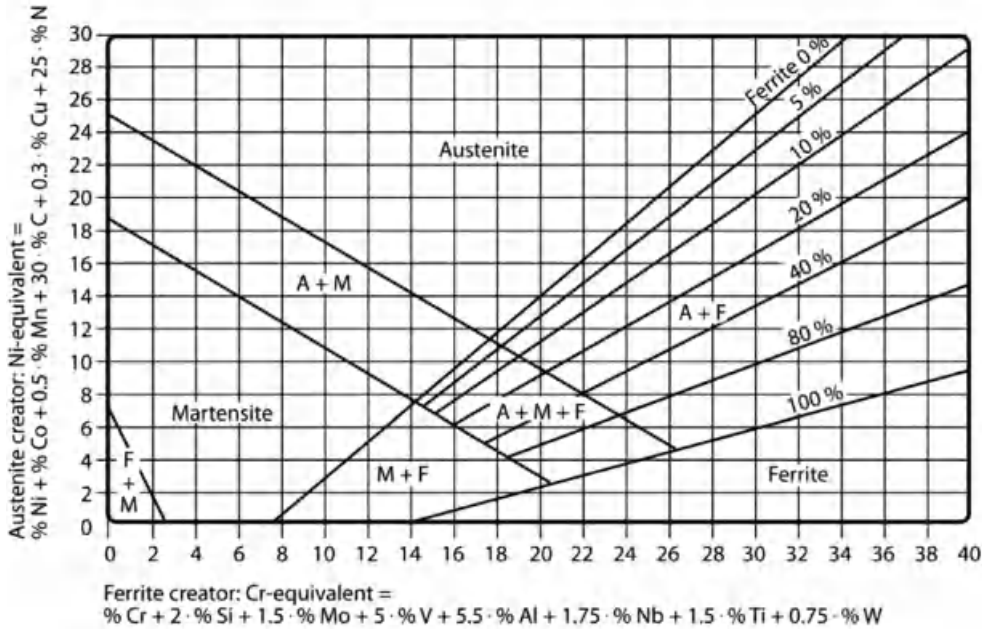


Figure 5.11 Microstructure diagram for steel (after Schaeffler).

The classification of steels is in accordance with DIN EN 10027-2 (1992), in conjunction with DIN EN 10020, in the form of a five-digit numbering 1.XXYY [16]. Here, the 1 refers to the main material group “steel”, XX describes the steel group, and YY describes the identifying number within the steel group. A distinction is made between nonalloyed and alloyed steels, as well as between quality steels and high-grade steels (Table 5.11). High-grade steels are steel types which are intended for heat treatment and, because of their special manufacturing conditions, they are

Table 5.11 Classification of steels in accordance with DIN EN 10027-2, in conjunction with DIN EN 10020 [16].

Non-alloyed steels		Alloyed steels				
Quality steels	High-grade steels	Quality steels	High-grade steels			
			Tool steels	Different steels	Chemically resistant steels	Structural, machine construction and container steels
1.0009– 1.0765	1.1004– 1.1830	1.0800– 1.0987	1.2002– 1.2891	1.3202– 1.3993	1.4000– 1.4988	1.5015– 1.8998

purer than quality steels. For practical reasons, alloyed steels are classified as low-alloy (total alloying elements <5%) and high-alloy (>5%). Low-alloy steels have essentially the same properties as nonalloyed steels [4], although as a result of the alloying elements they show much better hardening capability. Furthermore, the high-temperature strength (e.g., due to Mo) and tempering stability (e.g., due to carbide precipitation) can be increased [4]. A summary of the influence of the most important alloying elements on the properties of steel alloys is provided in Table 5.12.

Case-hardening steels: These are low-alloy or nonalloyed steels with a carbon content of <0.3 wt%, which have been specially developed for case hardening (see also Section 6.2.9.2). Higher carbon contents for these steels would lead to undesirable austenitization of the peripheral zone. In this case, the important alloying elements are Mn, Cr, Mo, and Ni. In particular, the hardening capability is improved by Cr and Mn additives, while Ni improves the core toughness and enhances the depth of hardening.

Nitrided steels (1.8504–1.8599): These are Cr–Mo quenched and tempered steels with additives of Al, V, and Ni. Mo improves the high-temperature strength and creep-rupture strength and reduces annealing embrittlement; Ni-alloyed steels are better suited to applications with larger cross-sections. The diffusion of nitrogen into the steel during the nitriding process (see also Section 6.2.9.3) vastly improves the edge hardness and the corrosion resistance for both low-alloy and nonalloyed steels.

Quenched and tempered steels: These are high-grade steels with high tensile strength and high endurance strength. Due to tempering, the martensite hardness obtained during hardening is in fact somewhat lowered, although the toughness is considerably improved. The tempering properties of nonalloyed steels can be attributed to the content of C and Mn, whereby increasing contents increase the yield point and tensile strength values. Although, with increasing Mn content, the through quenching and tempering is improved, a slightly coarse grain is formed, but this can be partly avoided by using very low-V content additives. An increased Si content enhances the hardness capability and tempering stability, as do higher Mn contents. A series of Cr-alloyed steels, in part with Mo, W and V, or Ni and Mo, has also been developed; these have a reduced tendency to embrittlement during annealing while, at the same time, their penetration hardening capability and through quenching and tempering are improved. In this case, the carbon content lies between 0.17 and 0.62 wt% and, with refractory metals, contributes to an improvement of the strength via the precipitation of special carbides.

Machining steels: These have been developed for efficient serial production on automated machine tools. The improved machinability is achieved mainly by the high S contents (0.18–0.30 wt%); this leads to the formation of brittle inclusions in the steel, at which the chip breaks away during machining. The addition of Pb has a similar effect, giving rise to finely distributed lead inclusions; however, for reasons of immission protection Pb is rarely used. In combination with Mn, soft, linear arrays of manganese sulfide inclusions form, thus improving the cutting speed. A slight increase in the content of P (up to 0.1 wt%) has a favorable influence on the possibility of obtaining smooth and glossy work piece surfaces.

Table 5.12 Influence of alloying elements on the properties of steel [17].

Alloying element	Mechanical properties										Magnetic properties										
	Hardness	Strength	Yield point	Elongation	Reduction of area	Impact value	Elasticity	High temp. stability	Cooling rate	Carbide formation	Wear resistance	Forgeability	Machinability	Scaling	Nitribility	Corrosion resistance	Hysteresis	Permeability	Coercive force	Resonance	Loss of watt
Silicon	↑	↑	↑	↑	2	↑	↑↑	↑	↑	↑	↑↑	↑	↑	↑	↑	↑	↑↑	↑↑	↑↑	↑	↑↑
Manganese at perlitic steels	↑	↑	↑	2	2	2	↑	2	↑	↑	↑	↑	2	↑	↑	↑	↑	↑	↑	↑	↑
Manganese at austenitic steels	↑↑	↑	↑	↑↑	2	↑	↑	↑	↑	↑	↑	↑↑	↑↑	↑	↑	↑	↑	↑	↑	↑	↑
Chromium	↑↑	↑↑	↑↑	↑	↑	↑	↑	↑↑	↑↑	↑	↑	↑	↑↑	↑↑	↑↑	↑↑	↑	↑	↑	↑↑	↑↑
Nickel at perlitic steels	↑	↑	↑	2	2	2	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑
Nickel at austenitic steels	↑↑	↑	↑	↑↑	↑↑	↑↑	↑	↑↑	↑	↑	↑	↑↑	↑↑	↑	↑	↑	↑	↑	↑	↑	↑
Aluminum	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑↑	↑	↑	↑	↑	↑	↑
Tungsten	↑	↑	↑	↑	2	2	↑	↑↑	↑	↑↑	↑↑	↑	↑	↑	↑	↑	↑	↑↑	↑↑	↑↑	↑
Vanadium	↑	↑	↑	2	2	↑	↑	↑↑	↑↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑
Cobalt	↑	↑	↑	↑	↑	↑	↑	↑↑	↑	↑↑	↑	2	↑	↑	↑	↑	↑	↑	↑	↑	↑
Molybdenum	↑	↑	↑	↑	↑	↑	↑	↑↑	↑↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑
Copper	↑	↑	↑	2	2	2	↑	↑	↑	↑	↑	2	↑	↑	↑	↑	↑	↑	↑	↑	↑
Sulfur	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑
Phosphorus	↑	↑	↑	↑	↑	↑↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑

↑ Increase ↓ Reduction

~ Ca. constant

— Not characteristic or unknown

Several arrows = more intensive effect

Rolling bearing steels (1.3501–1.3576): These contain 0.77–1.2 wt% C, in addition to Cr and in part also Mo and V. Rolling bearing steels are generally through-hardened steels, although high-temperature strength and stainless steels are also employed. The best known – and, without doubt, the best investigated – rolling bearing steel is 100Cr6. Rolling bearing steels are particularly subject to very high tensile–compressive loading and wear attack during operation. Because of the very high local (mostly point shaped) load transmission, special demands are placed on rolling bearing steels; these include a high degree of purity, a uniform distribution of the alloying and micro-structural components, sufficient toughness and, at the same time, a high surface hardness. In practice, rolling bearing steels usually have a high-strength martensitic-carbide microstructure. In order to obtain an optimal machinability, it is necessary for rolling bearing steels to produce uniformly grained carbides of medium size, without residual lamellar carbide (perlite), by soft annealing. For low-alloy case hardening steels, on the other hand, a microstructure with a uniformly distributed perlite is better suited.

Wear-resistant steels (1.3401–1.3433): The classical wear-resistant steel with high wear resistance and, at the same time, cold-hardening capability, is Mn hard steel (1.3401: X120Mn12). The highest wear resistance is obtained with alloys in which the C: Mn content is approximately 1: 10. For steel casting for high compressive loading, higher contents of Mn (up to 17 wt%) and chromium (up to 2.5 wt%) are chosen. For wear-resistant deposit welding, according to the wear requirements welding electrodes and rods of austenitic Cr–Ni–Mn steels are also used, besides those of Mn hard steel (e.g., in the welding of X15CrNiMn 18-8 rails with 6 wt% Mn). For wear resistance, a eutectoid microstructure is important; in this case, free ferrite is unfavorable, but free carbides are generally advantageous. For the same strength, a microstructure with a streaked perlite gives the highest wear resistance. However, with increasing strength the wear resistance is also increased, so that quenching and tempering is mostly advantageous.

Tool steels: These are classified, according to their application, into:

- Nonalloyed tool steels (1.1520–1.1830)
- Alloyed tool steels (1.2002–1.2891). These include tool steels for cold working, up to 200 °C working temperature; and tool steels for hot working, above 200 °C working temperature
- High-speed steels (1.3202–1.3397); these are used primarily for machining tools, but also for cutting and forming tools, with W, Mo, V and Co as the alloying elements. The high fraction of high-melting-point special carbides ensures a sufficient hardness when working at temperatures above 600 °C.

Stainless steels (1.4000–1.4690): These are high-alloy steels with <1.2 wt% C and >12 wt% Cr, which means that they can passivate. Austenitic Cr–Ni steels show a greater corrosion resistance. While Mo additionally improves the stability of the passive layer and thus lowers the susceptibility to pitting in media containing chlorides. Alloying with Cu improves the resistance to sulfuric acid. The addition of Ti and Ta/Nb binds carbon in the grain, preventing sensitization by chromium carbide (Cr_{23}C_6) precipitation; this must be prevented from occurring at the

grain boundaries due to the danger of inter-crystalline corrosion. When there is a danger of inter-crystalline corrosion, the C content should be simultaneously reduced to <0.03 wt%.

High-temperature strength steels (1.4901–1.4988): In order to achieve high-temperature strength and to be as stable as possible, these steels must possess a (preferentially austenitic) microstructure with high recovery and recrystallization temperatures. Precipitation hardening is achieved by the formation of special carbides, nitrides and intermetallic compounds, which allow cold or hot hardening by distending or forging, followed by annealing, above the working temperature. Up to working temperatures of about 600°C , steels capable of quenching and tempering, with 12 wt% Cr and additives of Mo and V are employed. For higher temperature ranges or greater stressing, Cr–Ni steels distinguished by their good creep–rupture strength even above 600°C are used. High-temperature steels have a relatively high Cr content of >12 wt%, and this results in a sufficient stability against scaling for normal requirements. In order to improve the creep–rupture strength, small amounts of Nb, Mo, and V are added. The temperature limit of these steels, which are frequently used in the construction of power plants, is about 750°C .

Cast steels: These are Fe–C alloys with a C content of <2 wt%, with and without additional alloying elements. For parts not subjected to high stressing, a nonalloyed cast steel can be used in the normalized state. However, for higher demands such steels must be quenched and tempered, or a low-alloy cast steel should be chosen; these are also mostly normalized. For greater chemical or thermal stressing, rust-proof and acid-resistant alloy types and heat-resistant cast steels with high contents of Cr, Ni, Mo, and Si additives (and also occasionally Nb) are available.

5.2.4

Hard Alloys

Hard alloys are multiphase metallic materials manufactured in melt-metallurgical processes and further processed in different ways [18]. Their microstructure is comprised of a relatively tough matrix of the metals iron, cobalt, or nickel (Table 5.13), in which hard phases, such as carbides, borides and, in a few cases also silicides, are embedded [19, 20]. According to the matrix metals, it is possible to distinguish between three groups of hard alloys.

Iron, nickel, and cobalt are distinguished by sufficient solubility for the hard phase-forming elements in the melt, and low solubility in the solid state. As a result, during cooling of the melt, a precipitation of the hard phases takes place. The base metals also possess high melting points, and this results in the high-temperature resistance values of the hard alloys. In particular, Co-based alloys allow maximum working temperatures in excess of 700°C . Some typical alloy concepts are listed in Table 5.14.

In combination with a metallic matrix with embedded hard phases, materials with a combination of high wear resistance and sufficient resistance to fracture can be obtained. The fraction of hard phases is generally in the range of 15–45 vol%, while

Table 5.13 Physical and mechanical properties of the base metals for hard alloys.

	Symbol	Crystal structure	Density ρ (g cm ⁻³)	Melting point T_s (°C)	Youngs modulus (MPa)
Iron	Fe	bcc; > 911 °C fcc > 1392 °C bcc	7.87	1535	210 000
Cobalt	Co	hcp > 417 °C fcc	8.89	1495	210 000
Nickel	Ni	fcc	8.91	1453	210 000

Table 5.14 Groups of hard alloys and examples of alloys.

Base metal	Alloying elements leading to hard phase formation	Other alloying elements	
Fe	Cr, W, Mo, V, (Nb, Ti)	C, (B, Si)	Mn, Ni, (Co)
Co	Cr, W, Mo	C, (B, Si)	Ni, Cu, Fe
Ni	Cr, (Nb, Mo, W)	B, Si, (C)	Cu, Fe, (Co)
Base metal	Composition	Description	
Fe-based	FeCr12C2.1	X 210 Cr 12	Cold working steel
	FeCr5Mo1VC0.4	X 40 CrMoV 5 1	Hot working steel
	FeW6Mo5Cr5V3C1.3-P	HS 6-5-3	High-speed steel
Co-based	CoCr29W5C1.2	Stellite 6	Co–Cr–W matrix with M ₇ C ₃
	CoCr20Mo20FeNiSiB2.5		Co–Cr–Mo matrix with M ₃ B ₂
Ni-based	NiCr18Si4B3C		Ni–Cr–Si matrix with M ₃ B
	NiCr18Mo18Si4Nb3B4C		Ni–Cr–Si matrix with M ₃ B ₂

materials with >50 vol % (hard compound materials, pseudo-alloys) are manufactured via powder-metallurgical processes. The volume fraction and composition of the matrix itself are decisive for the (heat) resistance and corrosion resistance. To a large extent, the precipitated hard phases determine the wear behavior. In this case, the important influential factors include the size, form, distribution, alignment, composition and volume fraction of the hard phase. The bonding between the hard phases and the matrix also has a major influence on the mechanical properties. Hard phases with a high fraction of metallic bonds (e.g., metal carbides) are preferred, as they form coherent or partly coherent precipitations from the metallic matrix.

During solidification of the hard alloy, primary (directly from the melt) and/or eutectic hard phases are precipitated. In the greatly simplified binary system (Figure 5.12), which consists of a matrix metal M and C, B or Si, during the solidification a sub-eutectic melt initially begins so as to form a primary metal matrix, which then grows into the melt in the form of dendrites. During further cooling, the metal cells formed in this way are surrounded by a eutectic system comprised of the metal matrix and the eutectic hard phases. In the case of super-eutectic alloys, coarser primary hard phases are initially precipitated out, but

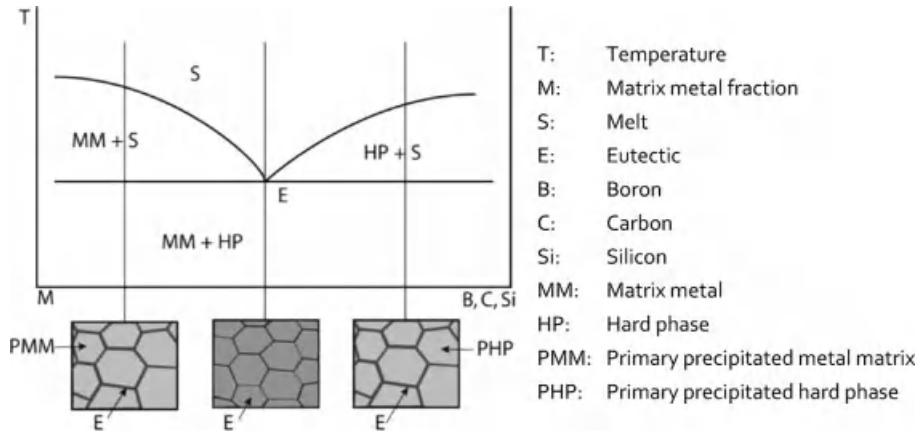


Figure 5.12 Schematic representation of the formation of hard alloy microstructures during solidification with a eutectic (after Ref. [20]).

during further cooling below the eutectic temperature, the eutectic will then form. Besides being precipitated from the melt, hard phases can form as a result of further cooling, or by heat treatment processes from the solidified mixed crystal. In this case, secondary hard phases are spoken of which, due to their size, are mostly allocated to the matrix [21]. In fact, they are considerably smaller than the primary hard phases, and have no significant influence on the wear resistance, such as for abrasive wear, but nevertheless they improve the supporting effect of the matrix. The cooling gradient has a decisive influence on the microstructure; with an increased cooling rate a finer-grain microstructure is formed than with a comparatively slow cooling.

Hard alloys are predominantly cast materials, the immediate use of which may be as cast parts, as cast welding filler materials, and/or as mechanically diminished alloy powders, whether atomized or following the melting down of different components during application in thermal-coating processes. Besides full-material components, hard alloys are also available as coating materials [22, 23], in particular when the mechanical properties of the hard metals preclude their use as construction materials, for example as large-volume parts. The use of hard alloys as coating materials involves, on the one hand, cost advantages, since cost-effective materials such as low-alloy steels can be used as construction materials. Moreover, the substrate materials exhibit a greater toughness, such that the resistance to fracture of components manufactured in this way is improved. In the manufacture of such compound materials, various thermal coating processes – such as deposit welding, thermal spraying or deposit brazing – are employed. The coating thicknesses obtained with these processes range from a few hundred micrometers up to several millimeters. The welding, soldering, or spray filler metals may be used in the form of wire, powder, cored wire, or fleece [24]. In this case, self-flowing NiCrBSi alloys, FeCrBSi alloys and CoCrWC alloys (Stellite®; Deloro Stellite Holdings Corporation) are of particular technical importance.

5.2.5

Super-Alloys

The term “super-alloys” refers to all metallic materials intended for technical applications at high temperatures in excess of 540 °C; this includes Fe-, Ni-, and Co-based alloys. By far the most important area of application for super-alloys is gas turbine manufacture, particularly of the hot gas turbine components (such as rotor, blades and vanes) and the gas turbine combustor, where the prevailing conditions are high temperatures and large temperature discontinuities, as well as high pressures and large mechanical stressing. Generally, oxidizing and corrosive atmospheres are also superimposed over these peripheral conditions. Under such process conditions, the materials required must be capable of withstanding such stressing over long periods of time. The material limit for the high-temperature use of metallic materials is the onset of re-crystallization, as this causes a pronounced deterioration of the material strength. The contribution of the grain boundary strength drops off rapidly, together with the effect of most solidification mechanisms (see also Section 5.1.2).

Within the relevant temperature range for gas turbines ($T \sim 950$ °C substrate temperature), both Ni and Co super-alloys possess very high strengths [25] whilst, at the same time, exhibiting the most favorable ratio of density to strength (Figure 5.13). For these operating temperatures, common Fe-based alloys are no longer suitable, as they have a maximum re-crystallization temperature of approximately 800 °C, even when making use of all available alloying technology. Neither are refractory metals, nonoxidizing ceramics (Si_3N_4 , SiC) and carbon fibers (C/C) suitable, for reasons of excessively high densities, insufficient stability against oxidation, insufficient fracture toughness, and poor machinability.

Figure 5.14 compares the creep–rupture strengths over 100, 1000, and 100 000 h for Fe-, Ni-, and Co-based alloys. As a basis for the calculation of unsteady gas turbines (e.g., in aircraft, where the engines are extensively overhauled within short time intervals), the 1000 h strength is decisive. However, for stationary plants (chemical plants and power plants), the 100 000 h strength is of primary interest. Whilst it is important to recognize the superiority of Ni and Co super-alloys compared to high-temperature steels, it is equally important to realize that, with increasing

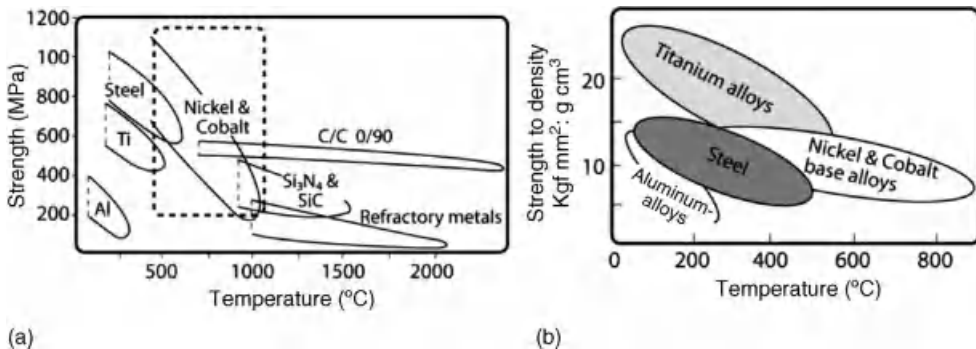


Figure 5.13 Temperature capabilities of material classes [26, 27].

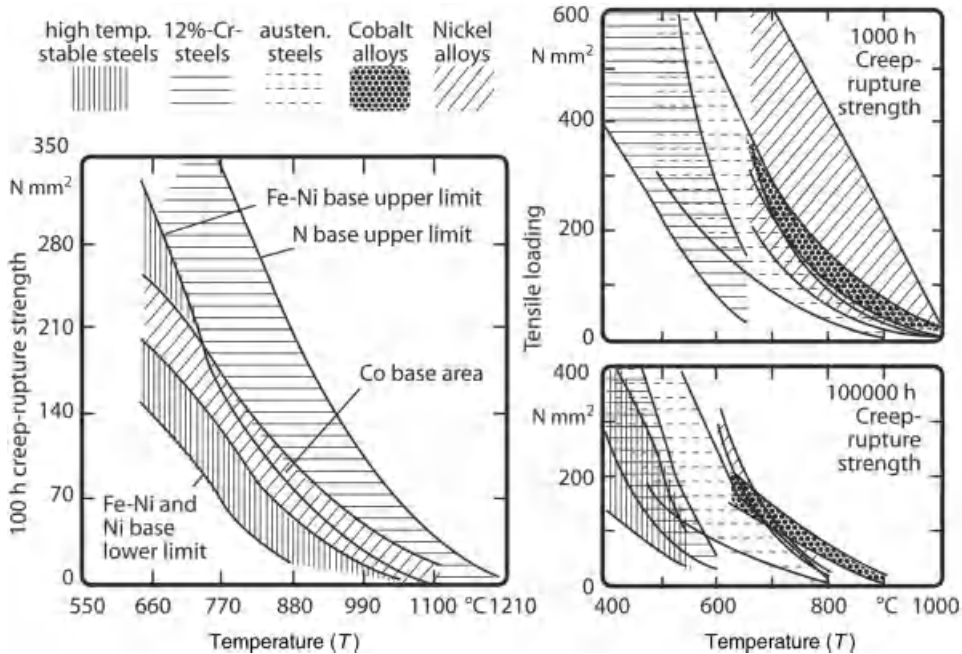


Figure 5.14 Creep-rupture strengths of the most important super-alloys.

stressing time and temperature, the superiority of Ni super-alloys is no longer so clear. It is for this reason that Co super-alloys are used preferentially in the field of power generation, while Ni super-alloys are used in aviation turbines (Table 5.15).

Super-alloys are classified according not only to their base metals, but also to their manufacture and further processing to cast and wrought alloys. Cast alloys allow the selective solidification of the microstructure and controlling of the grain size. In the ideal case, even single-crystal manufacture with excellent creep behavior is possible. The main purpose of wrought alloys, on the other hand, is the production of a very fine-grained microstructure with good forming properties and the possibility to produce a high dislocation density and formation under controlled conditions. This thermo-mechanical processing is employed almost exclusively for Ni-based materials. The production of the, mostly, semi-finished super-alloys takes place by way of melting in an electric furnace under a shroud gas, followed by continuous casting or diecasting and re-melting in vacuum in order to obtain the required degrees of purity and to minimize block-crystal segregation. In special cases – notably, when there is a desire to exploit the advantages of dispersion – powder-metallurgical production qualities have been introduced more recently, and these are also used for particularly fine carbide distributions. However, dispersion hardening is meaningful only for operating temperatures above 1000 °C, when the other hardening mechanisms fail. As strengthening elements, aluminum oxide and/or thorium oxide may be employed in so-called “oxide dispersion-strengthened” (ODS) alloys, either added directly to the powder mixture in aggregate form, or formed by internal oxidation in the material (Table 5.16).

5.2.6

Refractory Metals

Within the Periodic Table, transition metals belong to the d-block – that is, subgroups 3 to 12. Transition metals are distinguished by the fact that electron levels of higher order are filled before the shells of lower order are completely occupied. The same configuration of their outer electrons explains the similarities among the transition metals. Those transition metals with high melting points occupy subgroups 4 to 8, and the refractory metals subgroups 4 to 6. The term “refractory metal” derives from the Latin *refractarius* (= contrary, stubborn). Thus, the refractory metals are seen to have in common such properties as a high melting point (Figure 5.15), high densities, mostly high hardness and strength values, and a high modulus of elasticity (Table 5.17).

The transition metal with the lowest melting point is titanium ($T_S = 1660^\circ\text{C}$). Refractory metals are non-noble and exhibit a high affinity for B, C, N, and O. When

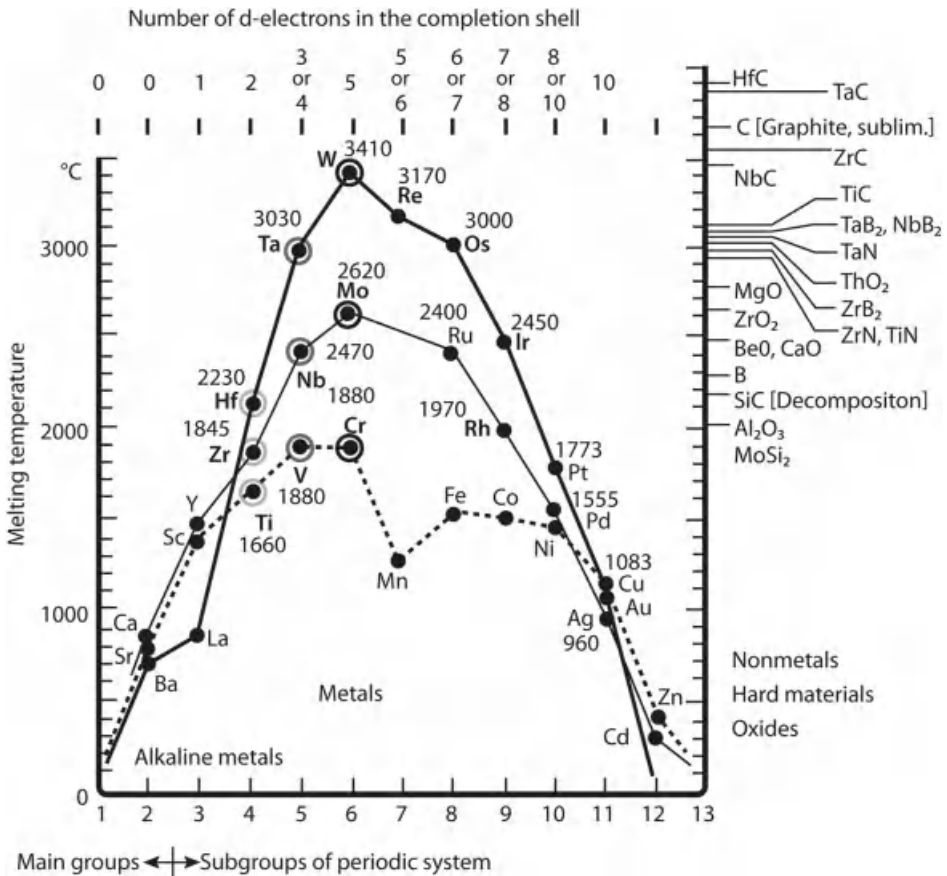


Figure 5.15 Melting points of metals, ordered in accordance with the Periodic Table.

Table 5.17 Properties of refractory metals.

	Symbol	Crystal structure	Density ρ (g cm ⁻³)	Melting point T_s (°C)	Modulus of elasticity (MPa)
Titanium	Ti	hcp > 882 °C bcc	4.51	1660	110 000
Zirconium	Zr	hcp > 862 °C bcc	6.51	1852	90 000
Hafnium	Hf	hcp >1760 °C bcc	13.31	2150	137 000
Vanadium	V	bcc	6.09	1890	137 000
Niobium	Nb	bcc	8.58	2468	103 000
Tantalum	Ta	bcc	16.68	2996	186 000
Chromium	Cr	bcc	7.14	1857	186 400
Molybdenum	Mo	bcc	10.28	2617	300 000
Tungsten	W	bcc	19.26	3407	405 000

exposed to the atmosphere, they form stable protective oxide layers (passive layers) on their surfaces, which is why they possess excellent corrosion resistance in many media. Because of their high tendency to react, their production is difficult, and must be conducted in complex shroud gas processes that require considerable energy input. Refractory metals are used primarily in the chemical industry, and also in reactor technology, furnace construction, and electro-technology. As alloying elements, they are indispensable in connection with Fe-, Ni-, and Co-based alloys. The carbides, oxides, nitrides and borides of the refractory metals are important hard materials for the design of tribological components.

5.2.7

Intermetallics

Intermetallics, which are better described as intermetallic phases, are formed from two or more metals with ordered lattices. Depending on the temperature, they show a more or less broad range of existence as a compound in the phase diagram. Intermetallics may be classified in two forms:

- The *daltonides* have a very narrow homogeneity range; that is, the range over which the composition of the alloy varies only very slightly from the stoichiometric composition (vertical line in the phase diagram).
- The *bertollides* show a more or less large deviation from the exact stoichiometry (concentration ranges in the phase diagram).

Although, strictly speaking, the term intermetallics is only correct when all of the elements involved are metals, it remains partly in use today and includes compounds such MoS₂ [28]. It has been documented that, as long ago as 2500 BC, in ancient Egypt, Asia Minor and Britannia, the intermetallics Cu₃As was used in the cementation process for the coating of bronze tools and other articles of practical value [29]. Westbrook has provided some extensive accounts of the history of intermetallics [29–32]. On the basis of the many possibilities for bonding, and the different sizes of

the participating atoms, a number of intermetallic phases exist, with some 5000 being recognized for binary phases alone [33].

When the forces of attraction between the different types of atoms are greater than between atoms of the same type, then compounds will be formed between the atoms of different types. According to their electrochemical behavior, compounds can form which show, in addition to purely metallic binding, partially covalent and ionic bonding. Thus, the description “intermediate phase” is an appropriate term, as the crystal lattice formed in intermetallics no longer leads to the properties of the participating single metals. This means that the properties of intermetallics can also not be derived from these. The resultant lattices are mostly very complex in terms of their structure, with an elementary cell perhaps including up to several hundred atoms. The crystal structures are mostly hexagonal close-packed, face-centered cubic or body-centered cubic. In spite of the great variety of intermetallic phases, it is possible to define a large number of rules that apply to certain groups of structures, and thus to predict the crystal structures within these groups [33]. The stability of intermetallics is determined essentially by the ratios of the atomic radii, the valence electron configurations, and the electronegativities of the components. According to whichever property is responsible for stability, it is possible to distinguish between Laves, Zintl, and Hume–Rothery phases. Although, in addition to these phases, other groups such as Hagg, Heusler or Frank–Kasper also exist, these will not be described at this point.

Laves phases: Among the classic intermetallic phases, the Laves phases constitute the numerically largest group [28], with several hundred representatives known to exist [33]. In the case of Laves phases, two inter-penetrating lattices, in which the atoms are not mutually in contact, are present in the form AB_2 . These crystallize in the most densely packed lattice types, the hexagonal close-packed or face-centered cubic (Table 5.18). The most important characteristic of the Laves phases is the ratio of the radii r_A and r_B , which has a value of $1.2 < r_A/r_B < 1.3$ (1.225 [34]; 1.228 [35]). Due to the difference in the radii ($>15\%$), Hume-Rothery phases or substitution mixed crystals can form. One decisive factor leading to predominantly metallic bonding is the difference in electronegativities, which is too small for the formation of ions. Moreover, the sum of the electronegativities is also small, so that the formation of covalent bonds is also not possible. Thus, which of the three lattice structures is ultimately formed is determined by the concentration of valence electrons.

Table 5.18 Stacking sequence for Laves phases [35].

Type	Lattice	Stacking sequence	Examples	Number
MgCu ₂	fcc	ABCABC...	KNa ₂ , BaPt ₂ , NaAg ₂ , CaAl ₂ , KBi ₂ , YFe ₂ , TaV ₂ , TiCo ₂ ...	500
MgZn ₂	hcp	ABAB...	CaLi ₂ , CsNa ₂ , BaPt ₂ , NaAg ₂ , TiMn ₂ , NbFe ₂ ...	350
MgNi ₂	hcp	ABACABAC...	TaCo ₂	50

Zintl phases: These are essentially formed between metals of groups 1 and 2 and elements of groups 14, 15 and 16, with the exception of C, N, and O. Sn and Pb also form such compounds and, in individual cases, so do Al, Ga, In, and Tl. On the basis of their physical properties, the Zintl phases are semi-conductors, and the tendency to form compounds is greater the more electropositive is one component and the more electronegative is the other. Both, binary and ternary Zintl phases have been identified. Compounds of the type AB have a common salt (NaCl) type lattice, while compounds of type AB₂ have a fluorospar (CaF₂) type lattice. Compounds of type ABC also have a fluorospar-type lattice. One common characteristic of Zintl phases is the ratio of the radii ($r_A/r_B \sim 1-2.4$).

Hume-Rothery phases: This common class of bonding is formed via the combination of transition metals with metals of the main groups, as well as Zn, Cd, and Hg which, as a result of their completely filled d-orbitals, behave in many ways as main group metals. In 1929, Hume-Rothery had already observed that, in the phase diagrams of certain binary chemical systems, the same sequence of phases was always present, and that the stability of the phases was related to certain concentrations of the electron cloud. The phases are determined by the valence electrons, such that the following general formulation of a compound A_mB_n applies:

$$\text{Valence electron concentration (VEK)} : \quad \text{VEK} = \frac{mE_A + nE_B}{m + n}$$

where E_A and E_B are the valence electrons of the elements A and B.

The number of valence electrons of the transition metals of groups 8–10 is set to zero for the determination [36]. The metals Fe, Co, Ni and their homologues then clearly give up no electrons in these phases; the reason for this is most likely their tendency to completely (Ni, Pt) or almost (Fe, Co) maintain the d10 electron configuration (Table 5.19).

Table 5.19 Determination of the valence electron concentration and some examples of Hume-Rothery phases.

Phase	Lattice	Composition	Number of valence electrons	Number of atoms	Valence electron concentration
β-phase	bcc	CuZn, AgCd	1 + 2	2	3: 2 = 21: 14 = 1.50
		CoZn ₃	0 + 6	4	6: 4 = 21: 14 = 1.50
		Ag ₃ Al	3 + 3	4	6: 4 = 21: 14 = 1.50
		FeAl	0 + 3	2	3: 2 = 21: 14 = 1.50
γ-phase	cubic ^{a)}	Cu ₅ Sn	5 + 4	6	9: 6 = 21: 14 = 1.50
		Cu ₅ Zn ₈ , Ag ₅ Cd ₈	5 + 16	13	21: 13 = 1.62
		Fe ₅ Zn ₂₁ , Pt ₅ Zn ₂₁	0 + 42	26	42: 26 = 21: 13 = 1.62
		Cu ₉ Al ₄	9 + 12	13	21: 13 = 1.62
ε-phase	hcp	Cu ₃₁ Sn ₈	31 + 32	39	63: 39 = 21: 13 = 1.62
		CuZn ₃	1 + 6	4	7: 4 = 21: 12 = 1.75
		Ag ₅ Al ₃	5 + 9	8	14: 8 = 21: 12 = 1.75
		Cu ₃ Sn	3 + 4	4	7: 4 = 21: 12 = 1.75

a) Cubic phase with its own structure.

As the intermetallic phases do not constitute a homogeneous group of materials, a general treatment of their properties is not possible. Nevertheless, all intermetallic phases can be said to have the common properties of high hardness and brittleness, essential to which is the formation of large elementary cells. In particular, the brittleness increases as the elementary cells become less symmetrical [37]. An additional common factor among intermetallic phases is that their properties are transferred to the entire alloy when they are produced via precipitation in technical alloys, and consequently their use must be carefully considered. Due to their many different phases, each with their own structures and special properties, the properties of the intermetallic phases can be described only for particular cases. From a technical standpoint, titanium-aluminides and nickel-aluminides represent the two most intensively investigated groups of intermetallic materials in recent years, with α_2 -phase (Ti_3Al) and γ -phase (TiAl) having found their way into engineering applications. However, the most important phases of nickel aluminides have been recognized as γ' -phase Ni_3Al and β -phase NiAl .

5.3

Non-Metallic Inorganic Materials

The group of non-metallic inorganic materials includes not only ceramic materials but also glasses and semiconductors (though the latter will not be dealt with here). In respect of their chemical structure, these hard materials which, on the basis of their high hardness, chemical stability and good high-temperature behavior, are of major importance for tribological applications. Typically, hard materials find application as:

- precipitations in metallic alloys (see Section 5.2)
- hard particles or fibers in a metal, ceramic or polymer matrix with composite materials (see Section 5.5)
- coating materials (see Chapter 6)
- structural materials, such as engineering ceramics or high-performance ceramics (see Section 5.3.2).

5.3.1

Structure of Hard Materials

The term “hard materials” encompasses all materials with a Vickers hardness of more than 1000 HV [38]. Essentially, these are the carbides, nitrides, borides, silicides and oxides of the refractory metals (subgroups 4 to 6 of the Periodic Table). Other important elements which form hard materials are aluminum, silicon, and the rare earth metals, such as yttrium (Figure 5.16). Hard materials are solid interstitial solutions; that is, the non-metals C, N, and O or the metalloids B and Si occupy the interstitial positions of the metallic lattice structures, or

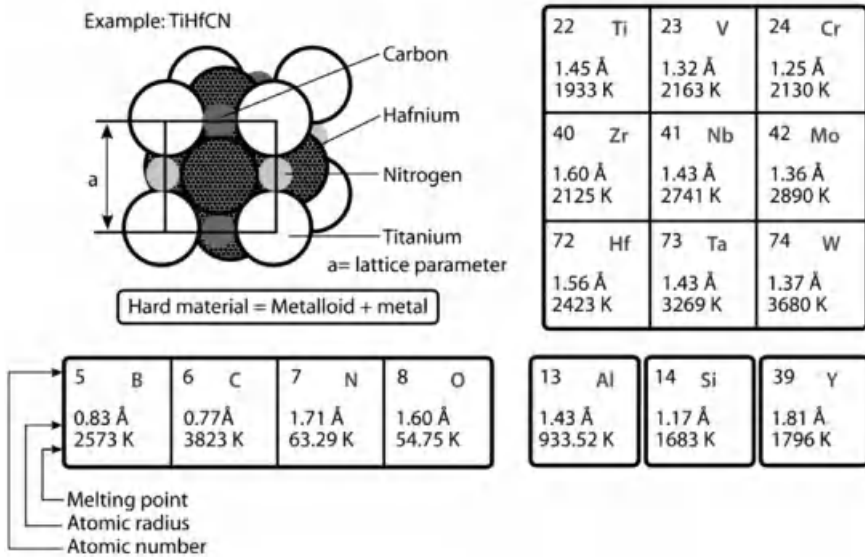


Figure 5.16 “Building blocks” for hard material systems [39, 40].

vice versa. Besides the high hardness values, the high melting points of hard materials especially stand out, these being above 2000 K for essentially all hard materials.

Classically, it is possible to differentiate between three groups of hard materials: (i) metallic hard materials; (ii) ionic (heteropolar) hard materials; and (iii) covalent hard materials (Figure 5.17). This classification is oriented to the character of the preferred chemical bonding. For technical hard materials, with the exception of diamond, different types of bonding exist in a hard material, though neither purely metallic nor purely ionic bonding will result in suitable hard materials [41]. Diamond is the only hard material which has *only* covalent bonding. The characteristic properties of the chemical bondings are decisive for the selection of the material.

Metallic hard materials are distinguished by good bonding to metallic alloys. In the composite system, this permits good cohesion between the metal matrix and the hard material particles, whilst on metallic substrates the best adhesion is achieved with metallic hard material layers. As a result of the high fraction of metallic bonding, metallic hard materials possess good thermal conductivity and comparatively good toughness compared to ionic and covalent hard materials (with the exception of diamond). Whilst the highest hardness values are obtained with covalent bonding, the greatest chemical stability on the surface is obtained with ionic bonding. This leads, on the one hand, to a favorable adhesive resistance, and on the other hand to very little tendency to react with the environment, even at higher temperatures. Ionic hard materials are good insulators. The material's behavior can be estimated according to its position in the “bonding triangle” (Table 5.20; Figure 5.17).

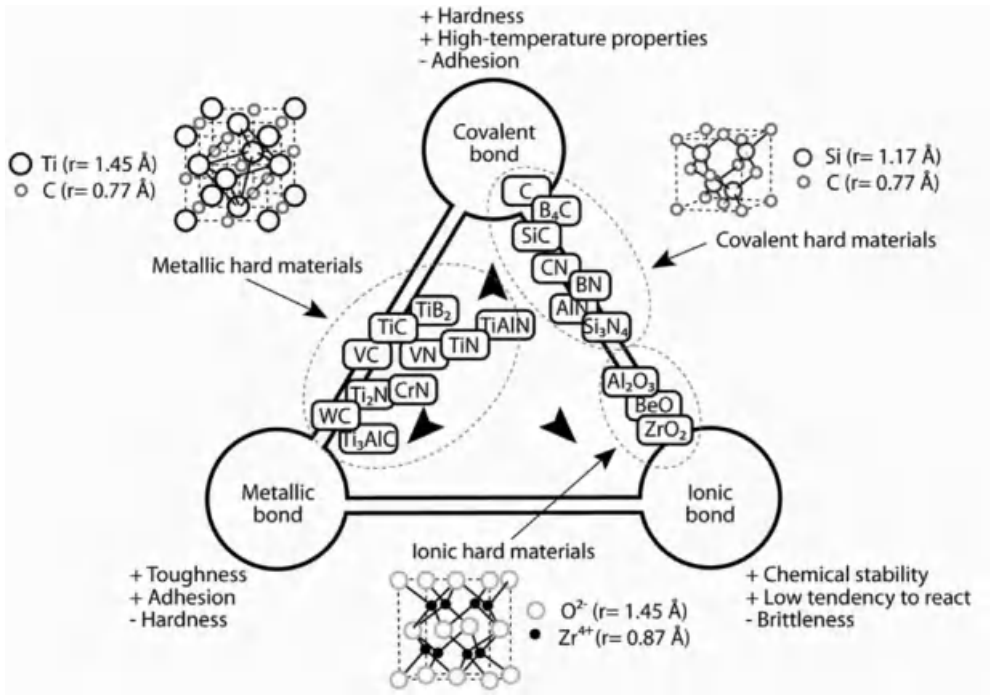


Figure 5.17 Classification of hard materials in the “bonding triangle” [42].

Table 5.20 Material properties depending on the character of their chemical bonding (after [43]).

Hardness	Brittleness	Melting point	Stability – ΔG	Coefficient of thermal expansion	Adhesion to metals	Reaction tendency	
Covalent	Ionic	Metallic	Ionic	Ionic	Metallic	Metallic	↑
Metallic	Covalent	Covalent	Metallic	Metallic	Ionic	Covalent	→
Ionic	Metallic	Ionic	Covalent	Covalent	Covalent	Ionic	↓
Borides	Oxides	Carbides	Oxides	Oxides		Borides	↑
Carbides	Nitrides	Borides	Nitrides	Nitrides		Carbides	→
Nitrides	Carbides	Nitrides	Carbides	Carbides		Nitrides	→
Oxides	Borides	Oxides	Borides	Borides		Oxides	↓

5.3.2

Engineering Ceramics

In applications where hardness and wear resistance, chemical and thermal stability, and a good weight-to-strength ratio are required, metallic materials are unable to sufficiently satisfy these demands, or indeed to satisfy them at all. In this case,

ceramic structural materials – which are also known as engineering ceramics, technical ceramics or high-performance ceramics – offer very promising alternatives. However, along with these positive features there are also negative properties, such as excessive brittleness, (in part) a poor thermo-shock stability, difficulties with machining, and a broad scattering of characteristic values. In respect of their classification, engineering ceramics can be divided into three main groups: oxide ceramics; non-oxide ceramics; and silicate ceramics. One important distinguishing feature is the glass phase fraction, which can be considerable for silicate ceramics but very low or even non-existent for oxide and non-oxide ceramics. As a rule, engineering ceramics are formed at room temperature from a raw mixture, and take on their typical material properties, usually as the result of a high-temperature sintering process.

5.3.2.1 Oxide Ceramics

Among oxide ceramics, aluminum oxide (Al_2O_3), zirconium oxide (ZrO_2) and aluminum titanate ($\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$ or Al_2TiO_5) are the most important technical materials, while the use of beryllium (BeO), magnesium (MgO), thorium (ThO_2), and titanium (TiO_2) oxides and spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$ or MgAl_2O_4), at least as structural materials, is limited to special cases. The properties of oxide ceramics are determined by the prevailing fractions of ionic and covalent bonding. The stability of these bonding types is responsible for the properties already mentioned, such as thermal stability and corrosion resistance, in addition to the insulating properties important for electrical and electronics applications.

Al_2O_3 constitutes the greatest share of the market and finds application as cutting ceramics, blasting shot and wear-protection coatings [e.g., chemical vapor deposition (CVD), physical vapor deposition (PVD), or thermal spraying]. In order to improve the thermo-shock stability and fracture toughness, Al_2O_3 is manufactured as a mixed ceramic, together with TiO_2 , TiC or ZrO_2 (zirconium-toughened alumina; ZTA). Far better behavior in respect of cyclical thermal and mechanical loading is shown by ZrO_2 , which is used for example, as a protective coating in combustion engines. In order to suppress the allotropic phase transformation (monoclinic \rightarrow tetragonal) of pure ZrO_2 , it is used almost exclusively with stabilizers, the most frequently used stabilizer being Y_2O_3 , added in amounts of 3–8 wt%. The addition of 8 wt% Y_2O_3 fully stabilizes the cubic phase (fully stabilized zirconium oxide; FSZ). As a rule, partially stabilized zirconium oxide (PSZ) is employed, in which the tetragonal phases are present in a cubic matrix [44].

5.3.2.2 Non-Oxide Ceramics

The term “non-oxide ceramics” describes all ceramic materials manufactured on the basis of borides, carbides, and nitrides. Besides diamond (C), the most important representatives are silicon nitride (Si_3N_4), silicon carbide (SiC), aluminum nitride (AlN), boron nitride (BN), and boron carbide (B_4C). By contrast with oxide ceramics, predominantly covalent bonding is found in non-oxide ceramics. As the participating elements, such as B, Al, Si, C, and N have small atomic diameters, the atomic spacing is small and the binding energy accordingly high.

This is (in part) the reason for the exceptionally high mechanical and thermal stability, which is reflected in the high hardness values and high melting points. For example, cubic boron nitride (cBN), with a Knoop hardness of 4650 HK100, has the highest hardness value of all known substances, except for diamond. The immense influence of the lattice type on the properties becomes apparent with the extremely low Knoop hardness of 6–30 HK100 for hexagonal boron nitride (hBN), which is also referred to as “white graphite.” Whereas, cBN may find application as a cutting material, hBN is known to be an excellent solid lubricant for high-temperature applications.

5.3.2.3 Silicate Ceramics

Silicates are the salts and esters of *ortho*-silicic acid ($\text{Si}(\text{OH})_4$) and its condensates. The Earth's crust is comprised almost entirely (>90%) of silicates and, indeed, silicate ceramics constitute the oldest group of all ceramics. The most important component is clay or kaolin, derived from feldspar and soapstone. In addition, alumina ($\gamma\text{-Al}_2\text{O}_3$) and zirconium are used to obtain certain special material properties, such as high strength. During the sintering process, a high glass phase fraction (predominantly of SiO_2) is usually formed in addition to the crystalline phases [45]. Silicate ceramics include:

- porcelain (alkaline aluminum silicates)
- steatite (magnesium silicates)
- cordierite (magnesium–aluminum silicates)
- mullite ceramics (mullite: $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ and corundum: Al_2O_3).

5.4

Organic Materials

The diverse use of polymers is the result of their relatively simple processing, comparatively inexpensive raw materials, favorable mechanical properties, and relatively low densities, in the range of 0.9 to 2.2 g cm^{-3} . The processability and mechanical properties can be influenced over a wide range by a suitable choice of additive materials, such as softening agents, stabilizers, lubricants and filler materials [8]. Of advantage are the low processing temperatures of approximately 250–300 °C for injection molding and extrusion production processes.

All polymers have in common the fact that they are essentially comprised of organic materials with macromolecular structures. The smallest structural elements are low-molecular-weight reactive molecules (monomers), that are linked by polymerization, polyaddition or polycondensation to form macromolecules (polymers) [46]. The macromolecular polymers produced in this way, in contrast to the cubic or hexagonal microstructure of metal atomic lattices, exhibit a filamentous or netted structure [47]. The most important monomers for the production of polymers are unsaturated low-molecular-weight carbon compounds (i.e., with C=C double bonds [46]), which are derived primarily from crude oil, but may also be produced

from natural gas or carbon:

- ethene (ethylene) C_2H_4
- propene (propylene) C_3H_6
- butene (butylene) C_4H_8
- ethine (acetylene) C_2H_2
- butadiene C_4H_6
- benzene, toluene C_6H_6 .

The linking of carbohydrate molecules to molecular chains (polymers) can take place by way of bonding between carbon atoms or by way of sulfur, nitrogen, or oxygen atoms. With C–C, C–N, C–O and C–S bonding, covalent bonding ensures a stable cohesion along the molecular chain, and this constitutes the main valence bonding. In addition to carbon, silicon can also form macromolecules by way of oxygen bridges, for example, polysiloxane: $-Si-O-Si-$. Bonding between different monomers results in “copolymers” – that is, regular arrangements of molecular blocks, or so-called “block polymers.” The cohesion of the molecular chains amongst each other derives from van der Waals forces (so-called “semi-valence bonding”), which is several orders of magnitude weaker than covalent binding energies. The forces of attraction can be attributed to the overlapping of molecular orbitals, or to the electrostatic interaction between permanent or temporary dipole molecules, whereby the formation of hydrogen bridges between neighboring oxygen and hydrogen atoms contributes the strongest binding energies. When subjected to tensile loading, polymers fail due to the severing of the semi-valence bonding (Figure 5.18), and this results in low strength values of around 10–100 MPa [46]. In contrast to metals, many polymers are – because of their organic character – stable in the presence of inorganic media, including mineral acids, lyes, and aqueous salt solutions. However, also in contrast to metals, they react sensitively with organic solvents, such as alcohols, acetone, and benzene. Nevertheless, it has been possible to develop polymers which are stable in the presence of these media; one such example is the polyethylene petrol tank in the Volkswagen Polo which, simultaneously, is highly resistant to atmospheric corrosion and insensitive to petrol.

Polymers with linear or branched molecular chains in their ultimate form are known as *thermoplasts* (Table 5.21). These can be re-melted; in other words, the

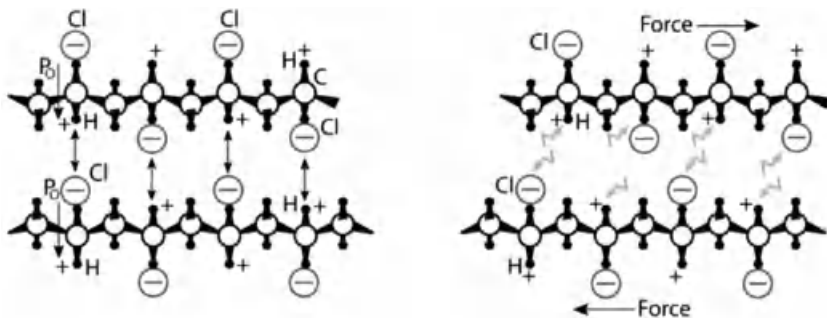

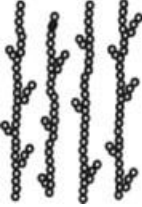
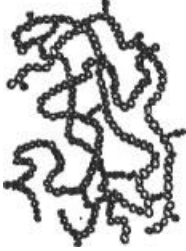
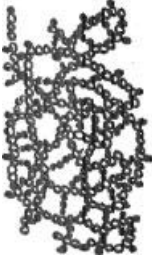


Figure 5.18 Breaking of semi-valence bonds as a result of tensile loading for the example of polyvinyl chloride (PVC) with van der Waals dipole bonding between Cl^- and H^+ .

Table 5.21 Classification of plastics according to their molecular structure.

Thermoplasts		Elastomers		Duroplasts	
	Linear molecular chains Capable of melting Soluble For RT soft to hard-tough or hard-brittle				Strongly networked molecular chains Not capable of melting Not capable of swelling Not soluble For RT hard

application of heat can alter the relative spacing of the molecular chains, so that they can slip over each other, causing them to be flowable and providing them with good shaping properties. However, when the molecular chains are linked to each other (“networked”), they can no longer be re-melted. A wide-meshed networking enables the formation of *elastomers*, and a close-meshed linking to so-called *duroplasts* (also referred to as *duromers*) (see Table 5.21) [48].

5.4.1

Thermoplasts

Thermoplasts are easily plastically deformable over a certain temperature range (they are then termed *thermoplastic*). Thermoplastic products can be manufactured by using primary shaping and forming processes, followed by machining. Below the decomposition temperature, thermoplasts can be repeatedly re-melted, which makes them suitable for recycling and also for welding. In thermoplasts, which represent the largest group of polymers currently in use (Table 5.22), there is no covalently bonded networking between the molecular chains. Completely disordered molecular chains forming an intertwined cluster are referred to as *amorphous* thermoplasts, while *semi-crystalline* thermoplasts are characterized by molecular chains in a parallel arrangement, according to the degree of crystallization (Figure 5.19).

Table 5.22 Typical thermoplasts and examples of their applications.

Abbreviation	Material name	Examples of applications
PA	Polyamide	Gearwheels, plain bearings, plain rollers, textiles, carpets
PC	Polycarbonate	CDs, DVDs, automotive glass, optical lenses, eyeglass lenses
PEEK	Polyether ketone	Rolling bearing cages, medical technology (stable up to 335 °C)
PET = PETP	Polyethylene terephthalate	Recyclable bottles, textile fibers, vascular prostheses
ABS	Acrylonitrile butadiene styrene	Automotive parts, Lego bricks, do-it-yourself equipment
POM	Polyoxymethylene, polyformaldehyde	Plain bearings, gearwheels, pump components, fan impellers, valve bodies
PMMA	Polymethyl methacrylate	Dental prostheses, tail lamps, reflectors, watch glasses, eyeglass lenses
PE-UKMW	Ultra-high molecular polyethylene	Pump components, gearwheels, sliding bushings, implants, endoprosthesis
PP	Polypropylene	Crash absorbers, child seats, bicycle safety helmets, seals
PTFE	Polytetrafluoroethylene	Plain bearings, shaft seals, vascular prostheses, non-stick coatings

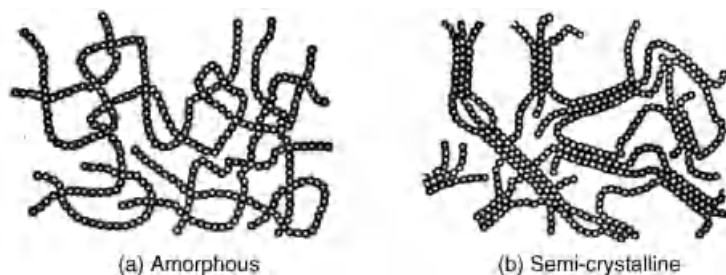


Figure 5.19 Molecular structures of thermoplasts. (a) Amorphous; (b) Semi-crystalline.

Table 5.23 Typical duroplasts and examples of their applications.

Abbreviation	Material name	Examples of applications
UP	Unsaturated polyester resin	Fiber-reinforced material components, buttons, heat-resistant and electrically insulating handles for cooking pots and pressing irons
EP	Epoxy resin	Fiber-reinforced material components for aviation and aerospace and automotive construction, structural adhesives (e.g., in boat constructions)

5.4.2

Duroplasts

Duroplasts are hard, glass-like polymer materials that are three-dimensionally networked via main-valence bonding. As the linkage is thermally stable, the duroplasts have neither melting capability nor swelling capability; moreover, they are stable in relation to solvents, and cannot be recycled. Their manufacture frequently takes place by way of polycondensation when, after hardening, they are no longer capable of plastic deformation. Duroplasts are used in the manufacture of light switches, and also frequently as components of fiber-reinforced materials (Table 5.23) [46].

5.4.3

Elastomers

Elastomers, which are also known as *rubber* or *vulcanized rubber*, are produced by the main-valence-bonded (chemical) networking of caoutchouc [49]. In 1839, the inventor, Charles Goodyear, found that when caoutchouc was subjected to heat with the addition of sulfur, it was transformed into rubber, in a process known as *vulcanization*. Like duroplasts, elastomers are thermally stable and cannot be re-melted, although compared to duroplasts they are only weakly networked. Up to the decomposition temperature, but also at very low temperatures, elastomers exhibit a pronounced

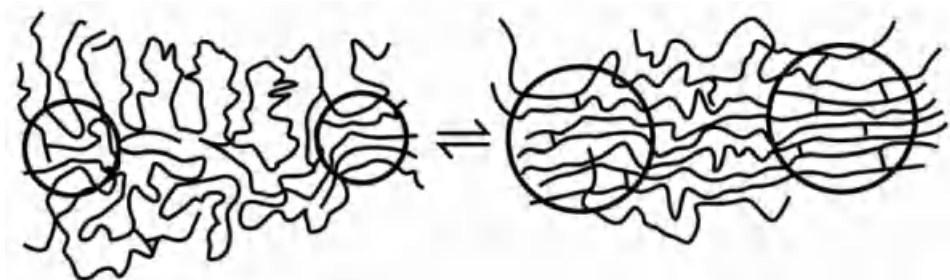


Figure 5.20 Elastic behavior of elastomers due to the stretching and contraction of the molecular chains.

Table 5.24 Typical elastomers and examples of their applications.

Abbreviation	Material name	Examples of applications
NR	Natural rubber	Rebound rubber, sand-blasting hoses, rubber-metal bearings, engine mounts, tires, bridge bearings, structural bearings
SBR	Styrene-butadiene rubber	Tires, rubber articles, conveyor belts, shoe soles
EPDM	Ethylene-propylene-diene rubber	Foamed automotive door seals, O-rings, floating ring seals, flat packings
NBR	Nitrile rubber	Seals, membranes, medical gloves, conveyor belts

elastic deformability. Such elasticity is due largely to the ability of the intertwined polymer chains to react to tensile loading by stretching, together with a disentanglement of the chains (Figure 5.20). Following removal of the tensile load, the chains again relax to their intertwined state. In order to prevent slipping of the chains over each other under tensile loading, the molecules are interlinked by sulfur bridging. The addition of a large amount of sulfur leads to the production of hard rubbers via vulcanization, whereas the addition of small amounts of sulfur leads to soft rubbers (Table 5.24).

5.5

Composite Materials

Within the field of composite materials, the continuously expanding requirements placed on technical components have prompted intensive research activities, as the combination of different materials has allowed the production of new materials with greatly improved properties. Composite materials are multiphase, macroscopic, homogeneous systems with phases of different principal material groups. The classification of composite materials is made according to the matrix material

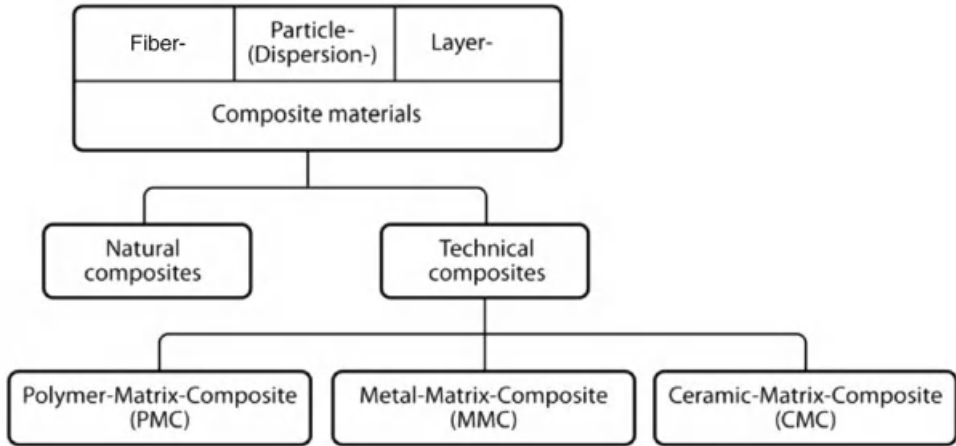


Figure 5.21 Classification of composite materials according to the matrix system.

(polymer, metal, ceramic) and the structure of the strengthening component (Figure 5.21). In this section, only composite systems of technical interest will be discussed.

In the case of a composite material, the matrix is reinforced with fibers, particles or layers in order to selectively improve certain properties. Such specific properties are the ratio of the tensile strength to the density (R_m/ρ), and the ratio of the modulus of elasticity to the density (E/ρ). These are determined by the properties of the matrix, and the strengthening components and their geometry and spatial arrangement (Figure 5.22). The interfacial boundaries between the matrix and the strengthening components may also have a considerable influence in this respect.

The strengthening components serve to bear the greatest part of the load acting on the component. The matrix, on the other hand, supports the strengthening components, provides cohesion and transfers the loads acting, as well as assimilating compressive loading and protecting fibrous composite materials for example, against buckling. The matrix also protects the strengthening components against ambient chemical attack. Depending upon the matrix material, polymers and metallic or ceramic materials are suitable as strengthening components.

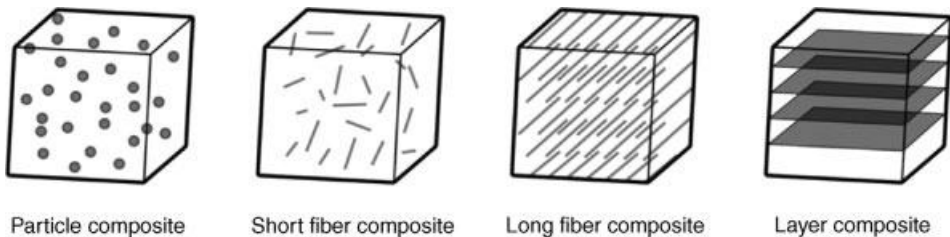


Figure 5.22 Basic composite material systems.

Fibers (long fibers, short fibers, long-fiber fabric): A distinction is made between short and long fibers. Long fibers can also be utilized as semi-finished textiles, in the form of fabrics or meshwork. Of technical importance are:

- carbon fibers (graphitic structure)
- glass fibers (SiO_2 with Ca, B, Al)
- aramide fibers (aromatic polyamides)
- polyethylene fibers (PE)
- boron fibers (C fibers with boron coating applied by CVD or W wires)
- ceramic fibers (SiC , Al_2O_3 partly stabilized with B_2O_3 and/or SiO_2)
- metallic fibers (W wires)
- metal carbide fibers (selectively solidified eutectic alloys, for example, Co–Cr–C or Co–Cr–TaC).

Modern fibrous composite materials find application as lightweight, high-strength components in the areas of aviation and aerospace engineering, as well as in the automotive industry, particularly in racing vehicles and in the high-price market segment. Increasingly, these materials are also finding use in the sports industry.

Particles and dispersions: Composite particle materials with hard material particles (oxides, borides, carbides, nitrides, silicides) are primarily employed as abrasive wear protection. They are the most commonly employed strengthening process, and are utilized with polymers, as well as with metals and ceramics. The strengthening effect of finely distributed hard particles in a metallic matrix derives from the impeding of dislocation movements. Here, there are two possible mechanisms. According to the Kelly–Fine theory, the particles are penetrated by the dislocations, whereas the theory of Orowan postulates that the dislocation lines migrate around the particles, leaving behind a dislocation ring around the particle. Both mechanisms absorb energy and therefore slow the migration of dislocations, thus enhancing the strength. By contrast with precipitations, embedded impurity particles (dispersions) are not soluble in the matrix at high temperatures, and therefore offer improved heat resistance. In electrochemically deposited dispersion coatings (see also Section 6.2.5), graphite, MoS_2 and polytetrafluoroethylene (PTFE) particles are also embedded to reduce friction. A frequently used filler material in natural rubber mixtures is carbon black which, besides its strengthening effect, also enhances ultraviolet (UV) stability and can be used to produce electrically conductive polymers [46].

Whiskers: Capillary single crystals with diameters $D \leq 1 \mu\text{m}$ are known as whiskers. Because of the lack of grain boundaries and virtual absence of lattice defects, their strengths are of the same order of magnitude as the theoretical values for ideal crystals. In metals, considerable improvements in performance have been demonstrated using SiC and Al_2O_3 whiskers, while the use of boron whiskers and whiskers of different metals have also shown improvements. In spite of their excellent mechanical properties, however, the use of whiskers has not become established, the main reason being the health hazards that can arise from the ingestion/inhalation of particle sizes similar to those of asbestos.

5.5.1

Polymer Matrix Composites (PMC)

The addition of filler particles can improve the mechanical properties and abrasion resistance of polymers. Best suited for this purpose are kaolin (aluminum silicate), lime (calcium carbonate, CaCO_3), glass beads, stone dust, siliceous sand, and to some degree, also carbon black [46]. Fiber-polymer composites (FPCs) contain carbon fibers, glass fibers, aramide, or polyethylene (PE). Although currently duroplasts are primarily employed as the matrix material for FPCs, the use of thermoplasts has shown a fairly rapid increase [46]. The manufacture of components from composite polymer materials can be divided into three process steps:

- The strengthening components are introduced; these may be in the form of long fibers, fabrics or meshwork, as well as pre-impregnated semi-finished materials (“prepregs”).
- The fibers are infiltrated into the polymer matrix.
- The composite materials are hardened (duromer matrices) or cooled (thermoplasts).

5.5.2

Ceramic Matrix Composites (CMCs)

Ceramic structural materials are distinguished by a number of properties, which makes them superior to polymers or metallic materials for certain applications. In particular, they have a high tensile strength and rigidity, even at high temperatures, they are characterized by a low specific weight and, in general, they have a good chemical stability. One disadvantage of many technical ceramics, however, is their low fracture toughness and the related low damage tolerance for defects. This means that even tiny defects, especially on the surface, may serve as the starting point for cracking. Due to their poor plastic deformation and the resulting reduction of stress peaks, even slight defects can lead to component failure. In contrast to polymers and composite metal materials, the strengthening of the matrix is required primarily to improve the damage tolerance. Here, the introduction of fibers to the ceramic matrix can hinder or even stop the propagation of cracks by initiating energy-absorbing processes, such as the tearing out of fibers, and the branching or redirection of cracks [50]. The ratio of the modulus of elasticity of the strengthening components to that of the matrix is therefore low. In the extreme case, both phases have the same rigidity. The development and application of composite ceramics essentially makes use of C and SiC fibers and, to a limited extent, of Al_2O_3 fibers. Likewise, Al_2O_3 , mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), C and SiC have also been employed as matrix materials for technical applications [51].

Although, developments aimed at improving the fracture toughness of engineering ceramics by the embedding of particles, single crystal fibers (whiskers) or flattened particles (flakes) have improved their cracking resistance only to a limited extent, they have led to applications in oxide ceramic cutting tools (Al_2O_3). Drastic

improvements in cracking resistance and improvements of properties such as ductility, fracture toughness and thermo-shock stability resistance, might also be realized by using C/SiC for the brake discs of automobiles.

5.5.3

Metal Matrix Composites (MMCs)

The particle and fiber reinforcement of metal alloys can take place in two different ways: (i) particles can precipitate out during solidification of the melt (precipitation hardening); or (ii) be added as dispersions (dispersion hardening). By the selective solidification of a eutectic alloy, fibers can be formed or incorporated by re-melting with the molten metal. As the mode of action of precipitations and selective solidification has been discussed previously (see Section 5.2), the following will be limited to the introduction of impurities as strengthening components (Table 5.25) for the MMCs. Due to the high melting points of the metallic alloys, it is necessary to take into consideration any chemical interactions between the impurity particles and fibers and the metallic melt. This presents no problems for the electrochemical deposition of dispersion coatings from aqueous electrolytes (see also Section 6.2.5), in which temperature-sensitive particles, such as PTFE, can also be embedded.

From the tribological standpoint, MMC systems can be divided into two groups with application-specific objectives:

- The strengthening of lightweight metals (Al, Mg, Ti), to improve their tribological, thermal, and mechanical loading capacities.
- A maximum wear resistance with metal–hard material composites, having the best possible combination of high hardness and high toughness, with Co, Ni, and Fe-based alloys as the matrix metals.

5.5.3.1 MMCs for Lightweight Constructions

Today, the range of applications for lightweight metal components is continually growing, with lightweight structural components – notably composed of aluminum but also of magnesium or titanium – having become standard in many areas, particularly in the automotive and aviation/aerospace industries. Although such lightweight metals have their limits when they must withstand high tribological, mechanical, or thermal loadings, their application limits can be extended by

Table 5.25 Strengthening components used in MMCs.

Type	Aspect ratio	Diameter (μm)	Examples
Particles	1–4	0.1–150	SiC, Al_2O_3 , cBN, B_4C , WC, WC/ W_2C , TiC, TaC, TiCN, NbC, Mo_2C , VC, Cr_3C_2 , diamond
Short fibers	10–10 000	1–5	C, SiC, Al_2O_3 , $\text{Al}_2\text{O}_3 + \text{SiO}_2$
Long fibers	>1000	3–150	C, B, W, Nb–Ti, Nb_3Sn , SiC, Al_2O_3

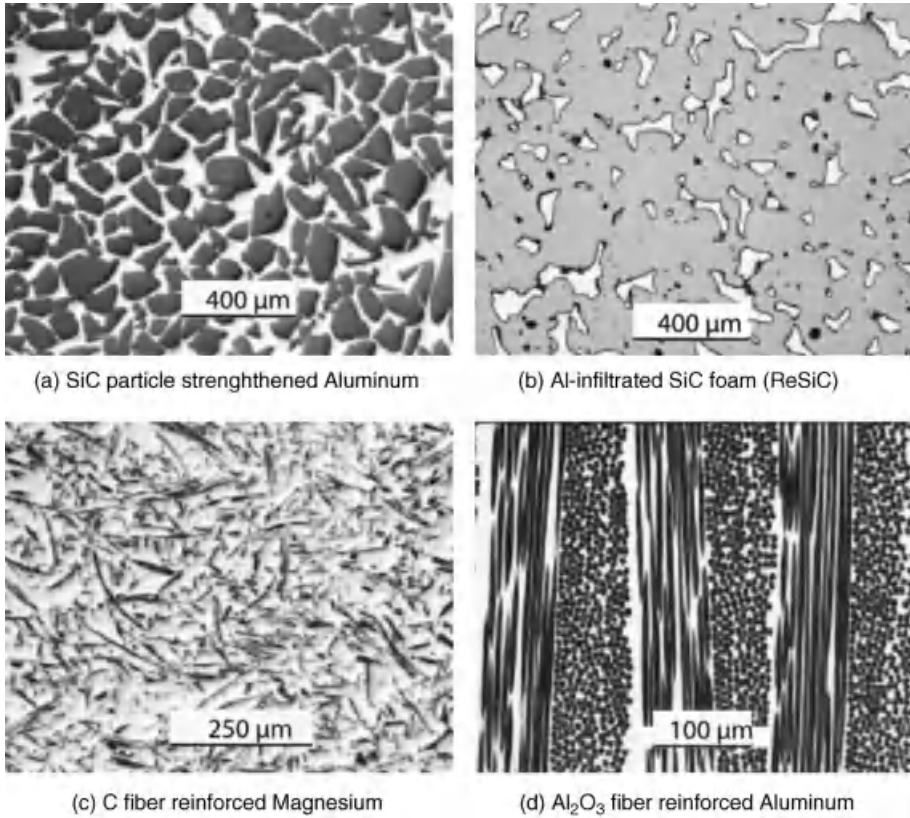


Figure 5.23 Photo-micrographs of reinforced lightweight metal alloys.
Source: EMPA, Switzerland [52].

strengthening them with particles and with short and long fibers, usually of SiC, Al₂O₃, and C (Figure 5.23) and, in part, also with B₄C. Both, fiber- and/or particle-reinforced composite lightweight metals can be manufactured in different ways; the simplest of these is the preferential addition of particles or short fibers to the metallic melt, followed by casting in the absence of any pressure. In order to obtain the most homogeneous distribution of the strengthening components possible, the melt must be stirred. Since the components manufactured in this way have no preferred direction of strengthening components in their microstructures, the material properties will be isotropic. In particular, sub-eutectic aluminum–silicon alloys are processed in this way. The addition of strengthening components increases the viscosity of the melt, limiting the maximum fraction of the strengthening components to approximately 30 vol% [52]. Then, by using a die-casting processes, previously manufactured semi-finished materials (preforms) of strengthening components may be infiltrated with metallic matrices. Such semi-finished materials are produced, for example, from short fibers dispersed in water, when the mix is pressed into a form and then dried. For the manufacture of MMC components, the

pre-formed porous semi-finished material is first introduced into a heated form, after which the metallic melt is driven into the mold by applying a pressure of 70–100 MPa (the pressure can be applied mechanically by a ram, or by using a pressurized inert gas). By using this process, it is possible to manufacture components with a fiber content of up to 80 vol% [52]. In particular, low-melting alloys (Al, Mg) are preferentially processed via this method. It is also possible to introduce long fibers and/or also fabric or foam into a metallic matrix by using similar processes. Unfortunately, the casting process has one major disadvantage, in that the fiber distribution is poorly controlled to a point where pre-fabricated semi-finished goods may not be present. A better distribution of the strengthening components can be achieved by using a powder-metallurgical manufacture. In this case, the ceramic particles are mixed with the matrix metal (which is present in the form of a powder) in order to obtain a homogeneous distribution in the component. The mix produced in this way is then compacted in a subsequent process step to create a green body, the density of which is about 80% that of the final product. In order to dehumidify the green body, the semi-finished material is first de-gassed under low pressure, after which the green body is further compressed, but this time at high temperatures. The product produced in this way can serve as the starting material for further processes, such as extrusion, forging, or rolling, whereby the particle size is then limited to 40 vol% in order to ensure good shaping properties.

5.5.3.2 MMCs for Maximum Wear Resistance

Wear protection in MMCs is achieved by particle strengthening, using hard materials. This development began during the very early 1900s, with the invention of the electric-arc furnace and the investigations conducted by Moissan, who used this system to produce artificial diamond. Although, in fact, diamond was not produced, some very hard compounds of tungsten and carbon were created that would soon be recognized as important in engineering [53]. Further research and development was conducted by the lamp industry with the successful manufacture of filaments from tungsten; however, as this required the use of very costly diamond drawing tools, a more cost-effective alternative was sought. Unfortunately, the initial attempts at using hard carbides to manufacture molds for tools and parts that were most subjected to wear proved to be unsuccessful. Consequently, two alternative approaches were pursued, and this led to the material concepts used today for extreme wear stressing.

The first approach followed the enrichment of alloyed steels with metal carbides. In addition to the alloyed steels used initially, Tamman achieved positive results with Ni–Cr and Co–Cr alloys, such that hard alloys (see also Section 5.4) were first developed at the start of the twentieth century. When using this melt-metallurgical method, the carbide content was limited to 45 vol%, since above this value the alloys could no longer be forged and, for many applications, were too brittle. However, with the introduction of powder metallurgy, it became possible to increase the particle content to more than 50 vol%. The so-called “pseudo-alloys,” which comprise a matrix of hard alloy and hard material particles (preferably of WC, VC, Cr₃C₂ or fused tungsten carbide WC/W₂C) are widely used in mining, strip mining, in the

construction industry, and for the extraction of materials. These are processed via thermal deposition welding coating processes (see also Section 6.2.7), thermal spraying (see also Section 6.2.6), and deposition brazing (see also Section 6.2.8), with powders, cored wires or fleeces being employed as filler materials. During the course of development, the range of hard materials was extended such that, today, borides, cBN, B₄C and diamond are all also used for strengthening. Nonetheless, the carbidic hard materials – which are distinguished by their excellent bonding to the metal matrix due to the high fraction of metallic bonding in the metal carbides – continue to dominate. Currently, sintered, tempered and annealed TiC–Fe composites with hardening capabilities are successfully employed as wear-resistant materials in ship building, sheet metal-forming, and compression molding under the designation “ferrotitanites.” These alloys contain approximately 50 vol% TiC, while the matrix is comprised of steels of different compositions (tool steel, heat-resistant steel, etc.), according to the purpose of the application. Following annealing at a Rockwell hardness of 38–42 HRC, the alloys have good machining properties and, after hardening, reach a Rockwell hardness of 68–71 HRC.

In parallel to melt-metallurgy, at the start of the twentieth century the first attempts were also made with the then new process of powder metallurgy to manufacture molds of tungsten carbide. The decisive break-through came in 1923, when K. Schröter of the Osram Studiengesellschaft mixed WC mono-carbide powder with 5–10 wt% Co, and then sintered the mixture at close to the melting temperature of Co. The (until then) unequaled strength values of the cemented carbide enabled their use for machining. Following purchase of the patent, the Krupp company launched the new cutting material on the market in 1925, under the name Widia (“wie Diamant”). Initially, this permitted the machining of cast alloys with a vastly improved performance, although only slight improvements were possible for the machining of steel, due to the high crater wear rate of the pure WC–Co cemented carbides. This problem was caused by the solubility of WC in the metals of the iron group (Fe, Ni, Co), and is the reason why WC may also be slightly attacked by the hot chips produced. Today, pure WC–Co compounds find application as thermal-spray wear protection coatings in many tribological applications (see also Section 6.2.6)

Between 1925 and 1931, under the direction of P. Schwarzkopf of the Metallwerk Plansee in Austria, crater wear-resistant cemented carbides were successfully developed with the introduction of carbides of the systems WC/TiC, Mo₂C/TiC, WC/Mo₂C, and also of the use of nickel as a bonding material, whereby sintering had to take place in a vacuum furnace. Parallel to this, in the USA, Fansteel introduced to the market (in 1930) a cemented carbide on the basis of TaC and Ni, while and in Germany Holzberger developed cemented carbides containing TiC, for which the Böhler company later acquired the rights. These new mixed-carbide-content cemented carbide types also brought about a veritable revolution of the cutting parameters that could be realized for the machining of steel that, above all, could be attributed to the formation of protective oxide layers on cemented carbides containing TiC and TaC. From 1934 onwards, cemented carbides with mixed carbides were marketed by virtually all manufacturers, whereby the cobalt-bound cemented carbide types on the basis of the ternary mixed carbides WC/TiC/TaC established themselves. Both, TaC

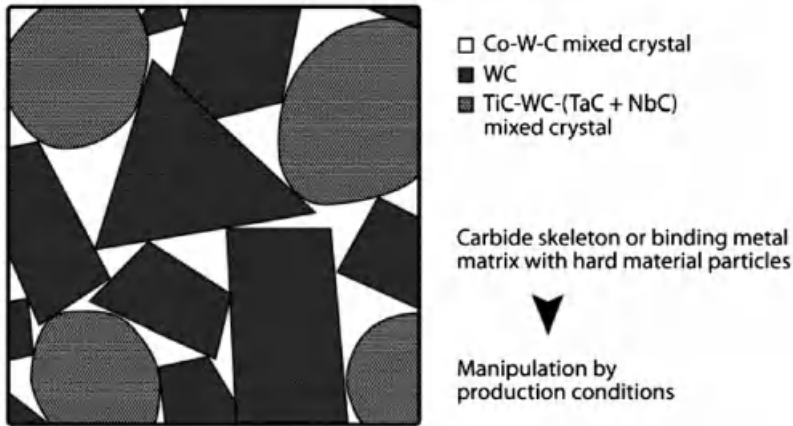


Figure 5.24 Schematic representation of a cemented carbide microstructure.

and small amounts of NbC or VC, were shown to inhibit grain growth in these types and, indeed, to this day WC–TiC–Ta/NbC–Co cemented carbides constitute the prevailing cemented carbide types for the machining of steel (Figure 5.24). The range of their use was further extended during the 1970s, with the introduction of high TaC contents, which improved their thermal cycling strength and therefore also allowed milling. Not only VC and Cr_3C_2 , but also Ta/NbC, find application as grain growth-inhibiting additives in WC–Co cemented carbides. Cr_3C_2 also serves as a basis for special corrosion-resistant cemented carbide alloys. The properties of Mo_2C are similar to those of WC, to a point where Mo_2C has repeatedly been proposed as a partial substitute for WC. Molybdenum has also taken on great importance as an additive in tungsten-free, TiC-based cutting alloys.

The first cutting materials on the basis of TiC– Mo_2C –Ni (titanite S) were developed by P. Schwarzkopf at Plansee due to the patent situation, and marketed from 1934 onwards [54]. Due to the better solubility of TiC in Ni, Ni is preferably employed as a bonding metal. In Germany, following the Second World War, the lack of raw materials led to a resumption in the development of low-tungsten content cemented carbides, with TiC/VC–Ni(Fe) alloys showing good results. Interest was also resumed in TiC– Mo_2C –Ni cemented carbides, such that between 1950 and 1960 the alloying of bonding metals with molybdenum improved to the extent that cutting materials became as important as the Al_2O_3 -based ceramics of the time, and indeed they are still in use today for certain applications. From the mid-1970s onwards, Rudy and colleagues developed very fine-grained, low-tungsten content cemented carbides with improved usage properties, by utilizing the spinodal decay of hard material components in the system Ti(C,N)–Mo(W)–Ni(Co). These (in part) low-tungsten-content cemented carbides contain nitrogen, and are known as “cermets” in technical terms; the term, which originated from the words “ceramics” and “metals,” has led to composite metal–ceramic components acquiring a whole new meaning.

In addition to alloy-engineering measures, process-technical innovations have – since the 1970s – become increasingly important in connection with improvements

in hard metal properties. Thus, whilst fine-grained hard metals were first successfully manufactured during the early 1970s, their improved hardness and flexural strength were not exploited industrially until the 1980s. In the case of hard metals which have high demands on their flexural strength, sinter-HIP technology was developed which provided not only a higher density but also a better micro-structural homogeneity.

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6

Surface Engineering

Today, important industrial sectors such as the automotive industry, the aviation industry and the power engineering industry, depend heavily on modern surface engineering processes. Yet, at the same time, the newer industrial sectors, such as medical engineering, micro-systems technology and micro-electronics, would not have been able to grow as rapidly without the methods of surface engineering. Consequently, approximately two-thirds of all technological innovations are considered attributable to material developments, as the commonly used materials are often no longer able to meet rising demands. Hence, in many industries, new materials with extended functionality and performance limits represent the driving force for new products, and the key to improved competitiveness. The potentials of surface engineering for separately optimizing the volume and surface properties of materials have proven to be both useful and necessary in many fields of engineering, in order to meet the requirements of modern leading-edge technology. The main driving forces behind the spread of surface technologies are the sparing use of resources, environmental protection, and increasing safety requirements. Although the value added by surface engineering and coating industries in Germany alone has been estimated at €20 billion annually [1], it can be assumed that, overall, only 10% of the actual potential of products amenable to surface coating is currently being exploited. It is generally recognized that approximately 85% of all component damage can be attributed to *surface attack* which, in addition to *mechanical attack* (such as wear), also includes *corrosion*. Clearly, a combination of different forms of surface attack is invariably responsible for component damage (Figure 6.1), and it is in this area that the correct application of surface engineering can offer valuable solutions.

The demands placed on technical surfaces differ greatly. The various requirements of industry and research were identified, recorded and evaluated in a Research Agenda – Surface Treatment survey, the “TOP 10” of which are listed in Table 6.1 [1]. The spectrum of requirements resulting alone from the ten surface properties named here shows a large and many-faceted variance. Moreover, it is also clear that the surface of the future must accommodate more functionality than ever before. It is clear that a surface is no longer simply a feature of a component; rather, in future it must also serve to determine essential physical characteristics, such as corrosion or wear properties. This potential, which is inherent in technical surfaces, is the main

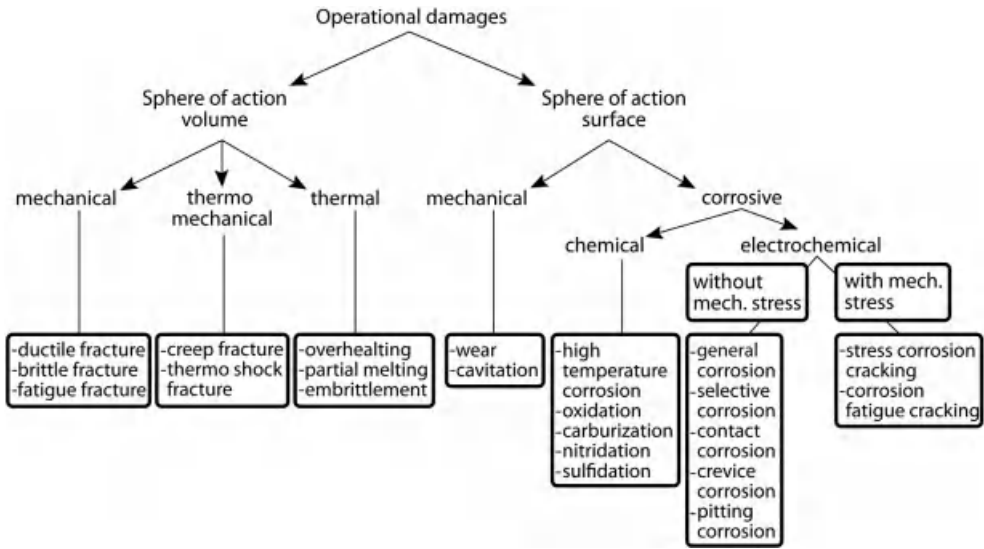


Figure 6.1 Operationally related types of damage to technical materials (after Ref. [2]).

reason for the constantly growing interest in surface engineering and its increasing added market value.

An overview of the market shares for the important surface engineering processes in Germany in 2005 is shown in Figure 6.2. Here, by far the greatest share of the market was shown to relate to electroplating processes, while heat treatment processes included thermo-chemical diffusion methods, such as nitration and carbonization. A significant share was also found in mechanical treatments, which included blasting procedures and, most importantly, cutting procedures such as polishing, grinding, and honing.

Table 6.1 The TOP 10 requirements for the technical surfaces of the future [1].

Properties	Named by (%)
Self-cleaning properties	100
Sensor technology	71
Tribologic properties	65
Scratch resistance	63
Hardness, elasticity	62
Environmental compatibility	57
Processability/applicability	56
Long-term stability	56
Chemical stability	49
Optical properties	48

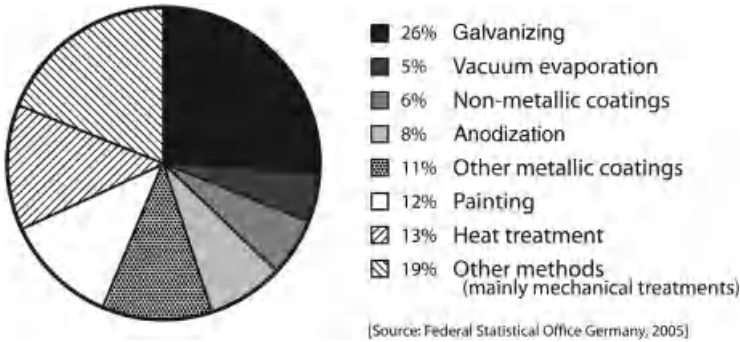


Figure 6.2 Market shares of surface technologies in Germany, in 2005.

6.1

Introduction to Surface Engineering

The surfaces of materials can assume a wide range of different functions (Figure 6.3). First, they can match the properties of the different materials. An example of this is the flue gas inlet of a power plant to the wash tower of a flue gas desulfurization facility where, as with refuse incinerators, the most severe corrosion attacks identified to date are seen to occur. In order to protect the construction against corrosion, the walls must be lined with very costly, high alloyed steel materials, including

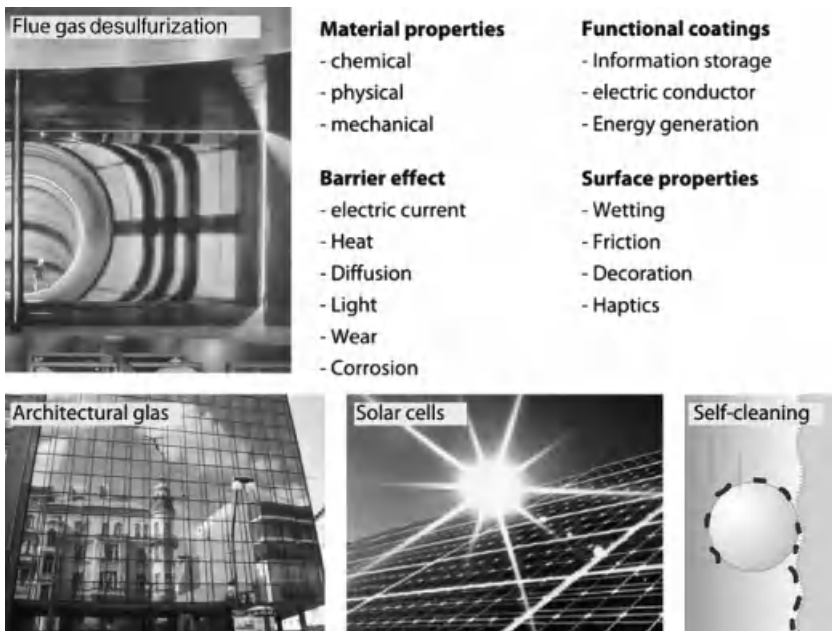


Figure 6.3 Functions of technical surfaces.

nickel-based alloys. But, to manufacture these constructions entirely from such materials would be neither economically feasible nor technically possible, and consequently inexpensive structural steels are covered with several millimeters of protective plating. There is no doubt that the most common function of technical surfaces is their barrier effect, with coatings being used as barriers against electric current, heat, diffusion, and light. An example of this is architectural glass, with which both the introduction of heat and lighting conditions can be manipulated. Coatings can also furnish barrier protection against surface damage, such as wear and corrosion, while surfaces can also serve to implement functions. Likewise, magnetic properties may serve as information carriers, and electrical properties for conducting current or for energy generation, such as in photovoltaic applications. With present-day methods of surface engineering, it is also possible to influence surface properties, such as wetting or friction, one aspect of which is the huge decorative (and lucrative) coating market. The haptics (tactile nature) of objects is likewise a surface phenomenon that can be realized on a selective basis.

6.1.1

Methodical Approach for Coating Development

A coating has no end in itself, as a coating development will always depend on the intended application (top-down method; see Figure 6.4). It is essential that a process is clearly understood by the surface engineer, as the “customer” is often unable to define a requirements profile from the surface engineer’s point of view. Consequently, the surface engineer must not only be able to think in terms of the application, but also be capable, in collaboration with the customer, to describe the load complex as completely as possible: only then can a theoretical choice of material for the surface be made. The customer will expect the surface engineer to have the required knowledge of materials, at which point – according to the application, construction and function – the suitable process technology can be selected. Coating

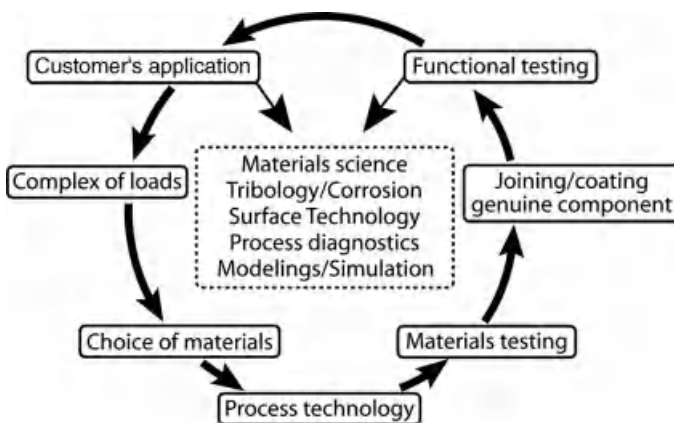


Figure 6.4 Methodical development approach in surface engineering.

development includes the initial selection of materials on simple samples, with the aid of materials analysis and materials testing. The goal here is to determine a suitable process “window” to manufacture a composite material, in consideration of the requirements profile for the application. The next step includes the component application, together with possible adaptations of the component geometry in order to obtain the best suited coated construction; the final stage will be to conduct application-oriented functional tests. A good surface engineer will require a basic knowledge in respect of materials technology, tribology, corrosion and surface engineering, while additional knowledge of process diagnostics, modeling and simulations will be indispensable for a thorough understanding of the processes utilized.

The development of coated tribo-elements includes the matrix (Figure 6.5) for the analysis and characterization of:

- coating properties
- compound properties
- system properties

The analysis of coating properties is mainly used for the development of appropriate process windows for the coating process. All surface engineering processes result in composite materials with other properties than those of the surface or the base material alone. The composite material must be fundamentally viewed as a unit, and capable of functioning as a unit, while the surface is always part of the coated tribo-element. The material and shape properties of the coating and the base material influence each other and act together as compound properties. Thus, for example, the internal stresses in the surface area can influence the strength characteristics of the component. One decisive factor (among others) for the utilizability of a hard-wearing protection layer is the supporting effect of the base material. In this case, the fundamental prerequisite is a sufficient bonding between the surface material and the base material. The development of coated components is always a system development, in which the system comprises the base material, coating material and the boundary layer (interface) between the base material and the coating, as well as the component geometry. In technical applications, the coated tribo-body is exposed to external loads. As the third step, therefore, the system boundaries must be extended with the surrounding medium, the complex of loads, and the counterbody. Tribological system properties are not material properties; rather, the coefficients of friction, wear resistance or corrosion resistance are quantities that are valid only when considering the tribological or corrosion system.

6.1.2

Bonding Mechanisms

The properties and design of a surface depend essentially upon the production history, with such a surface property state being of fundamental importance for follow-on surface treatments. Indeed, these properties determine the bonding mechanisms which arise between the surface of the base material and the coating,

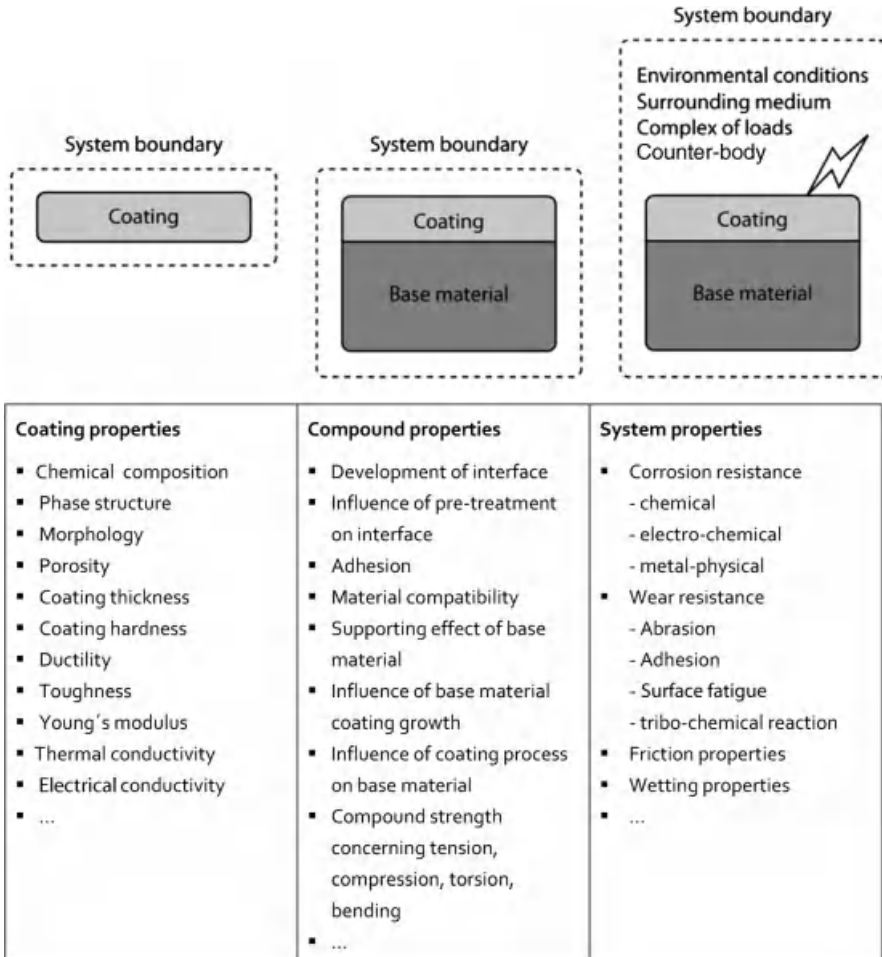


Figure 6.5 Evaluation matrix for characterization of coated tribo-elements under consideration of material and shape properties of coating, base body, counter-body, intermediate material, and surrounding medium and complex of loads.

the so-called *interface*. For every coating, its adhesion to the base material is of decisive importance since, without adequate bonding, no functioning layer system can be created. In fact, an inadequate bonding may even result in disadvantageous behavior, to a point where an uncoated base material would perform better in a direct functional comparison.

The major decisive factors for sufficient adhesion are the interactions and interactive forces in the boundary layer between the base material and the coating. The smallest possible distance between the uppermost layer of atoms in the materials (ca. 0.1–0.5 nm), and chemical reactions between the atoms favor good bonding. Yet,

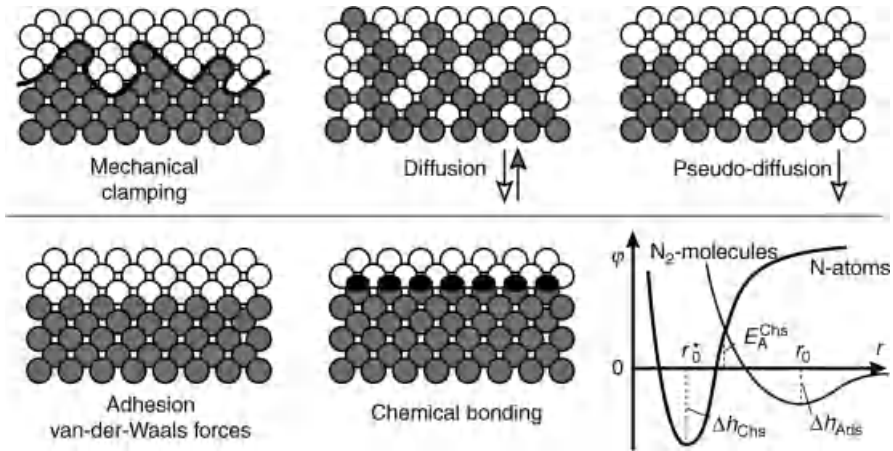


Figure 6.6 Bonding mechanisms between the surface material and base material.

whilst the process technology can influence this distance, chemical reactions are influenced primarily by the choice of materials. Low intrinsic stresses in the coating may also prove to be advantageous for good bonding stability, while the applied load complex may also influence the bonding. In general, it is possible to distinguish fundamentally between five different models for the interface (Figure 6.6) (as will be explained below). Whilst these bonding mechanisms are based on the assumption of an ideal case, in practice a single bonding model will rarely act alone in the interface; rather, a combination of the models will be found.

6.1.2.1 Mechanical Clamping

According to the theory of mechanical anchorage, a type of interlocking linkage exists that is responsible for the bonding. The prerequisite for such a bonding mechanism is the presence of coated caverns, hollow spaces and under-cuttings. By assuming a gapless covering, the bonding can be detrimentally influenced by the number, form, and size of the caverns; notably, the greater the number of caverns and the larger the hollow spaces, then the better the bonding. But the coated surface may also play a role since, the larger the surface the greater the number of existing possibilities for mechanical anchorage. Both, mechanical and chemical surface-roughening techniques can be used in order to enlarge the surface.

6.1.2.2 Diffusion

With a diffusion transition, the base material and the coating material are mutually soluble. This allows the formation of an inter-diffusion zone in which a matching of the two materials takes place, resulting in a matching of the chemical composition. The lattice structures of the two materials approximate each other, and also the intrinsic stress states. The formation of an inter-diffusion zone is essentially influenced by the different rates of diffusion.

6.1.2.3 Pseudo-Diffusion

If, during the application of a coating material, atoms from the coating are introduced to the lattice of the base material (due to an intensive application of external energy) and subsequently remain there, the situation is referred to as “pseudo-diffusion”; in this case, no solubility exists between the two materials, so that no diffusion will take place. Pseudo-diffusion may be observed with ion bombardment when the particle energy of the impacting ions is sufficiently large to penetrate the material lattice (interstitial diffusion). The diffusion is then not the result of a concentration equalization between two phases of different composition.

6.1.2.4 Adhesion

Such an interface is always formed when the materials involved are not mutually soluble, so that neither diffusion processes nor chemical reactions can take place. Under the assumption that a solid body is held together by internal cohesive forces, and that the surface represents only a cross-section of the body, the adhesive forces (surface energy) will develop as a result of the inner cohesive forces and enable bonding to another phase. The bonding derives from van der Waals forces, which are attributable to interactions between electric dipoles. Examples of van der Waals forces include hydrogen bonds, dipole–dipole bonds, dipole-induced dipole forces, and dispersion forces. The different linkage forces will vary in strength and in their ranges; the bonding stability of such a coating system will depend on the strength of these interactions.

6.1.2.5 Chemical Bonding

Between the base material and the coating, chemical reactions give rise to the formation of a bonding transition at the boundary surface. This may be in the form of inter-metallic linkages, oxides or other compounds which, as a rule, have a thickness of several atomic layers. It is possible to distinguish here between metallic bonds, ionic bonds and covalent bonds (the bonding energies rise in this order), the bonding energies of which are several orders of magnitude greater than the van der Waals bonding. Metallic bonding is found in metals and inter-metallic alloys, while ionic bonding occurs predominantly in many oxides (CaO), metallic chlorides (NaCl) and metallic hydroxides (NaOH). Examples of preferred covalent bonding are SiC and B₄C. Ceramic materials are characterized by the presence of different types of bonding. The only hard material with purely covalent bonding is diamond.

6.2

Processes of Surface Engineering

Equally as varied as the functions of surfaces are the processes of surface engineering. The goal of surface engineering is to provide an increase in the value of a material, and in order to structure and design technical surfaces it is important to have an understanding of a three-dimensional (3-D) surface area. Typically, the

surface engineer recognizes the surface as a part of an object that forms the boundary surface to the environment. All materials possess surface areas that have properties which differ from those of the base material (see Chapter 2.1). As a result of manufacture and interaction with the environment, several boundary layers are formed on all metals. All surface engineering processes have in common that the outer boundary layers must first be removed by using suitable pretreatment methods.

In surface engineering, a distinction can be made between surface modification processes and surface-coating processes (Figure 6.7):

- *Surface modifications* are processes which penetrate into the material and thus alter the surface properties; this can be in the form of thermal (e.g., by diffusion, as with nitration or carbonization), chemical, or also mechanical processes (e.g., by shot-blasting to achieve residual compressive strengths).
- For *surface-coating processes*, new materials are applied to the surface. The coatings can be applied as single layers and, as a rule, layer systems, alloy layers, composite layers or even gradient layers are produced.

The boundaries between modification and coating are not always entirely clear. For thermal diffusion processes, the material also grows outwards, just as with some coating processes the coating material can penetrate into the base material. Furthermore, many of these processes are used in combination.

Surface engineering processes are production technologies, classified in accordance with DIN 8580 (Table 6.2) into six principal groups. Allocation to these groups is based on whether a coating is applied to a surface (coating), or the surface is modified in the boundary area of the work piece.

The processes of surface engineering can be distinguished by the aggregate state of starting materials for the coating production (Figure 6.8). Depending on the requirements profile and the function, the appropriate surface engineering with regards to suitable coating materials, coating thickness, deposition temperatures and

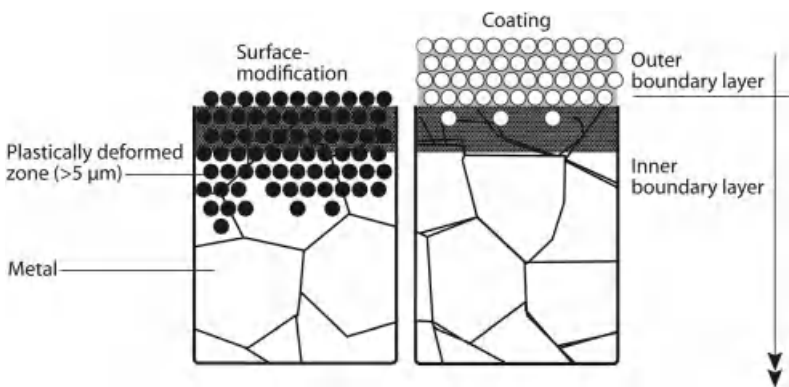


Figure 6.7 Classification of processes according to surface modification and surface coating processes.

Table 6.2 Classification of production processes in accordance with DIN 8580.

Group	Criterion	Process examples
Primary shaping	Achieving cohesion	Casting, sintering, electrolytic deposition
Forming	Maintaining cohesion	Forging, stamping, rolling, extruding, creasing, crimping, flanging, flattening, flexing, stretching
Separating	Reducing cohesion	Sawing, filing, abrading, ramming, turning, milling, drilling, lapping, planing, honing, broaching, grinding, thermal separation, polishing, cutting, electro-erosion machining
Joining	Increasing cohesion	Assembling, screwing down, riveting, clinching, welding, gluing, soldering
Coating	Increasing cohesion	Varnishing, electrolytic deposition, physical vapor deposition (PVD), chemical vapor deposition (CVD) thermal spraying, hot-dip galvanizing, electro-surfacing, surface brazing, plating
Altering material properties		Heat treatment, hardening, annealing

process-related restrictions concerning coatable geometries can be selected. For tribological applications, the following processes are suitable (as described in the following sections):

- Converting processes
- Physical vapor deposition (PVD)
- Chemical vapor deposition (CVD)
- Sol–gel processes
- Process for (electro-)chemical metal deposition
- Thermal spraying
- Deposition welding
- Deposit brazing
- Thermo-chemical diffusion processes

6.2.1

Converting Processes

Coatings formed by redox reactions between a metallic surface and an aqueous electrolyte solution, whereby the metal is electrochemically converted, are referred to as *conversion coatings*, and consist of inorganic salts or metallic oxides. In the electrochemical converting process, anodic oxidation (anodizing) takes place with an applied external current, used above all with non-noble metals. The chemically formed coating (phosphatizing, chromating, burnishing) takes place without the application of an external current, when the metallic surface is subjected under

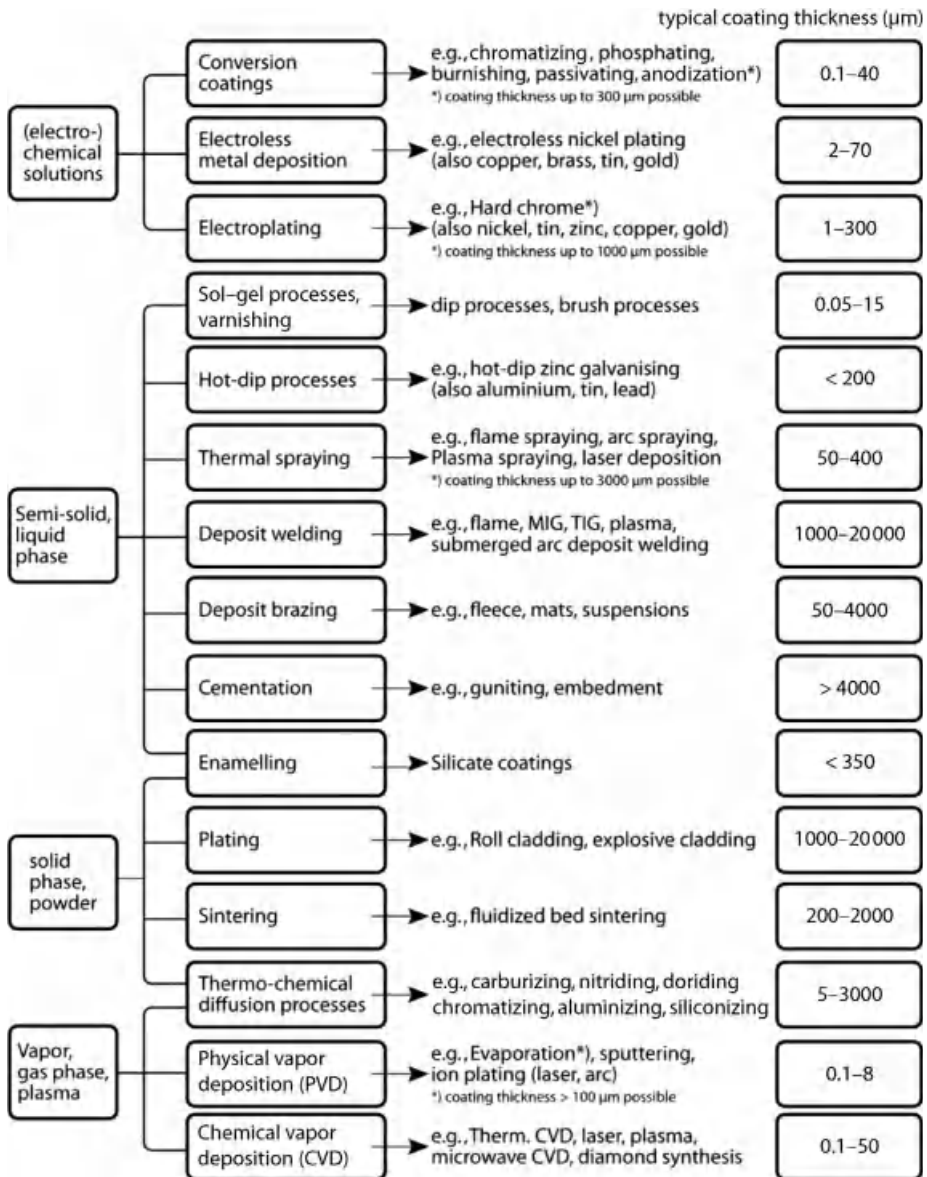


Figure 6.8 Classification of processes of surface engineering by aggregate state of starting materials with approximations for typical coating thicknesses (without organic coatings, e.g., enameling or gumming).

specific conditions to a redox reaction, with a liquid medium of corresponding composition (electrolyte solution).

Conversion coatings offer protection against corrosion, and may serve as an undercoating for paints and enamels on metallic surfaces. In addition, the coatings

Table 6.3 Classification of the function of converting processes (after H. Hoffmann [5]).

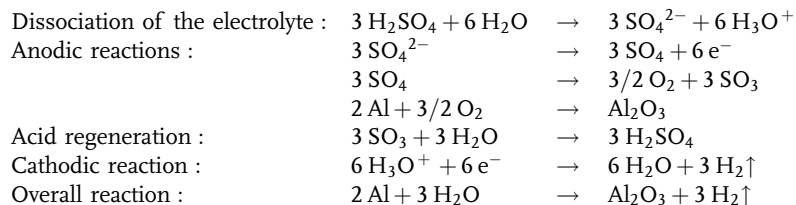
	Anodizing	Phosphatizing	Chromatizing	Burnishing
Bondcoat	+	+	o	+
Corrosion protection	+	+	+	o
Wear protection	+	+	–	–
Reduction of friction	o	+	–	–
Decoration	+	O	+	+

(+ : suitable, o: suitable with restrictions, –: unsuitable).

are used to influence the visual appearance of the base metal (e.g., improved gloss, a particular color) [3]. Conversion layers alter the frictional properties and can also improve wear resistance, while other properties of the coatings are their low electrical and thermal conductivity and their inherent color [4]. An overview of the functions of the different converting processes is provided in Table 6.3.

6.2.1.1 Anodizing

The term “anodizing” refers to the electrolytic (i.e., anodic oxidation) of metallic surfaces. Electrolytic oxidation is used primarily for aluminum components, as well as for work pieces and components of magnesium, titanium, zinc, and their alloys. These materials are each capable of forming a natural oxide layer of about 0.05 μm thickness, but with the anodic oxidation process coating thicknesses of up to 300 μm can be achieved (the usual coating thicknesses are in the range of 5–40 μm , or up to 80 μm for magnesium). The term “eloxal” derives from the electrolytic oxidation of aluminum for the production of protective coatings, from which the likewise frequently used term “eloxation” also emerges. During anodizing, the metallic surface is converted to a very hard, scratch-resistant metal oxide layer with excellent adhesive strength. As an example, Figure 6.9 illustrates the anodic oxidation of the DC-sulfuric acid process for the electrolytic oxidation of aluminum. Here, the work piece is connected as the anode in an electrolytic bath, and a DC current is applied; the cathodes are located at the edge of the bath. The application of a current causes the evolution of atomic oxygen at the anode, which reacts with the metallic surface and forms the metal oxide. This entails the following reactions [6]:



The coating formation mechanism is the result of the oxidation of aluminum due to the evolution of atomic oxygen at the anode. Initially, a thin, electrically insulating

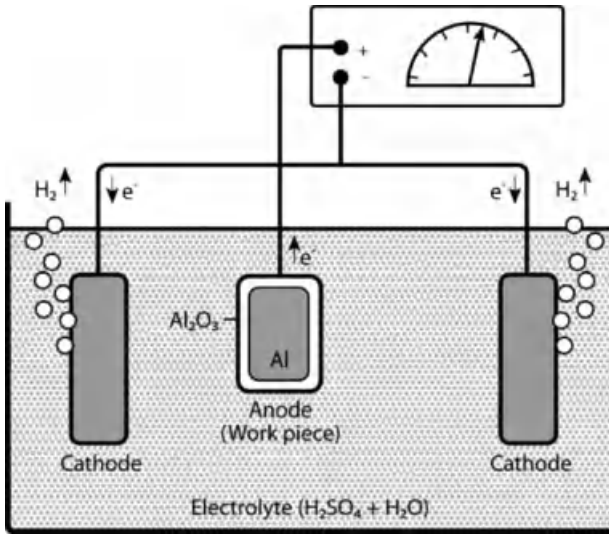


Figure 6.9 Schematic diagram of anodic oxidation for the example of the DC-sulfuric acid process for the electrolytic oxidation of aluminum materials.

and pore-free Al₂O₃ barrier layer is formed; this barrier layer will continue to grow for as long as the aluminum ions are able (due to the applied current) to diffuse through the layer. Normally, the process breaks down at a layer thickness of about 1 μm, but in order to obtain thicker coatings on aluminum, high-conductivity electrolytes are utilized, which results in the punctiform re-dissolution of the barrier layer (Table 6.4). The locally thinned regions are electrolytically penetrated, which leads to the electrolyte penetrating into the break-down channels and causing a re-formation of the barrier layer [5]. The barrier layer grows into the base material, while the finely porous, thicker eloxal layer forms in the residual oxidized regions at the perimeter of the break-down channels. This layer exhibits columnar pores and a honeycomb-like hexagonal structure (Figure 6.10), whereby the cell diameter depends upon the anodizing potential. Due to the constant re-dissolution of the barrier layer at the pore base, the thickness of the porous layer grows, while the thickness of the barrier layer remains constant. The layer formation stops when the re-dissolution on the surface of the barrier layer and the new formation at the interface are in equilibrium [6]. For the hard anodizing of aluminum with the DC process, the electrolyte is cooled to about 0 °C, allowing thicker layers of >100 μm to form. The Al₂O₃ layer grows from the original component surface two-thirds inwards and one-third outwards.

Because of the two-layer structure, eloxal coatings that consist of a thick barrier layer and a main porous layer are referred to as *duplex coatings*. The main porous layer can be sealed following processing for better corrosion protection; in addition, the porous layer can be colored for decorative purposes by including dyes. It is also possible to improve the sliding and static friction properties by impregnating the layer with particles, such as polytetrafluoroethylene (PTFE) or a lubricant.

Table 6.4 Anodizing electrolytes. After Refs [5, 7, 8].

Material	Electrolytes	Special properties	Applications
Aluminum	Boric acid, citric acid	Very low capacity for re-dissolution of the Al_2O_3 barrier layer	Dielectrics for electrolytic capacitors
Aluminum	Sulfuric acid, oxalic acid, chromic acid, aliphatic carbonic acid	Pronounced capacity for re-dissolution of the Al_2O_3 barrier layer (Eloxal process) Direct current – sulfuric acid Direct current – oxalic acid Direct current – sulfuric/oxalic acid Alternating current – oxalic acid Alternating current/Direct current – oxalic acid	Corrosion protection, wear protection, decoration, organic acids and chromic acid for color anodizing
Aluminum	Alkali carbonates, alkali phosphates, phosphoric acid	Very pronounced capacity for re-dissolution of the Al_2O_3 barrier layer	Glossy anodizing
Magnesium	Potassium fluoride, sodium phosphate, potassium hydroxide, aluminum hydroxide, potassium permanganate	HAE electrolyte, named after <i>Harry A. Evangeliste</i> – the process utilizes alternating current, layer thicknesses of up to 80 μm are possible, no capacity for re-dissolution of the oxide layer DOW-17- electrolyte	Corrosion protection, wear protection, decoration
Magnesium	Ammonium difluoride, sodium dichromate, <i>ortho</i> -phosphoric acid	To reduce friction, impregnating with a lubricant is meaningful	Corrosion protection, wear protection, decoration
Titanium	Sulfuric acid	The layers are comprised of zinc ammonium phosphate and zinc chromate	Undercoating for enamels
Zinc	Phosphoric acid, chromium oxide, NH_4 , ammonium fluoride		

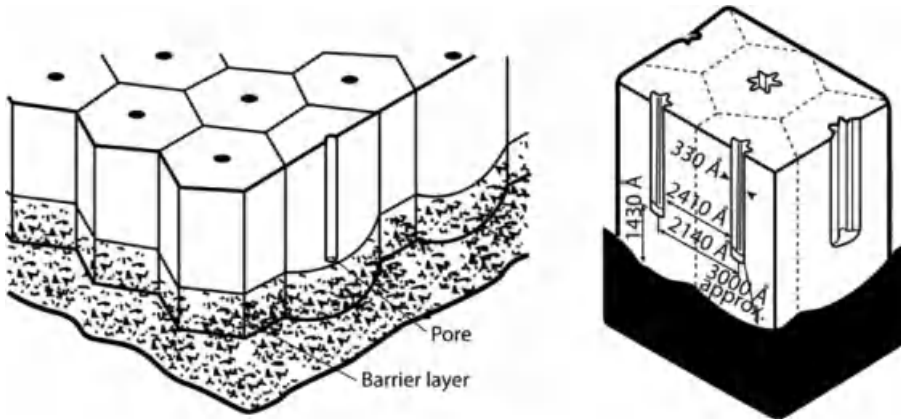


Figure 6.10 Structure of the aluminum oxide layer with the eloxal process. (a) Structure of the grown oxide cell [9]; (b) Individual cells with pore channel [10].

The individual anodizing process steps are performed in sequentially arranged baths, into which the work pieces are usually placed as rack parts. Rinsing steps are carried out between the degreasing, conditioning, anodizing, coloring, and compression process steps (Figure 6.11).

Plasma electrolytic oxidation (PEO), which is also known as *plasma anodizing*, represents a further development in anodizing. The process is mainly used with aluminum, titanium, and magnesium, with the conversion processes being based on

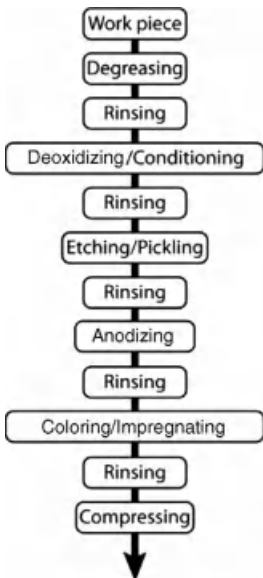


Figure 6.11 Bath sequence and anodic oxidation facility. Illustration courtesy of AHC Oberflächentechnik GmbH of the AIMT Group, Kerpen, Germany.

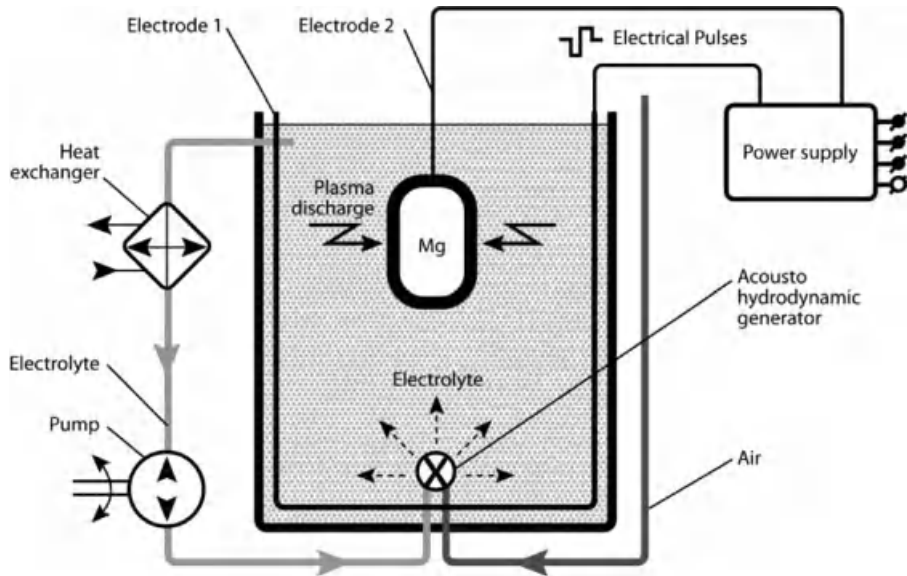


Figure 6.12 Principle of the plasma electrolytic oxidation process. Illustration courtesy of Keronite International Ltd, Cambridge, UK.

those of electrolytic oxidation. The major advance compared to classical anodizing is the utilization of a plasma, whereby the plasma phenomena influences the electrode processes as new layered structures are formed on the surface. The coating sub-processes can be divided into thermally induced and diffusion-induced reactions, while chemical reactions and macro-particle transport in the electrolyte also take place in parallel [11].

The principle of plasma electrolytic oxidation is illustrated schematically in Figure 6.12. In this case, the oxide layer forms in a chromium-free, slightly alkaline electrolyte and, as with anodic oxidation, the work piece is connected to an external current source and constitutes the anode. When a pulsed alternating current is fed through the bath, this leads to the formation of a controlled plasma discharge such that sparks are produced on the surface of the work piece, causing it to become fused over a short time and to react with the activated oxygen. This results in the formation of three oxide layers of different morphologies, each having good adhesive strength in relation to the metallic substrate (Figure 6.13). A barrier layer with a thickness of approximately 100 nm constitutes the direct bonding to the work piece, and both nonporous and porous oxide layers are formed over this. Typically, the oxide layer will grow partly over and partly under the surface. The process stages of PEO may be summarized as follows:

- Plasma chemical process by electrical discharge at high potentials, spark discharge
- Substrate is fused and reacts with the activated oxygen

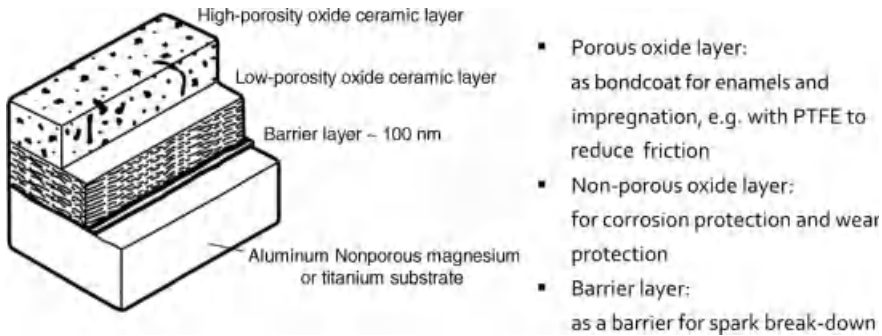


Figure 6.13 Structure of a plasma-anodized coating. Illustration courtesy of AHC Oberflächentechnik GmbH of the AIMT-Group [8].

- Electrolytes: aqueous solution of, for example, fluorides, borate, or phosphate
- Formation of amorphous oxide layers containing crystalline regions

When compared to a classical anodizing process, the main advantages of PEO are that it is safe, environmentally acceptable, and that alkaliferous and chromate-free electrolytes are used. Also, the process and component temperatures are low, at 12–30 °C. Moreover, there is generally no need for any complex pretreatment of the work piece surfaces, which allows a higher production rate. Typically, the coating will grow at a rate of 0.3–1 $\mu\text{m min}^{-1}$ on aluminum surfaces, and at up to 2 $\mu\text{m min}^{-1}$ on magnesium surfaces. The hardness values of the oxide-ceramic coatings are between 500 and 2000 HV, according to the base material and the thickness of the ceramic layer; such hardness values are therefore superior to those obtained with anodic oxidation. This opens up new areas of application for anodizing in connection with heavy tribological stressing; typical examples include brake pistons for sport planes, engine pistons for the automotive industry, rotor discs for turbines and compressors, hydraulic cylinders, and compressor rotors.

6.2.1.2 Phosphatizing

Phosphatized coatings are formed by the reaction of a metallic surface with the phosphatizing solution, which is comprised of diluted phosphoric acid (H_2PO_4) and other additive components. On the metallic work piece, a virtually insoluble coating of metallic phosphates, oxides, and hydroxides is formed. Phosphatized coatings have been used since the very early twentieth century, notably for the corrosion protection of low-alloy steel components. The first large-scale technical application was developed by Parker Rust-Proof in the USA, and dates from the year 1918; indeed, the common term of “Parkerizing,” which is still used today, derives from the name Parker. Besides Parker[®], other brand names such as Bondern[®], Coslettieren[®] and Atramentiern[®] are in use [2]. Phosphatizing finds application for low-alloyed steel (<5 wt% alloying elements), zinc, and zinc alloys, as well as some aluminum alloys. Depending upon the cations present in the phosphatizing solution, it is possible to distinguish between:

- Alkaline phosphatizing without additional cations (“non-layer-forming phosphatizing”)
- Zn phosphatizing with Zn^{2+} , $\text{Zn}^{2+} + \text{Ni}^{2+}$, $\text{Zn}^{2+} + \text{Ca}^{2+}$ or $\text{Zn}^{2+} + \text{Mn}^{2+}$
- Mn phosphatizing with Mn^{2+}
- Fe phosphatizing with Fe^{2+}
- Tri-cation phosphatizing with Zn^{2+} , Mn^{2+} , Ni^{2+} , especially for aluminum alloys

Phosphatizing is predominantly employed for the purposes of:

Corrosion protection and bondcoat: Due to the presence of pores and cavities in the coating, the corrosion protection of pure phosphate coatings is very poor and offers only temporary protection [7]. However, with follow-on treatments, such as enameling, painting, applying plastic coatings, oils, waxes, or chromatizing, the corrosion protection can be improved. Compared to many organic coatings, phosphatized coatings are impermeable to water vapor, and therefore well suited to the prevention of under-rusting. Moreover, the rough coatings represent an excellent bondcoat for the application of further coatings (Figure 6.14). In conjunction with additionally applied waxes, soaps or oils, phosphatizing offers adequate corrosion protection for many applications. Here also, the phosphatized coating assumes the function of an bondcoat. Hot-dip zinc galvanized steel, to which an additional coating of enamel is to be applied (e.g., for car bodies) is generally phosphatized or chromatized. In this case, the phosphatizing system serves as an integral part of the hot-dip zinc galvanizing facility.

Reduction of friction and improvement of wear protection: In particular, zinc and manganese phosphate coatings offer good protection against adhesive wear, and thus good emergency running and run-in properties, which are further improved by greasing. Consequently, they are often applied to moving machine elements, such as for gearwheels, piston rings, or valves. Manganese phosphate alloys show a partic-

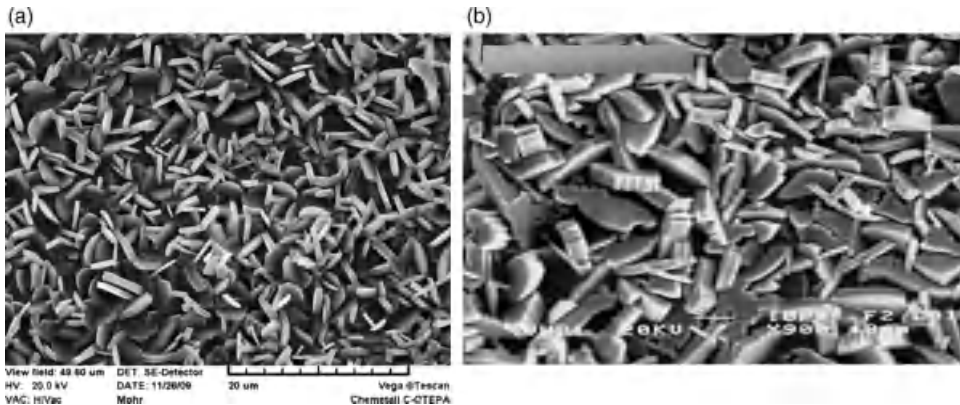
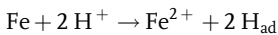


Figure 6.14 Scanning electron microscopy images of phosphate coatings. (a) Zn phosphatizing onto a hot-dip zinc galvanized steel. (Illustration courtesy of Christoph Mohr, Chemetall GmbH, Frankfurt); (b) Tri-cation phosphatizing onto aluminum. (Illustration courtesy of aluMATTER).

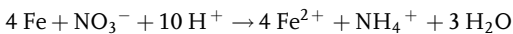
ularly good adsorption capability for lubricants, while zinc phosphate coatings are used for the cold-forming and deep-drawing of sheet metal, wire drawing, or tube drawing. The phosphatized surfaces of the semi-finished products to be formed may also be treated with lubricants, such as oils or soaps; this greatly reduces the loading of the semi-finished products to be formed, and allows more complex forming processes.

Thin phosphate coatings (ca. 0.3–1 μm) are produced in alkaline phosphate solutions prepared from wet phosphoric acid (pH range 3.5–6) [7], to which no other metal ions are added. Since, for alkaline phosphatizing, the metallic ions necessary for coating formation are derived from the component surface, a parabolic time law governs the growth of the coating. In other words, as the coating thickness is increased, the coating rate will fall off, such that the increase in coating thickness is time-limited. Hence, when a work piece is completely covered with a metallic phosphate coating, the reaction will cease immediately. This process, which is frequently described as “non-layer-forming phosphatizing,” is very slow and requires high temperatures ($>95^\circ\text{C}$) and long treatment times [12]. However, the process can be accelerated by adding oxidizing agents to the phosphatizing solution. With so-called “layer-forming phosphatizing,” the electrolyte contains additional cations (Mn^{2+} , Zn^{2+} , Fe^{2+} , Ca^{2+} , Ni^{2+} , Cu^{2+}), such that the kinetics of the redox reaction becomes transport-controlled. That is, the rate of coating formation will depend upon the availability of cations on the substrate surface, and this will lead to a further reduction in process time. In this way, coating thicknesses of 5–15 μm , and in part up to 30 μm , can be achieved.

The first process step of phosphatizing is a pickling reaction, in which the cations of the substrate material are dissolved. In the case of low-alloy steel components, this takes place in accordance with the following reaction [13]:

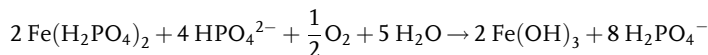
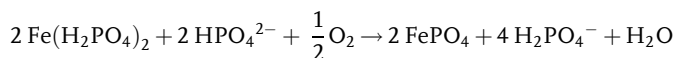


According to this reaction, the phosphatizing solution is neutralized (i.e., the pH value is increased). The atomic hydrogen H_{ad} which initially is set free is adsorbed onto the substrate surface, which polarizes the metallic surface and inhibits formation of the metal phosphate. It is for this reason that an oxidizing agent is added to the electrolyte in the form of a nitride, nitrate, chlorate, or borate, to convert the adsorbed hydrogen and de-polarize the metallic surface [5]. For phosphatizing solutions to which nitrate has been added and a low-alloy steel component, the following reaction takes place:



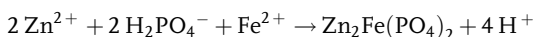
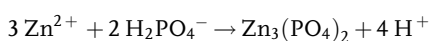
Due to the rise in pH value at the interface, the solubility of the phosphatizing bath (for example, of iron phosphates at the electrolyte–metal interface) is lowered and the phosphates or hydroxides are precipitated out [14]. The precipitated iron phosphate (FePO_4) crystals become embedded in the crystal lattice of the component surface,

where they form a very fine crystalline phosphate layer; other sources speak here of (X-ray) amorphous coatings [13].



Cleaning in advance of the phosphatizing itself involves the use of alkaline cleaners, in order to remove in particular any fatty impurities. After cleaning, the components are rinsed twice, although it is often difficult to remove alkalis from steel components. However, when alkalis are subjected to the phosphatizing bath, the bath would undergo an unacceptably high reduction in pH, such that this process step needs to be repeated. Following alkaline phosphatizing, cleaning is performed in completely de-mineralized water, followed by drying. Coatings produced in this way require at least six separate baths, which clearly involves a considerable technical complexity. Consequently, *iron-wash phosphatizing* was developed during the 1980s and is still very widely used today. In this case, the phosphatizing bath also serves to clean the components, the process being limited to three to four baths. In the majority of cases, the phosphatizing solutions are applied by spraying, while the reaction times range between 0.5 and 5 min [14], at temperatures of between 45 and 60 °C.

Layer-forming phosphatizing will be described as an example of Zn phosphatizing (though, in principle, this description also applies to Mn and Fe phosphatizing). In order to produce zinc phosphate coatings on low-alloy steels, it is necessary to use phosphatizing baths in which zinc ions are present in dissolved form, although as a result of a pickling reaction, iron ions are also initially dissolved. The coating is formed in accordance with the following reactions [14]:



This means that the coating produced is comprised of zinc phosphates and iron–zinc phosphates. The zinc phosphatizing process is not only more complex than alkaline phosphatizing, but activation of the component surface may also be necessary when particularly fine-grained phosphatized coatings are required. In this case, salts of nickel or copper are added to the bath for the purpose of activation. By way of an exchange reaction, nickel or copper crystals are precipitated on the surface, and serve as heterogeneous nucleation centers. Alternatively, an activation bath containing an alkaline form of a colloidal titanyl phosphate is placed before the phosphatizing bath; the titanyl phosphate then accumulates on the component surface, causing the heterogeneous nucleation centers to become available. Likewise, with zinc phosphatizing, attempts have been made to considerably reduce the

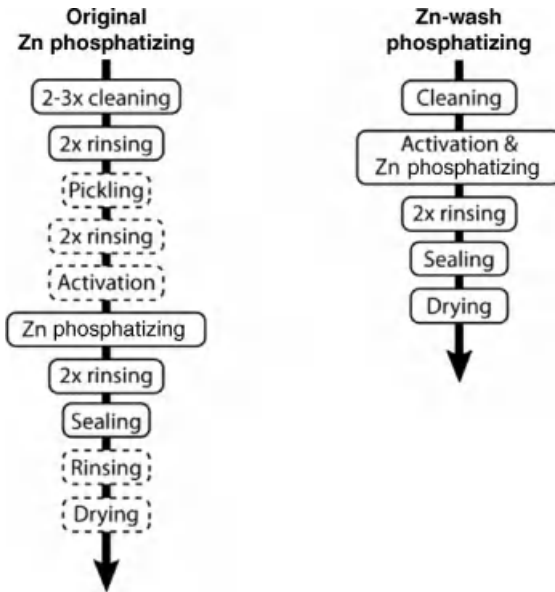


Figure 6.15 Process chains for Zn phosphatizing.

number of process steps; the result was a zinc-wash phosphatizing process in which the activation and phosphatizing steps were combined. The different procedures for zinc phosphatizing are illustrated schematically in Figure 6.15. In contrast to alkaline phosphatizing, in this case the coatings are also sealed. The zinc phosphate coatings are composed of needle-shaped crystals although, even with a thick coating on the surface of the component, the tiny interstices remain free. During sealing, the phosphatized component is immersed for example, in chromic acid, which accumulates between the interstices. A subsequent thermal treatment leads to (presumably) the formation of insoluble iron-chrome-spinel from the reaction between chromic acid and the steel base [13].

The component is then either immersed in the phosphatizing solution, or sprayed with it. Iron and zinc phosphatizing can be implemented with both processes, whereas manganese phosphatizing can be implemented only via the immersion process. In the case of immersion, the parts to be phosphatized are first degreased, pickled and rinsed, and then suspended in the warm phosphatizing solution (95–98 °C = hot phosphatizing, 40 °C = cold phosphatizing). Typically, a long-duration process will require 30–60 min, and a short-duration process 3–10 min. For spray phosphatizing, the exposure time is very short, at approximately 12 s [2].

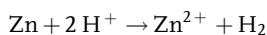
6.2.1.3 Chromatizing

Chromatizing is generally employed with aluminum and zinc materials [13]. In the case of zinc, chromatizing takes place principally on a previously electroplated zinc coating, or as post-processing of a hot-dip zinc galvanized steel plate. Other base materials which can be chromatized include magnesium, copper, cadmium, bronze,

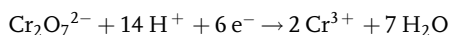
silver, and tin [3, 4, 13]. According to the color of the coating formed, it is possible to distinguish between transparent, blue, yellow, olive-green and black chromating. The color, and thus also the properties of the conversion layer, depend on the composition of the chromating solution, although the pH value, temperature, duration of treatment, motion of the bath, and condition of the surface of the material treated will also influence the visual properties [3, 4, 13, 15].

The coating is formed by a dissolution and precipitation process as a conversion layer, although when selecting the chromating solution the relationship between the pH of the medium and the metal corrosion and coating formation is decisive. Chromic acid solutions (H_2CrO_4) containing hexavalent and/or trivalent chromium salts, as well as impurity ions such as sulfates, chlorides, nitrates, fluorides or acetates, are usually employed as chromating solutions in order to influence the color and hardness of the coating [3]. The stepwise formation of a chromate coating on zinc is as follows [4]:

- Dissolution of the zinc:



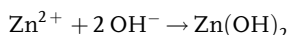
- Simultaneous reduction of a part of the Cr(VI) ions, present in the form of dichromate, by the hydrogen evolved:



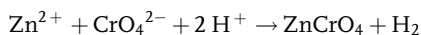
- Due to consumption of the hydrogen ions, the pH value will rise, resulting in the precipitation of chromium hydroxide:



- Part of the zinc ions formed according to the first equation form zinc hydroxide and precipitate out:



- The other part of the zinc ions react with the Cr(VI) ions, present in the form of dichromate, to form zinc chromate:



The inherent color of the chromate coating is *transparent*, but as the thickness of the coating is increased (to ca. $0.08 \mu\text{m}$) it begins to appear *blue*, as a result of interference colors. Transparent coatings are very thin (ca. $0.01 \mu\text{m}$) and offer poor corrosion protection; they are used only as a very low insulating resistance [15].

The inclusion of chromate ions produces a *yellow* coating. In fact, yellow chromating can be precipitated in the *dark yellow* (brown) color range, resulting in comparatively thick coatings ($>1 \mu\text{m}$) which offer excellent corrosion resistance. When the coatings exhibit a yellow color they are moderately thick (ca. $0.1\text{--}1 \mu\text{m}$) and

suitable as bondcoat for organic coatings. Besides layer-forming compounds of low solubility (e.g., on zinc: $\text{Cr}(\text{OH})_3$, Cr_2O_3 , ZnCr_2O_7 , or ZnCrO_4), small amounts of soluble Cr(VI) are incorporated into the layer. *Olive-green* coatings additionally incorporate anions from the phosphoric acid. The chromating solution is accordingly adjusted for the production of thick coatings (coating thicknesses on aluminum 2.5–10 μm and ca. 1.25 μm on zinc). *Black* shades are obtained by the inclusion of silver chromate or other silver compounds (the coating thickness is in accordance with the base chromating) [4, 13]. In addition, it is also possible to stain the coating, and for this purpose both alizarin and diazo dyes, as well as eloxal colors, are well suited. The soluble chromates incorporated into the coating are responsible for two special characteristics of yellow, black, and olive chromating [5]:

- At damage points, chromate compounds with poor solubility are again formed with the soluble chromates. This self-healing effect of chromating is unique, and leads to a superior corrosion protection. This self-healing effect is not found with other chromium coatings from electroplating, PVD or CVD processes, thermal spraying, or thermo-chemical diffusion processes, where no soluble chromates are present in the coating.
- Soluble chromates [e.g., Cr(VI)] can pass into the environment as a result of wash-out. These are highly toxic and carcinogenic, so that chromating (yellow, black, green) is becoming increasingly forbidden. Alternative processes therefore increasingly utilize Cr(III) electrolytes, whereby chromite [Cr(III)] is incorporated into the coatings.

Chromatized coatings are applied by immersion, flooding, spraying rolling, or roll coat techniques. As with phosphating processes, they entail the process steps that are summarized in Figure 6.16. Following chromating, the coatings are present in a

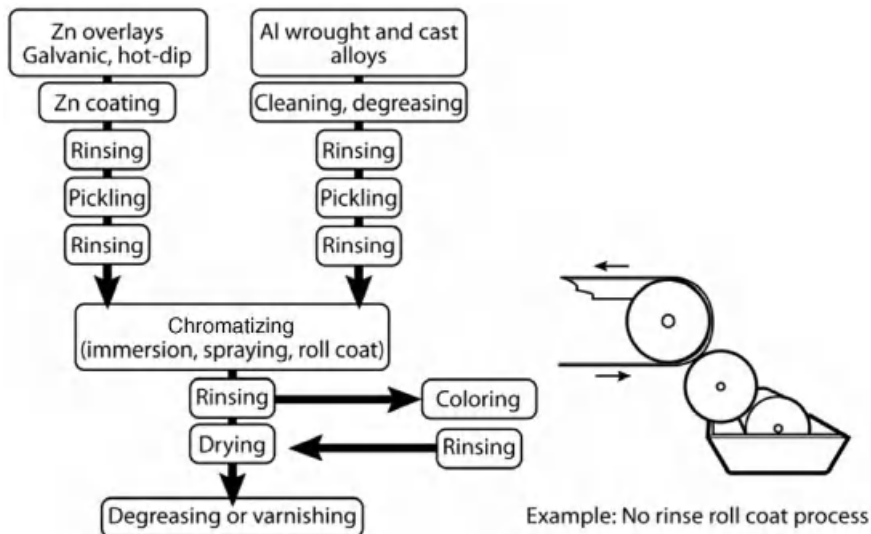


Figure 6.16 Process steps for chromating [3].

gel-like amorphous form that are sufficiently resistant to abrasion only after drying [3, 4]. For the chromating of aluminum bands immediately treated with the application of a post-processing color or an adhesive coating, the chromated coating is dried without being rinsed in water; the process is then referred to as “no-rinse chromating” [15].

Chromated coatings find application as undercoating in order to improve the adhesion of enameled coatings on components, or as corrosion protection. By way of example, magnesium is frequently chromated in order to protect against corrosion, up to the time of assembly or final processing. Olive-chromated aluminum is used in architecture, for example as roof cover plates, window blinds, antennas, or in airline terminal halls. For such purposes, chromating is much less costly than anodizing and, because of their inherent color, chromated coatings can also be used for decorative purposes. Chromating, following electroplated zinc coating and cadmium coating, forms part of the normal process sequence for conserving the gloss of a surface. For example, small parts such as screws, nuts and bolts, when manufactured in mass production, are often chromated after being zinc-plated. As the conversion layers exhibit insulating properties suitable only for low currents, aluminum is generally chromated when the electrical conductivity of aluminum device parts must be maintained. In electro-technics, brass, copper and silver are often chromated to protect them against becoming tarnished [3].

6.2.1.4 Comparison of Chromating and Phosphatizing

As chromating and phosphatizing solutions contain both chromic acid and phosphoric acid, it is not possible to define exact boundaries between the two processes. Apart from the chemical composition of the solutions and the coatings – which in the one case contains primarily phosphorous compounds and in the other case contains primarily chromium compounds – the following differences exist between the two processes:

- Phosphatizing solutions always contain, in addition to metallic phosphates, an oxidizing agent as an accelerator, in order that in practice the coatings are formed within acceptable times. In chromating solutions, no further oxidizing agents are necessary, as hexavalent chromium itself is a strong oxidizing agent. Furthermore, the chromates, Cr(VI) and chromites Cr(III), formed during the reaction have very low solubilities, so that the solution requires no further additives in this respect either for the formation of compounds with very low solubilities.
- Another difference between chromated and phosphated coatings concerns the coating structure. Thus, the former are amorphous, with thicknesses up to about 1.5 μm on zinc and maximum 10 μm on aluminum, while the latter are predominantly crystalline and can be deposited in thicknesses of up to around 30 μm .
- Chromating is not suitable for wear protection, nor for the reduction of friction in machine elements or shaping processes.

6.2.1.5 Burnishing

So-called *burnished coatings* represent another possibility for the corrosion protection of steels. The manufacture of burnished coatings can be classified according to four different processes [16]:

- Inoxidation of the iron, using steam at temperatures of 700–1000 °C in closed retorts.
- Burn-in processes; that is, heating the iron following the application of a blackening medium.
- Anodic oxidation in hot electrolytes.
- Treatment of the work pieces in oxidizing molten salts.

The last-named process represents the most frequently used in industry, as is apparent from the standard for burnished coatings. In accordance with the DIN 50938 standard, the burnished coating is described as a thermally produced dark brown to black oxidic conversion coating, manufactured by immersion in acidic or alkaline salt solutions. With this process, mixed oxides of FeO (wuestite) and Fe₂O₃ (hematite) are formed on the surface of the treated components. The coating thicknesses are only of the order of 0.75–2.5 μm, so that the components have a high dimensional stability during coating [3, 5]. Because of the character of the oxides, these thin layers are not dense and, if untreated, will offer virtually no corrosion protection. In order to improve the protective effect, burnished components are continuously oiled or greased, which causes the pores to be closed. Whilst the most familiar application for the burnishing process is in the coating of weapons, the process is also very often employed in the construction of machines and tools; in this case, the coatings can be used up to a temperature of 300 °C. The coatings are also stable against flexural and abrasive stresses, but the electrical conductivity and magnetic properties of the base material are only slightly influenced.

Burnishing utilizes molten salts or solutions of salts at temperatures in the range of 320–360 °C, with exposure times between 15 s and 15 min, resulting in a brown-colored coating on the component. These molten salts contain sodium nitrite, sodium nitrate, and sodium hydroxide in a mixture ratio which is specific to the component. Due to the high temperatures of the burnishing process, the components may become distorted; however, in order to avoid this a burnishing process has been developed that takes place at about 150 °C in aqueous salt solutions that may be either acidic or alkaline. With this burnishing variant, it is possible to distinguish between single-bath, double-bath, and triple-bath burnishing, though double-bath processes are used most frequently in industry. The process details and sequence for two-bath burnishing are listed in Table 6.5. An examination of the immersion times indicates that this process requires longer exposure times than the above-mentioned processes using hot molten salts.

In addition to the hot burnishing described, so-called “cold processes” – such as the NU-BLAK[®] cold burnishing process – are also available. With this process, it is also possible to produce iron oxide coatings on goods surfaces at room temperature with thicknesses of about 0.15 μm. In terms of corrosion protection capabilities, however, cold-burnished coatings and hot-burnished coatings are very similar [5].

Table 6.5 Process sequence for two-bath burnishing [5].

Process step	Constituent	Immersion time (min)	Temperature (°C)
Degreasing	Alkalis	10	50–85
Rinsing (threefold cascade)	Water	1 per step	RT
Pickling	Diluted acid	3–10	RT – 50
Rinsing (threefold cascade)	Water	1 per step	RT
Burnishing I	Burnishing solution	10–15	138–140
Rinsing	Water	3	RT – 40
Burnishing II	Burnishing solution	10–15	141–145
Rinsing	Water	3	RT – 40
Rinsing (threefold cascade)	Water	1 per step	RT
Oiling	Dewatering oil	5–10	RT

RT = room temperature.

6.2.2

Physical Vapor Deposition (PVD)

Today, PVD coatings have become a permanent part of the engineering sciences. They appear everywhere in daily life, as data storage media on CDs and DVDs, as thermal insulation on automotive glass and architectural glass, as a diffusion barrier for grocery packaging, or as decorative coatings for jewelry, fittings, and accessories. Since the 1980s, PVD coatings have become established over a wide range of technical applications relating to wear protection and the reduction of friction. Yet, besides coating development in its own right, much experience in methodical product development has been acquired, initially for tools and later also for components.

With PVD processes, the deposition of ions, atoms or molecules from the gaseous phase or plasma is utilized to synthesize tribological protective coatings on tools and components with layer thicknesses of about 1–6 μm . These PVD processes run as batch processes in fine vacuum or high vacuum ($\sim 10^{-4}$ to 10 Pa) at temperatures between about 140 and 600 °C (Figure 6.17). Moreover, because the coating temperatures are below the tempering ranges of many metallic base materials, any loss of hardness or deformation of components during coating can be excluded. For the coating of plastics, the coating temperature can be reduced to below 100 °C (so-called “low-temperature” processes).

The starting materials required for the chemical compounds (e.g., metals or ceramics) are, according to different physical principles, thermally vaporized or sputtered (momentum exchange), and then condensed onto the components. Other components of the coating material can be supplied in the form of reactive gases. According to the type of vaporization of the coating material, it is possible to

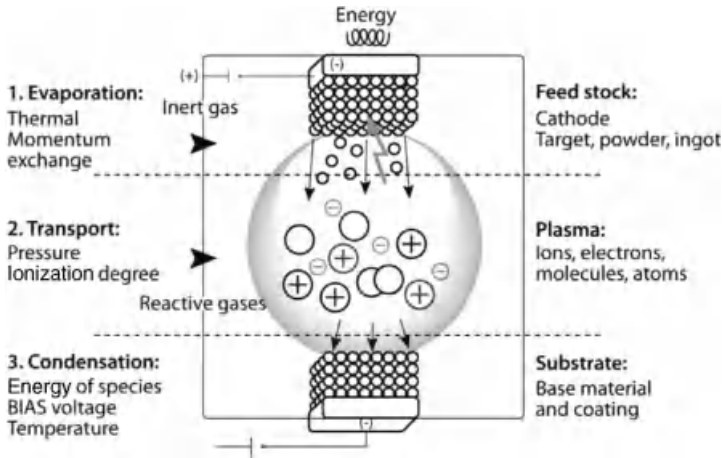


Figure 6.17 Schematic representation of the principle of PVD processes.

distinguish between thermal evaporation, cathode sputtering, and ion-plating process groups.

All PVD processes can be broken down into three phases: (i) when the starting material is transformed from solid to gaseous form; (ii) a transport phase, when the particles are transported to the substrate (the component treated) within the coating chamber; and (iii) a layer growth phase on the substrate, which occurs as a result of condensation. The different phases of a PVD coating process are described in detail in the following.

6.2.2.1 Generation of a Gaseous Phase or Plasma

As a rule, the starting material for the coating process is in solid form (target, powder, or ingot), but when the energy is introduced the material is transformed to a gaseous or plasma phase. PVD processes can be distinguished according to the method by which the gaseous or plasma phase is produced. If the starting material is ionized in a plasma, to yield high-energy ionized particles for the coating synthesis, the process is termed *ion plating*. The gaseous phase can be generated by using the following physical principles (Table 6.6).

Thermal evaporation: With thermal evaporation in a high vacuum (10^{-4} Pa), the target material is electrically heated in a suitable container. Depending on the material, the container may be a ceramic crucible, a tantalum boat, or tungsten wire spirals. When a sufficiently high vapor pressure is reached atoms, ions and clusters of atoms are emitted from the surface of the material being evaporated, and precipitate as a layer onto the substrate and the surrounding surface. The thermal energy required for evaporation is supplied to the material to be evaporated, alternatively in the form of an electron beam, a laser, or an electric arc (Figure 6.18). The evaporation rate and the amount evaporated are functions of the molecular mass of the starting material, and also of the saturated vapor pressure and the temperature of the evaporation source.

Table 6.6 Process variants in PVD technology.

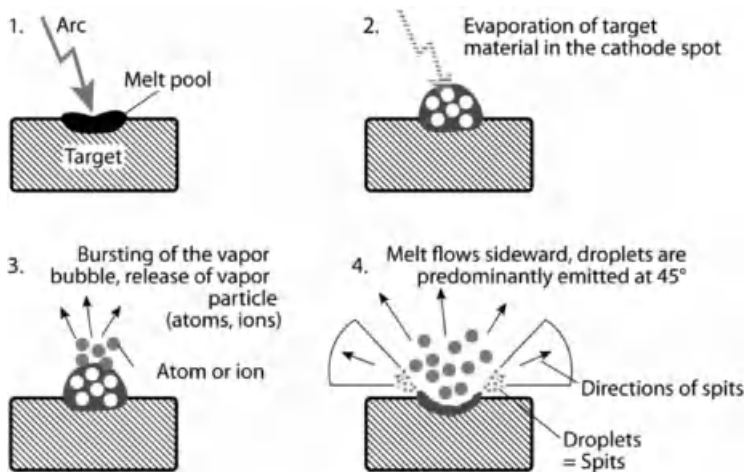
Process variants	Energy source
Thermal evaporation	
- Vapor deposition process	Electric current
- EB-PVD: Electron beam PVD	Electron beam
- LVD: Low-voltage arc deposition	Electron beam
- PLD: Pulsed laser deposition	Laser beam
- AIP: Arc ion plating	Electric arc
Sputtering by momentum exchange	
- Cathode sputtering	Kinetic energy, glow discharge
- MS: Magnetron sputtering	Kinetic energy, glow discharge
- MSIP: Magnetron sputter ion plating	Kinetic energy, glow discharge
- IB: Ion beam sputtering	Kinetic energy, glow discharge
- HIS [®] : High-ionization sputtering	Kinetic energy, glow discharge
- HIP: High-ionization pulsing	Kinetic energy, glow discharge
- HPPMS: High-power pulse magnetron sputtering	Kinetic energy, glow discharge
Hybrid processes	
- ABS: Arc bond sputtering	AIP for cleaning + MSIP for coating
- IBAD: Ion beam-assisted deposition	Ion implantation + MSIP

$$\text{Evaporation rate } G : G = 0.044 \cdot p_D \sqrt{\frac{M}{T}}$$

p_D : saturated vapor pressure

M : relative molecular mass

T : temperature of evaporation source

**Figure 6.18** Thermal evaporation for the example of an electric arc. (AIP = arc ion plating).

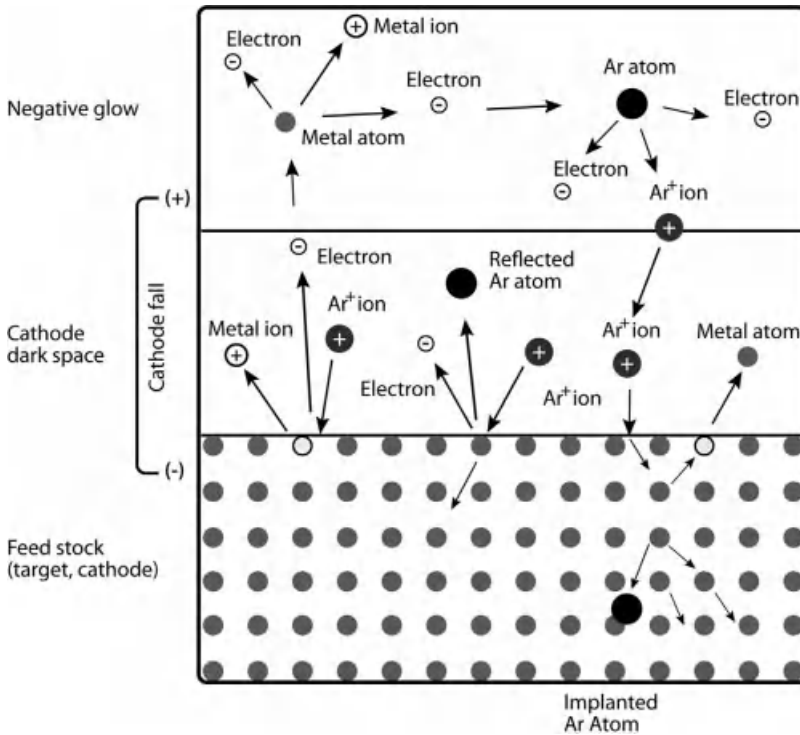


Figure 6.19 Collision and ionization processes on the sputtering target with cathode sputtering.

The saturated vapor pressure describes the pressure of the vaporous phase of a material at which the liquid and gaseous phases are in equilibrium. For a pure material, the saturated vapor pressure is a function of the temperature alone:

$$\text{Saturated vapor pressure } p_D : p_D = A \cdot e^{\frac{B}{T}}$$

A: Integration constant

B: Heat of evaporation (material-specific constant)

T: Temperature of the evaporation source

Cathode sputtering: With cathode sputtering, following the generation of a high vacuum in the deposition chamber, the process gas is led in up to a pressure of 0.1–10 Pa. In this case, a noble gas (e.g., argon) is used as the process gas in order that no chemical reactions take place between the target and the process gas. With the application of a negative voltage to the target (cathode), a glow-discharge plasma is produced [17], such that the electrons which are set free collide with gas particles and ionize further inert gas atoms. During the collision, in turn, new electrons are set free. During the ionization process, the recombination of electrons with gas ions occurs simultaneously, with the emission of electromagnetic radiation – this is the reason for the glow of plasmas. Due to the applied negative voltage, the positively charged gas ions (Ar^+ ions) will be accelerated to the target, with the impact of the ions on the target resulting in different physical processes (Figure 6.19) [18, 19]:

- The impinging ions collide with the target, transferring energy to it. By momentum transfer, the atoms and ions required for deposition are ejected and the target is sputtered. As a result of the impact, secondary electrons can also be set free from the target.
- Ions can, however, also be simply neutralized and reflected at the target. These reflected neutral particles impinge without breaking on the substrate, where they can be implanted.
- For a sufficiently high energy of the impinging ions, inert gases can be implanted, which recombine with the electrons in the target. Lattice atoms in the target are simultaneously displaced as a result of collision processes, which can also lead to the release of metal atoms. The impact of the ions on the target can result in different physical processes.

An important measure of the sputtering effectiveness is the *sputtering yield*, or *sputtering rate*, S . The sputtering rate S_0 , which describes the ratio of the number of ejected atoms to the number of impinging ions, is a function of the atomic binding energies of the target atoms among each other, the energy of the impinging ions, and the angle of incidence θ of the impinging particles (Figure 6.20). S' takes the angle of incidence θ in relation to the target normal into consideration:

$$\text{Sputter rate } S_0 : S_0 = \frac{k}{\lambda} \cdot \frac{4 \cdot M_1 \cdot M_2}{(M_1 + M_2)^2} \cdot \frac{E_i}{E_B}$$

$$\text{Sputter rate } S' : S' = \frac{S_0}{\cos \theta}$$

k : constant

λ : mean free path length of the ions

M_1 : mass of the impinging ions

M_2 : mass of the target atoms

E_i : energy of the impinging ions

E_B : binding energy of the target atoms

θ : angle of incidence of the impinging ions in relation to the target normal

6.2.2.2 Particle Transport

The transport phase describes the motions and processes of the particles (atoms, ions, clusters of atoms, droplets) in the gaseous phase within the coating chamber. During the transport phase, the partly neutral and partly charged particles move through the plant with partially ionized gas, which – when viewed as a whole – is electrically neutral. This fourth state of matter is referred to as a “plasma” (from the Greek – formation), the properties of which are primarily influenced by the charge carriers found within it. All PVD plasmas are low-pressure plasmas with a working pressure of less than 10 Pa, although a distinction can be made between “cold” and “hot” plasmas. PVD plasmas, in which the particles are transformed by thermal evaporation to the plasma state, are as a rule hot plasmas; that is, a thermal equilibrium is present in the plasma (T_p) between the ions (T_i) and the electrons (T_e), such that $T_i \approx T_e \approx T_p \leq 2 \times 10^4$ K. By contrast to these, “sputtering plasmas” are

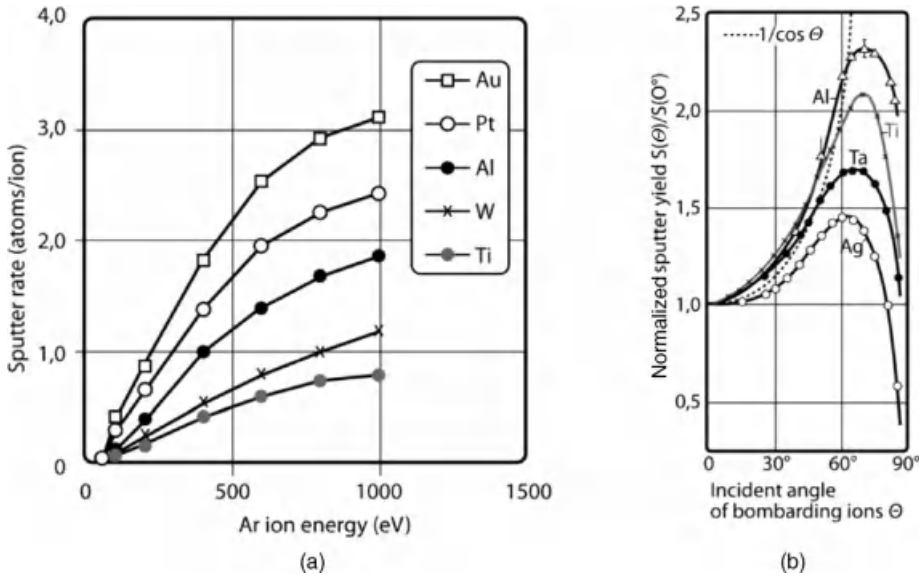


Figure 6.20 Sputter rate for different target materials. (a) As a function of sputtering energy; (b) As a function of the angle of incidence.

cold plasmas, where the ion temperature T_i corresponds approximately to the condition $T_i \approx T_p \approx 300$ K, while the temperature of the electrons T_e is several thousand degrees ($T_i \ll T_e \leq 10^5$ K). Cold plasmas are in a state of thermal nonequilibrium. The energy of the particles is largely responsible for the subsequent layer-forming process.

During the transport phase, collision processes can occur with other gaseous particles (volume collision rate), or with the wall (wall collision rate). In both cases, the particles lose energy that is required for layer formation and layer adhesion. The prevailing pressure in the vacuum chamber is particularly important, as this greatly influences the transport phase. The number of volume collisions between layer-forming particles and other gaseous particles increases with the number of particles, and thus with the coating pressure. The overall pressure is comprised of the pressure from the particles produced, the pressure of the process gas, and the residual gas pressure. The residual gas pressure is the pressure in the coating chamber following the generation of a high vacuum. This must be sufficiently small (as a rule $< 10^{-4}$ Pa) in order to maintain a low level of impurities due to foreign atoms in the growing layer.

The mean free path length λ describes the mean path over which a particle moves without colliding with another particle. The mean free path length of a gaseous molecule in air is approximately 68 nm under standard conditions (see Table 6.7). The mean free path length is a function of the pressure, gas type, and temperature:

Table 6.7 Mean free path lengths λ for gaseous molecules at different pressures.

Pressure range	Pressure (Pa)	Molecules (cm^{-3})	Mean free path length
Ambient pressure	101 300	$2.7 \cdot 10^{19}$	68 nm
Low-vacuum	$10^5 \dots 10^2$	$10^{19} \dots 10^{16}$	0.1 ... 100 μm
Medium-vacuum	$10^2 \dots 10^{-1}$	$10^{16} \dots 10^{13}$	0.1 ... 100 mm
High-vacuum (HV)	$10^{-1} \dots 10^{-5}$	$10^{13} \dots 10^9$	10 cm ... 1 km
Ultra-high-vacuum (UHV)	$10^{-5} \dots 10^{-10}$	$10^9 \dots 10^4$	1 km ... 10^5 km
Extreme ultra-high-vacuum (EHV)	$<10^{-10}$	$<10^4$	$>10^5$ km

$$\text{Mean free path length } \lambda \text{ [cm]} : \quad \lambda = \frac{k \cdot T}{\sqrt{2} \cdot \pi \cdot p \cdot (r_1 + r_2)^2}$$

k : Boltzmann constant ($k = 1.38 \times 10^{-23} \text{ J K}^{-1}$)

p : gas pressure (Pa)

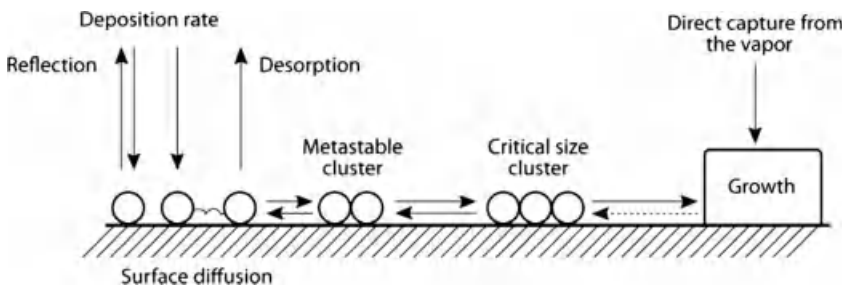
T : gas temperature (K)

r_1, r_2 : collision radius of the gaseous particles (cm).

The application of a negative electrical voltage to the substrate (the *bias voltage*) accelerates the positively charged layer-forming ions to the substrate, which the charged particles strike with a high kinetic energy. This leads to a dense layer morphology and, at the same time, the charged particles are deflected from the recipient wall, thus avoiding collisions with the wall. When viewed globally, the mean kinetic energy of the particles is a function of the mean free path length; that is, of the coating pressure in the chamber, the degree of plasma ionization, the bias voltage, and the distance between the substrate and the target [17].

6.2.2.3 Condensation, Layer Growth

The layer growth is influenced by the properties of the impinging particles and atoms, as well as the surface of the substrate (Figure 6.21). When atoms impinge on a solid

**Figure 6.21** Surface reactions during layer formation.

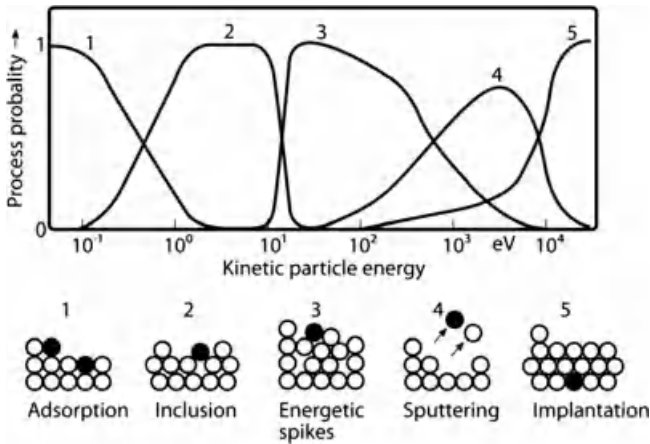


Figure 6.22 Type of particle bonding to the substrate as a function of the particle energy.

surface, they are either immediately reflected, or they impart sufficient energy to the solid that they then become loosely bound as so-called “adatoms.” The continued impinging of these atoms leads them to accumulate, with the resultant formation of nucleation centers. Above a critical nucleation size, these structures can (corresponding to the heterogeneous formation of nucleation centers on the substrate surface) grow to create crystallites. During the further course of their growth, the crystallites grow together to islands and, finally, produce a more or less contiguous layer [20]. The properties of the growing layer are influenced by a number of factors, including mass, chemical constitution, and energy state of the particles, as well as velocity, collision rate, and angle of incidence. By virtue of its roughness, chemical composition and temperature, the substrate may also influence the properties of the layer. The kinetic energy of the impinging target particles plays a decisive role in respect of the type of bonding to the substrate (Figure 6.22).

The relationship between process parameters and layer structure has been investigated on the basis of structure zone models. Besides the inert gas pressure, the coating temperature and bias voltage were also considered, permitting control of the layer morphology over wide regions (Figure 6.23). The typical columnar growth of many monolayers, in conjunction with the simultaneous lateral growth of the crystallites, results in an increase in the internal stresses with increasing layer thickness, imposing a limit on the maximum layer thickness. The roughness of the layer is often greater than for fine-crystalline layers or multilayers. The renewed formation of nucleation centers during growth of the layer gives rise to compact fine-crystalline structures with quasi-isotropic behavior, where internal stresses can be relieved, permitting a greater layer thickness. The same is observed with multilayers. For well-suited material combinations, the hardness of multilayers is enhanced, with a simultaneous improvement in toughness, while crack formation is laterally deflected, thus preventing premature failure. Furthermore, multilayers also offer the possibility of sealing off pinholes or layer defects, permitting vastly better

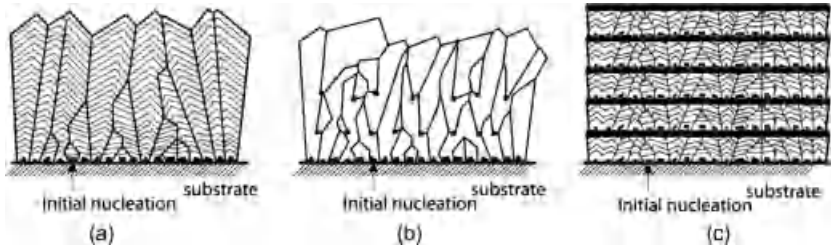


Figure 6.23 Influence of deposition conditions on layer morphology. (a) Columnar growth; (b) Fine-crystalline growth; (c) Multilayer structure.

corrosion protection. Increasingly, complex layer architectures are replacing simple monolayers (Figure 6.24). Notably, the development of nanostructured layers (e.g., nanocrystalline oxides, nanolaminates or nanocomposites) offers improved mechanical, thermal, and physical layer properties [21].

6.2.2.4 PVD Process Technology

The layer-forming particles propagate linearly from the target outwards, as a result of which shadowing regions can be only partly coated by borings and under-cuttings or, in the case of total shadowing, not at all. For complex geometric forms, differences in layer thickness will therefore arise along the contour when the layer-forming particles come from a single direction (with static coating and plane cathode surface). In the

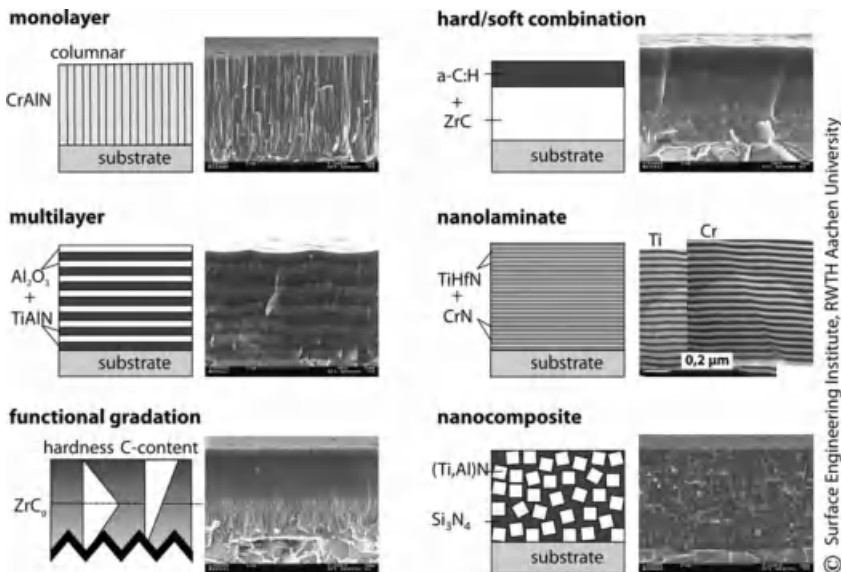


Figure 6.24 Coating architectures for increasing the PVD coating performance. Illustration courtesy of IOT, RWTH Aachen.

case of borings the rule states that, for a uniform coating, the aspect ratio of the depth to the diameter of the boring should be about 1:1. Rotating or translating the substrate, or a combination of rotating and translating, can lead to a reduction in the shadowing effects. Consequently, in many industrial plants planetary gears are employed, so as to enable a uniform layer thickness over the contour of a complex component.

With bias-supported coating, a negative voltage is applied to the substrate; however, due to this negative potential the substrate will be bombarded with positively charged ions. This effect is utilized during the coating process in order to improve the adhesion of the coating and to seal off the growing layer. Unfortunately, however, this also lowers the rate of layer growth, as more particles are reflected at the same time. As the kinetic energy of the impinging ions is transformed into thermal energy, the use of high bias voltages leads to a greater thermal loading of the substrate. Growth-induced internal stresses and, in part also the grain size, can be manipulated according to the bias voltage.

The steps of a PVD coating process are illustrated in Figure 6.25. Together with the coating itself, pretreatment of the substrate surface is of great importance, as the bonding of layers to the base material depends heavily on a smooth, clean, and contamination-free boundary surface between the layer and the substrate. Depending on the condition in which the components are supplied, a mechanical pretreatment (shot-blasting, polishing, lapping, grinding) of the surfaces may first be necessary. The substrates are then chemically cleaned (e.g., with alcohol, and in basic and aqueous solutions in ultrasonic baths) to remove any contamination and grease, and placed in drying ovens to remove any water residues from their surfaces. They are then placed with a suitable tooling device in the PVD plant (charging). In the next step, the substrates are subjected to plasma cleaning by ionic etching in the coating plant. The application of a negative bias voltage to the substrates causes

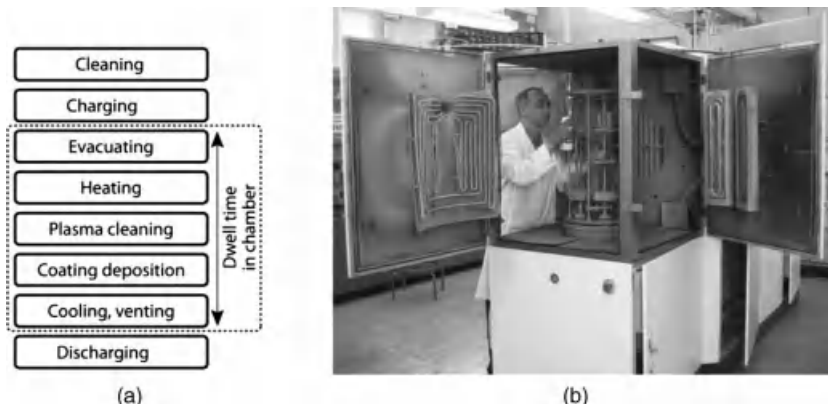


Figure 6.25 (a) Process steps for PVD coating; (b) Open coating chamber of a PVD plant with planetary gear charging table. Illustration courtesy of CemeCon AG.

positive gaseous ions (argon or metallic ions) from a low-pressure plasma discharge to be accelerated towards the substrate surface, where they erode away any impurities by collision processes (sputtering). This serves to remove oxide layers and other forms of contamination. Notably, with metallic substrates a highly polar surface, which guarantees good bonding of the layer atoms, will result.

All PVD processes can be carried out reactively; that is, inexpensive metallic targets can be employed and, with the introduction of a reactive gas to the coating chamber during the coating process, so that the layers are deposited with the required composition (e.g., $\text{Ti} + 1/2 \text{N}_2 \rightarrow \text{TiN}$). The chemical reaction between the metallic target material and the reactive gas takes place not only on the surface of the substrate, but also on the surface of the target. For the case of electrically isolating layers, such as Al_2O_3 , the plasma processes on the target are disrupted. This can result in electric arc discharges (so-called *arcing*), or in the complete break-down of the process. The term “target poisoning” is then referred to, which leads also to a lower rate of layer formation. When processed technically, the use of pulsed power injection can reduce this effect.

According to the substrate, an intermediate layer is first deposited which serves to promote adhesion between the substrate and the coating, or it may be employed to reduce the stress concentration at the boundary surface. According to the size of the chamber, the charging, and the required layer thickness, the overall dwell time of the components in the coating plant is in the range of 6–10 h, during which the actual coating time rarely exceeds 1–3 h. It is not only the substrate, but also the targets, that must be subjected to a thorough cleaning since, prior to their being placed in the plant, any pronounced impurities must first be removed by mechanical and chemical pretreatments. Any oxide layers that have formed on the target surface must be removed by pre-sputtering of the target immediately prior to plasma cleaning [22].

The two most important industrial thermal evaporation processes for tribological PVD coating are arc ion plating (AIP) and low-voltage discharge (LVD). Notably, magnetron sputter ion plating (MSIP) processes have become well established in the area of cathode sputtering.

Magnetron Sputter Ion Plating (MSIP) With MSIP, the particles are produced by cathode sputtering. In order to enhance the collision rates and the resulting degree of ionization, a permanent magnet is switched in behind the target (Figure 6.26). This magnet deflects electrons into a circular path, and this in turn causes an additional ionization of the plasma. At the site of a plasma ring produced in this way, the target material will be preferentially sputtered, and this will result in the formation of a so-called *sputter track* in the target. The use of a magnetic field assumes the presence of a target without ferromagnetic materials.

Electrically conductive cathode materials are deposited with the aid of a DC power supply. When applying a DC voltage to dielectric materials, the impinging charges cannot be led away, such that a counter-charge would build up and hinder the sputtering process. Up until the late 1990s, a radiofrequency (RF; 13.56 MHz) technique was used to sputter dielectric materials, but this had a significant influence on fast-moving electrons, in contrast to the heavy, slowly moving, ions. Typically, in

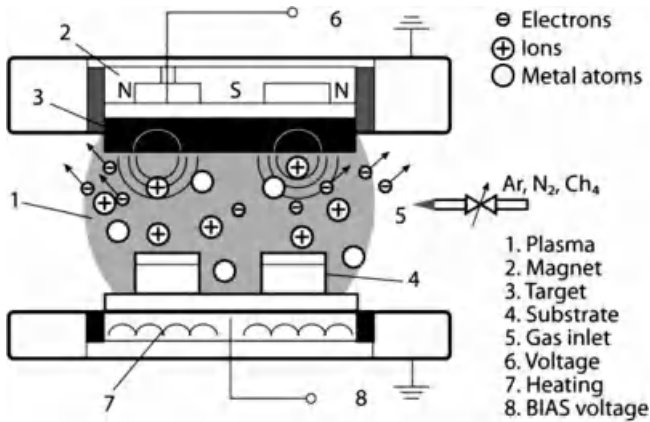


Figure 6.26 Schematic illustration of the magnetron sputter ion plating (MSIP) process.

the positive half-wave of the RF, many more electrons could reach (and thus charge) the electrodes, until an equilibrium was established between the ionic and electron currents [17]. Unfortunately, RF technology was not established for tribological applications, mainly because the coating rates were extremely low, bonding of the coating layer was unsatisfactory, and such process technology was very expensive. In both the DC and RF processes, the degree of ionization of the plasma was less than 4%. Since the 1990s, however, pulsed medium-frequency power (20–350 kHz) has been investigated, and is today in use industrially. The most recently developed power supply is high-power pulse magnetron sputtering (HPPMS), which operates in the low-frequency range (50–650 Hz), and with a high degree of ionization (up to 40%) for cathode sputtering.

The main advantages of this new pulsed process technology, when compared to DC voltage, are (Figure 6.27):

- an increased ionization rate;
- dielectric materials (e.g., Al_2O_3) can be synthesized;
- complex layer structures can be produced;
- nonconductive substrates can be coated;
- improved aspect ratio;
- lowering of the coating temperature;
- improved bonding of the coating layers; and
- more dense coatings with a high degree of hardness, high strength, and smoother surfaces

Arc Ion Plating (AIP) Among PVD processes, arc ion plating – an electric arc-induced evaporation – has the greatest energy, due not only to the high degree of ionization but also to the high kinetic energies of the ions that are set free. The properties and applications of an electric arc in vacuum have been described in detail [23]. Particle production occurs via an anodic or cathodic electric

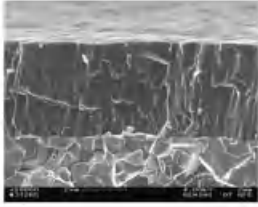
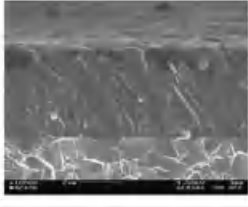
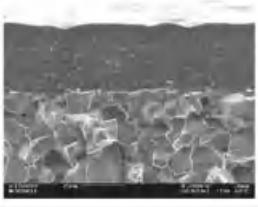
DC (TiCrAlSi)N	MF (TiCrAlSi)N	HPPMS (TiCrAlSi)N
Composition (At %): <ul style="list-style-type: none"> ▪ Al: 40.4 ▪ Cr: 12.6 ▪ Ti: 37.7 ▪ Si: 9.3 Universal hardness: 29 (+/- 3.4) GPa Young's modulus: 442 (+/- 14.7) GPa H/E: 0.066	Composition (At %): <ul style="list-style-type: none"> ▪ Al: 42.8 ▪ Cr: 13.6 ▪ Ti: 35.7 ▪ Si: 7.9 Universal hardness: 31 (+/- 2.1) GPa Young's modulus: 410 (+/- 18) GPa H/E: 0.075	Composition (At %): <ul style="list-style-type: none"> ▪ Al: 38.6 ▪ Cr: 15.2 ▪ Ti: 38.1 ▪ Si: 7.1 Universal hardness: 35 (+/- 3.7) GPa Young's modulus: 390 (+/- 11) GPa H/E: 0.089
		

Figure 6.27 Comparison of (TiCrAlSi)N layers with different power supplies. Information courtesy of IOT, RWTH Aachen.

arc-induced evaporation, where the cathodic electric arc represents the preferable variant.

In AIP, the layer synthesis is based on an arrangement whereby an electric arc is ignited over the material that has been configured as cathode in a high vacuum, with an earthed wire (Figure 6.28). This results in the exclusive evaporation of electrically conductive target materials. Similar to the situation with electric arc welding, the electric arc is maintained and guided in either uncontrolled (random arc) fashion or controlled (steered arc) fashion over the target surface. As a considerable part of the conductive medium consists of ionized cathode material, a stable, self-maintaining electric arc can form in vacuum, even in the absence of any ionizing gaseous particles [24]. In the region of the cathode spot, the target material melts and the layer material evaporates. The cathode material evaporated by the electric arc possesses a high degree of ionization (up to 90%), while the ions reach very considerable velocities normal to the surface of the cathode. By applying a negative bias voltage to the substrate, the positively charged ions are accelerated and focused, which favors the deposition of denser layers, with better adhesion [25].

One characteristic of the electric arc in vacuum is the random motion of the cathode spot, which moves with a velocity of about 100 m s^{-1} [26], while the life of the focal spot is on the order of 10^{-6} to 10^{-7} s [27] and the diameter of the focal spot is a few micrometers. In the cathode focal spot, current densities of up to $i = 1.012 \text{ A m}^{-2}$ are obtained [28], which results in an extremely rapid heating of

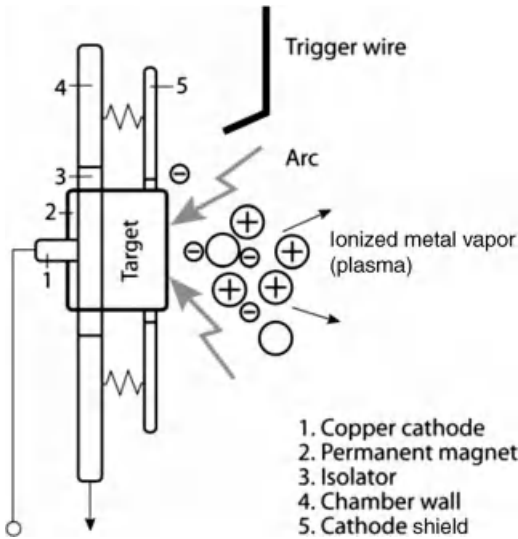


Figure 6.28 Schematic diagram of the arc ion plating (AIP) process.

the microscopic regions in the cathode surface. The evaporation current can also be varied over a wide range, independently of the melting point of the target. Refractory materials normally require higher currents for electric arc evaporation, while the degree of ionization depends, for example, on the melting temperature of the cathode material [29].

Low-Voltage arc Discharge (LVD) The low-voltage arc discharge process was developed in 1977 by the Balzers company, in Liechtenstein (today Oerlikon Balzers AG) and, from the very beginning, has been used primarily for the production TiN and TiCN high-speed steel (HSS) substrates [30]. Low-voltage arcs are characterized by initiating the discharge in a process gas, with an arc drop voltage that lies below the ionization voltage of the process gas. This requires that the cathode for the discharge path functions as an electron emitter, with a lowering of the work function. This is achieved by thermo-emission of the cathode for the discharge path, operated as a hot cathode. In this case, the emission current is equal to or greater than the discharge current [19].

The functional principle of the low-voltage arc discharge process is illustrated in Figure 6.29. Typical here is the spatial separation of the hot cathode and the coating chamber, on the floor of which the coating material is contained in a crucible. The inert gas flows via an opening in the ionization chamber into the coating chamber; the arc discharge then burns between the hot cathode and the anode of the crucible in the process gas, with an ionization rate of about 50%. A reactive gas can also be introduced into the coating chamber. A longitudinal magnetic field generated by magnetic coils at the coating chamber concentrates the discharge and focuses it onto

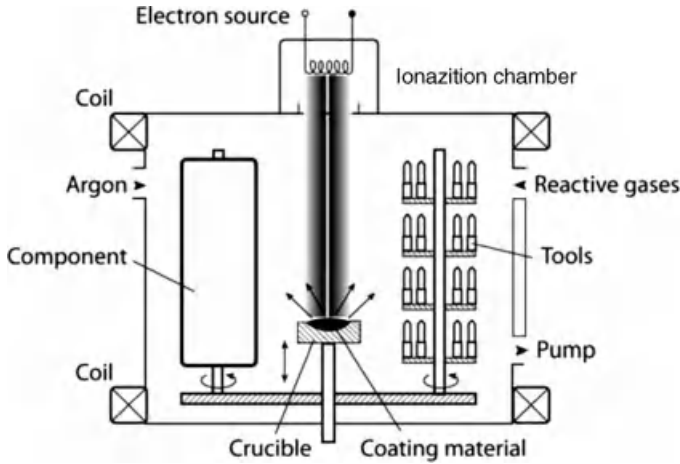


Figure 6.29 Schematic diagram of the low-voltage arc process.

the anode [19]. The components to be coated are then rotated around the arc discharge on a charging table that is driven by a planetary gear. The thermionic electric arc is used first to heat the substrate, and second in the subsequent etching process. During plasma etching, the substrate table is configured as the anode and the substrate surface is cleaned with the aid of the arc discharge. The anode is then switched over to the crucible containing the coating material [31].

6.2.2.5 PVD Tool Coating

The first commercial use of PVD for the coating of cutting tools with TiN was launched in 1980, by Gühring. This process was subsequently improved in 1988, with the use of TiAlN, which is somewhat harder than TiN and offers a greater stability against oxidation. Compared to CVD technology, the decisive advantages of PVD were:

- considerably lower deposition temperatures, which also permitted the coating of tool steel; and
- the possibility not only to synthesize meta-stable layer systems, such as TiAlN, but also to determine internal stresses in the coating with the deposition process.

In the meantime, approximately 80% of all cemented carbide tools are coated, using both CVD and PVD. Initially, reliance was placed on a very simple formula for the development of layers: “. . . the harder the coating, the better the wear protection”. Hence, attention was focused predominantly on hard material systems (nitrides, carbides, borides) and indeed, to the present day, the PVD tool market is dominated by classical hard material coatings such as TiN (41%), TiCN (24%), and TiAlN (27%) [32].

Since the mid-1990s, however, there has been a significant increase in the use of combined systems, such as TiN/TiAlN multilayers, or hard–soft combinations such



Figure 6.30 Commercial coating systems for tool coating and examples of their application. Illustration courtesy of IOT, RWTH Aachen.

as TiAlN + WC/C. It has also been recognized that hardness alone is not sufficient; in addition, the wear protection of hard material coatings improves the endurance of tools, the processes are becoming increasingly faster, the cutting volume can be increased, and the consumption of cooling lubricants can be reduced by using of coated tools. It is important that, due to a reduced usage of cooling lubricants, the coatings must also increasingly possess good frictional properties in order to compensate for the lack of lubrication. The reduced use of cooling lubricants has also led to higher temperatures in the cutting process ($>600^{\circ}\text{C}$), which the layers must be capable of withstanding. As a consequence, nanostructured PVD coatings such as TiSiN-, TiAlN-, TiAlSiN- and TiAlBN-based nanocomposites with high aluminum contents have more recently (since 2001) appeared increasingly on the market. The trend towards the use of coating materials that offer high stability against both heat and oxidation continues, with the preferred systems of today being, for example, CrAlN, CrAlSiN, and PVD- Al_2O_3 .

Today, it is not only cutting tools for turning, drilling, thread cutting and milling that are PVD-coated, but also tools used for forming and casting (Figure 6.30). For the pressure die-casting of lightweight metals, PVD coatings offer protection not only against wear but also against metal corrosion and heat cracking. This means, in turn, that the use of stripping agents can be reduced, the process cycles shortened, and the component quality improved. In plastic injection molding, the PVD coatings simplify the product removal of the molds, and also protect against corrosive, adhesive and abrasive attack by the plastic melt. In this way, significant improvements in service life can be achieved with cold forming, and also with cup extrusion, precision blanking, and deep drawing. Moreover, some initial investigations have also indicated some very promising results for forging.

6.2.2.6 PVD Component Coating

The breakthrough of thin-film technology for components during the mid-1990s was accompanied by the development of modern diesel motors. The main driving force for such improvements was the increasingly stringent European Union

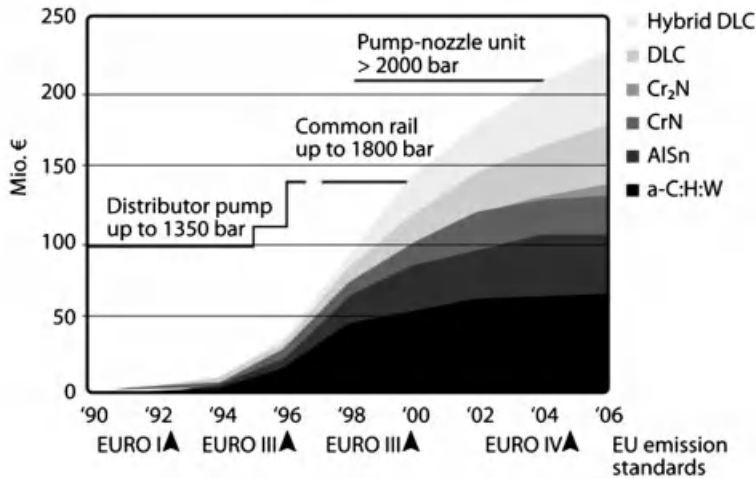


Figure 6.31 Market development of component coating in the automotive industry. Information courtesy of IonBond AG, 2006 [34] and Robert Bosch GmbH, 2007.

environmental restrictions and pollution regulations. In order to improve specific performance, modern motors run at extreme injection and ignition pressures (>2000 bar); this means that besides a high power density, reductions in the emission of pollutants and in fuel consumption are also achieved. By reducing the sulfur content of diesel fuel (1995: <500 ppm; 2002: <50 ppm), however, certain critical system lubricating effects are lost [33]. Hence, these extreme operating conditions require new material concepts.

An initial pilot use of a PVD coating at Robert Bosch GmbH was made in connection with the vanes of a vane cell pump for diesel injection in 1994/95 while, at the same time, Oerlikon Balzers Coating AG introduced its WC/C coating. The first successful mass production of a component using PVD technology was a bush bearing for the rocker arm of a pump nozzle unit for diesel motors. Moreover, by 2001 a total of 3.5 million sets had been coated with carbon-based systems. Nowadays 70% of all modern diesel pump components are being coated. Perhaps most importantly, the spread of the PVD component market has occurred extremely quickly (Figure 6.31), having today reached a volume that is almost comparable with that of PVD tool coating. Yet, the entire coated component market is several times larger than that for PVD.

Today, more than 60% of all coated components are treated with carbon-based coatings, which are now available commercially in a huge variety (Figure 6.32). These coatings are produced in both PVD and plasma CVD processes, and are frequently marketed as so-called diamond-like carbon (DLC) coatings. In addition to carbon (a-C, ta-C), DLC coatings in part contain hydrogen (a-C:H) and/or metals (a-C:H:Me, a-C:Me) such as tungsten or chromium, and in part also other dopings. A classification of carbon coatings was published in 2005 as a VDI directive (VDI 2840).

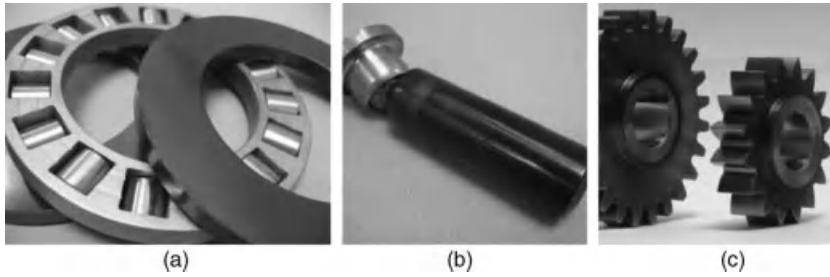


Figure 6.32 Components coated with graded a-C:H:Zr. (a) Roller bearing; (b) Piston; (c) Gearwheels. Illustration courtesy of IOT, RWTH Aachen.

With the further development of plasma processes, the initial difficulties encountered with the adhesion of coatings and the excessively high deposition temperatures have been largely eliminated. From an industrial point of view, it can be said that [35]:

“...in the next 10 years, component loading will increase in all machines and systems. Coating systems will be further optimized. Present-day systems, such as CrN, a-C:H:Me and DLC, have not yet reached their full developmental. These coatings will be further developed for specific applications. In addition, new coating systems will appear on the market.”

With increasing coated component volumes, the costs of coating will also invariably be reduced. Today, the coatings industry assumes a continued increase in turnover to about €550 million by the year 2010, while the entire Asian market can hardly be assessed. With the increasing volume of coated components and savings in production technology, according to calculations made by Oerlikon Balzers AG, the costs of PVD component coating already dropped by 60% between 2000 and 2007 [36].

6.2.3

Chemical Vapor Deposition (CVD)

Chemical deposition from the gaseous phase (CVD) is a coating synthesis process, in which the components of the gaseous phase react close to or on the substrate to be coated. In order for the chemical reaction(s) to take place, additional energy is required, which can be supplied in the form of heat, light, or plasma [37]. The gaseous components react in the vicinity of the work piece surfaces of the substrate material, with the formation of permanently adhering layers on these surfaces (Figure 6.33) [38]. In contrast to the PVD process, layer formation with CVD depends upon the thermodynamics of the chemical reaction.

The chemical reactions take place in reactors (Figure 6.34) in which the earliest plant technology is based on thermal CVD processes, where the substrate is heated (mostly electrically) in the reactor to the deposition temperature. There are two different types of reactor for thermal CVD processes: the hot wall reactor; and the cold

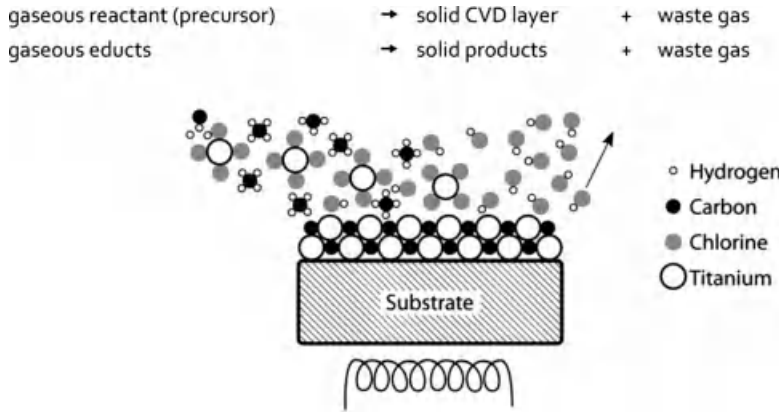


Figure 6.33 Schematic representation of layer formation from TiC in the thermal CVD process ($\text{TiCl}_4 + \text{CH}_4 \xrightarrow{800-1.000\text{ }^\circ\text{C}} \text{TiC} + 4 \text{HCl}$, at a pressure of $p = 10^3 - 1.5 \cdot 10^4 \text{ Pa}$).

wall reactor. In the hot wall reactor, the substrate is heated indirectly in a furnace, so that not only the substrate but also the reactor is heated. In contrast, in the cold wall reactor only the substrate is heated. Regardless of the type of energy supply, a CVD plant is comprised of the main components:

- Dosing system for reactants and carrier gases
- Reactor
- Vacuum unit with cleaning of the waste gases

One of the oldest examples of the CVD process is the formation of soot during combustion, due to the incomplete oxidation of firewood. The first technical utilization of the CVD process dates from 1880, when the carbon filaments of the first light bulbs were strengthened to improve their service life. This process, in which carbon was deposited by thermal dissociation, was developed by Sawyer and

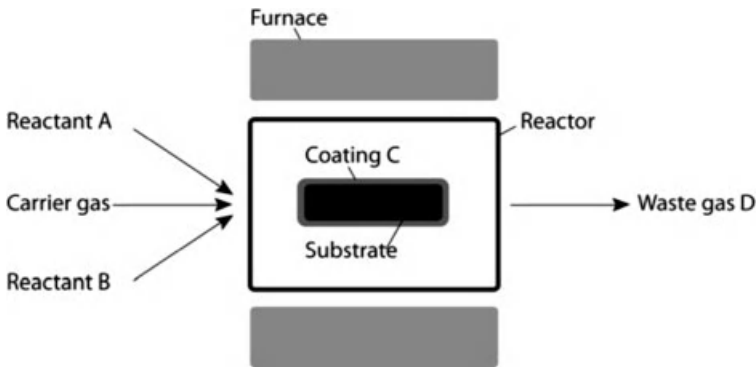


Figure 6.34 Functional principle of the CVD process in an “open” reactor; that is, with gas flow-through (schematic representation).

Man. Eleven years later, Mond succeeded in manufacturing nickel from nickel carbonyl [39], while in 1893 Lodyguine was able to deposit tungsten from a carbon filament by reducing WCl_6 with H_2 . During this time, CVD processes were developed for the economic manufacture of high-purity, fire-resistant metals, such as Ti, Ni, Ta and Zr, for example, in the:

- Van Arkel process : $TiI_4 \xrightarrow{1200\text{ }^\circ\text{C}} Ti + 2 I_2$
- Mond process : $Ni(CO)_4 \xrightarrow{150\text{ }^\circ\text{C}} Ni + 4 CO$

The emphasis of CVD processes on coating rather than on the extraction of metals has been apparent only since the 1960s. Consequently, not only has the area of application for CVD processes been extended, but the significance of the processes in connection with coating technologies has also increased. Subsequently, CVD coating processes have assumed a special importance in the manufacture of thin semiconductor layers and surface coatings designed to protect against wear and corrosion.

The success of CVD coating technology in the electrical and electronics industry, particularly during the early 1970s, also paved the way for the application of CVD technologies in other areas, including high-temperature tools, turbine blades, ceramic fibers, and solar cells [37]. Other important dates in the history of CVD coatings are:

- 1960: Introduction of, and differentiation between, the terms PVD and CVD
- 1960: Manufacture of semiconductors by CVD
- 1960: Realization of TiC coatings on tools by CVD
- 1963: Introduction of plasma CVD in the electronics industry
- 1968: Industrial application of CVD-coated cemented carbide tools
- 1980: Manufacture of diamond layers by CVD
- 1990: Use of metal-organic CVD processes (MO-CVD)
- 1995: Use of plasma CVD coatings on machine elements.

The numerous CVD process variants find application in widely different industries, the most important being in the manufacture and finishing of tools and of semiconductors, in the surface protection of components and tools, and in the chemical industry. Important applications of CVD technology include:

- Semiconductor coatings (e.g., Si, Ge) for micro-electronics, opto-electronics and solar cells
- Synthesis of materials for materials manufacture
- Fiber and powder coatings for materials manufacture
- Scratch resistance for transparent plastic components, lenses, eyeglass lenses, and plastic disks (e.g., SiO_x)
- Diffusion barriers on plastic films and plastic bottles for the packaging industry (e.g., SiO_x , a-C:H) and for high-temperature applications (e.g., gas turbine components)
- Wear and corrosion protection and reduction of friction for tools and components (e.g., TiB_2 , SiC, B_4C , BN, TiN, Al_2O_3 , ZrO_2 , DLC, and diamond).

6.2.3.1 Thermodynamics of the Chemical Reaction

The thermodynamic investigation of a chemical reaction enables a basic understanding for parameterizing the CVD deposition process. Before undertaking a CVD process, it is necessary to investigate the feasibility of the chemical reactions required. This can be determined on the basis of a calculation of the thermodynamic equilibrium for the given parameters, such as temperature, pressure, and educt concentration [40]. The basis for assessing whether a reaction will take place under the given conditions is the free molar reaction enthalpy, ΔG_R (Gibbs enthalpy).

$$\text{Gibbs enthalpy : } \Delta G_R = \Delta H_R - T \cdot \Delta S_R$$

H_R : Reaction enthalpy

S_R : Reaction entropy

T : Temperature

Given the initial condition that:

$\Delta G_R < 0$: The reaction takes place spontaneously.

$\Delta G_R = 0$: The reaction is in the equilibrium state.

$\Delta G_R > 0$: The reaction is possible only with the simultaneous introduction of energy, that is, the reaction products decompose again to educts.

The calculation of ΔG_R is based on the free molar standard reaction enthalpy ΔG_R^0 under standard conditions ($T = 25^\circ\text{C}$, $p = 1.013 \times 10^5 \text{ Pa}$). The free molar standard reaction enthalpy can be calculated from tabulated molar standard enthalpies of formation H_B^0 and molar standard entropies S^0 .

Free molar standard reaction enthalpy :

$$\Delta G_R^0 = \Delta H_R^0 - T \cdot \Delta S_R^0$$

$$\Delta H_R^0 = \sum \Delta H_B^0(\text{Products}) - \sum \Delta H_B^0(\text{Educts})$$

$$\Delta S_R^0 = \sum S^0(\text{Products}) - \sum S^0(\text{Educts})$$

The molar free reaction enthalpy ΔG_R changes continuously during the course of the reaction with the changing composition of the reaction mixture. This is described mathematically by the equation:

$$\text{Van't Hoff's reaction isotherm : } \Delta G_R = \Delta G_R^0 + R \cdot T \cdot \ln \frac{a_C \cdot a_D}{a_A \cdot a_B}$$

ΔG_R : free molar reaction enthalpy, Gibbs enthalpy

ΔG_R^0 : free molar standard reaction enthalpy

R : as constant ($8.314 \ 472 \text{ J mol}^{-1} \text{ K}^{-1}$)

T : temperature

a : amount of substance activity, corresponding to the amount of substance

A, B: educts

C, D: products

For a reaction which takes place spontaneously ($\Delta G_R < 0$), the free molar reaction enthalpy ΔG_R continuously increases during the course of the reaction, as the reaction quotient (activity quotient) ($a_C \cdot a_D / a_A \cdot a_B$) becomes increasingly larger, until a state of equilibrium $\Delta G_R = 0$ is reached. Then:

$$0 = \Delta G_R^0 + R \cdot T \cdot \ln \frac{a_C \cdot a_D}{a_A \cdot a_B}$$

The reaction quotient in the state of equilibrium plays a central role in the derivation of the law of mass action. It is given in the form of the equilibrium constant K :

$$\text{Law of mass action : } \Delta G_R^0 = -R \cdot T \cdot \ln K$$

In a gaseous mixture, the partial pressures of the different gases are proportional to the numbers of molecules with which the respective gases are present in a given volume. The partial pressure of a gas is therefore at the same time, a measure of the amount of the respective substance. The partial pressures p_{A-D} can therefore be used in place of the amounts of the substances a_{A-D} in the equation for the law of mass action. This enables the calculation of suitable process windows for the two most important process parameters, pressure and temperature, for the required reaction.

For many reactants employed in CVD processes, thermodynamic data are available, so that the calculation of favorable process parameters for the reaction is possible (Figure 6.35). As long as the process gases are steadily introduced, the activity of the reaction will be maintained. The activity is thus directly dependent upon the temperature T and the partial pressures of the gases in the reactor. The required coating temperatures for typical CVD reactions are listed in Table 6.8.

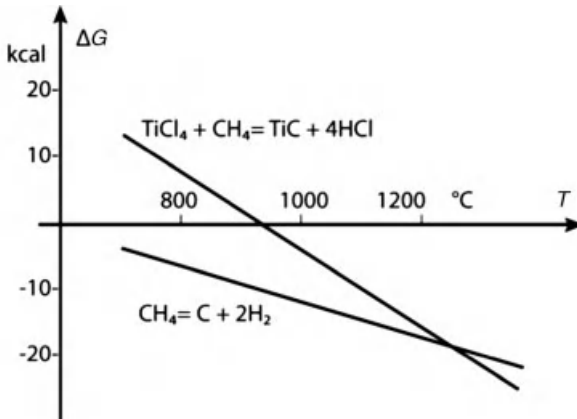


Figure 6.35 Calculation of the Gibbs enthalpy for estimating the deposition temperature of TiC and C layers with the CVD process [41].

Table 6.8 Deposition temperatures for typical CVD reactions.

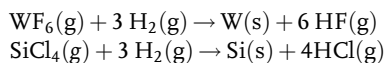
Educts		Products	Deposition temperature (°C)
2 TiCl ₄ + 2 NH ₃ + H ₂	→	2 TiN + 8 HCl	800–1100
2 AlCl ₃ + 6 CO ₂ + 3 H ₂	→	Al ₂ O ₃ + 6 HCl + 3 CO	800–1300
TiCl ₄ + 2 BCl ₃ + 5 H ₂	→	TiB ₂ + 10 HCl	900–1600
12 WF ₆ + C ₆ H ₆ + 33 H ₂	→	6 W ₂ C + 72 HF	325–600
CH ₃ SiCl ₃ + H ₂	→	SiC + 3 HCl + H ₂	1400–1800
B ₂ H ₆ + 2 NH ₃ + H ₂	→	2 BN _{hex} + 7 H ₂	300–350
CH ₄ + H ₂	→	C _{Diamond} + 2 H ₂	700–1100

6.2.3.2 Reaction Chemistry

The basic prerequisite for CVD synthesis is the availability of volatile compounds (precursors) that contain the components of the coating material. Gaseous precursors can be employed directly, but liquid or solid precursors must be evaporated before being introduced into the reactor (liquids in a bubbler, solids in a tube evaporator using a carrier gas and heating), atomized, or introduced in the form of an aerosol. Halogenides (fluorides, chlorides, bromides), which are already available in gaseous or liquid form for many metals, are particularly well suited as volatile compounds.

Most classical processes are based on the principle of *chemosynthesis*, according to which halogenides are transported in the form of reducing or oxidizing gases with the introduction of energy to the surface of the substrate. Above 700 °C, however, most halogenides are very aggressive, and this must be taken into account for CVD plants. Chemosynthesis includes such reactions as hydrogen reduction, co-reduction, metal reduction, oxidation and hydrolysis, and carbidization and nitrogenization.

Hydrogen Reduction Due to its lower manufacturing temperatures, hydrogen reduction has a great advantage compared to equivalent degradative reactions. This method is principally employed to deposit the halogenides of transition metals, especially those of Groups 5 (vanadium, niobium, tantalum) and 6 (chromium, molybdenum, tungsten). The reduction of the halogenides of the Group 4 metals (titanium, zirconium, hafnium) is more difficult, because they are more stable. The hydrogen reduction of non-metallic halogenides, such as those of silicon and boron, is the most important manufacturing process for semiconductors and high-strength fibers. Typical reduction reactions are:



Co-Reduction The CVD deposition of binary chemical compounds can be realized by co-reduction reactions. In this way, ceramic materials, such as oxides, carbides, nitrides, borides and silicides (e.g., titanium boride) can be produced:

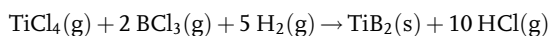
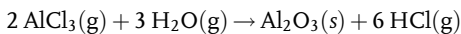
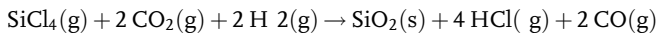
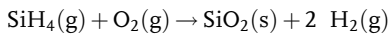


Table 6.9 Free reaction enthalpy ΔG° of metal chlorides [37].

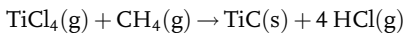
Reducing agent	Melting point (°C)	Boiling point (°C)	Chloride	Free reaction enthalpy ΔG° (kJ mol ⁻¹)			
				425 °C	725 °C	1025 °C	1325 °C
H ₂			HCl	-98	-100	-102	-104
Cd	320	765	CdCl ₂	-264	-241	-192	-164
Zn	419	906	ZnCl ₂	-307	-264	-262	-254
Mg	650	1107	MgCl ₂	-528	-482	-435	-368
Na	97	892	NaCl	-223	-238	-241	229
K	631	760	KCl	-369	-341	-295	-

Metal Reduction Although hydrogen is generally used as the reducing agent, elements such as zinc, cadmium, magnesium, sodium, and potassium have a higher affinity for chlorine. The free reaction enthalpies for these elements are summarized in Table 6.9. The free reaction enthalpy ΔG° for the chlorides of these metals is more negative than that of hydrogen chloride at the given temperatures; hence, these metals can be used to reduce the halogenides of titanium, zirconium or hafnium when this is not possible with hydrogen. In order for these metals to be used, it is important that the chloride byproducts are volatile at the process temperature. For this reason, the use of sodium or potassium can be excluded, due to the high boiling points of their chlorides (>1400 °C) [37].

Oxidation and Hydrolysis Reactions The two most important CVD reactions are oxidation and hydrolysis; examples include the production of oxides, where O₂ and CO₂ are the reaction elements. More recently ozone (which is a stronger oxidizing agent) has been employed for the CVD deposition of SiO₂. Typical oxidation and hydrolysis reactions include [37]:

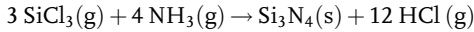


Carbidization and Nitrogenization The CVD deposition of carbides takes place by the reaction of gaseous carbohydrates (e.g., methane CH₄) with halogenides:



Ammonia is the principal process gas for the CVD deposition of nitrides. Ammonia (NH₃) has a positive free energy of formation ($\Delta G_R > 0$) – that is, it is unstable. Upon degradation, its products become the educts for the CVD

reaction. An example for the use of ammonia is the CVD deposition of silicon nitride [37]:



Another possibility is the thermal degradation reaction (*pyrolysis*) of the precursor gases. Here, a molecule is decomposed into its elements and/or elementary molecules on the hot substrate surface. Typical examples are:

- Carbohydrate degradation : $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{s}) + 2 \text{H}_2(\text{g})$
- Halogenide degradation : $\text{WF}_6(\text{g}) \rightarrow \text{W}(\text{s}) + 3 \text{F}_2(\text{g})$
- Carbonyl group degradation : $\text{Ni}(\text{CO})_4(\text{g}) \rightarrow \text{Ni}(\text{s}) + 4 \text{CO}(\text{g})$
- Hydride degradation : $\text{SiH}_4(\text{g}) \rightarrow \text{Si}(\text{s}) + 2 \text{H}_2(\text{g})$

Alternatively, with *disproportionation* a gaseous substance in equilibrium is transformed by temperature reduction to a solid component (powder synthesis). Alkyl substances (CH-compounds), acetonitriles (CN-compounds), alcoholates, or cyclopentadienyl compounds also find use as metal-organic (MO) compounds. Although, the use of MO compounds allows the temperature for synthesis to be drastically reduced (to ca. 300–800 °C), the compounds and the required plant technology are very expensive. Consequently, MOCVD is used only when purity and coating quality are of primary importance, such as in the synthesis of GaN for light-emitting diodes (LEDs).

6.2.3.3 Coating Deposition Kinetics

In contrast to thermodynamic considerations, the kinetics is concerned with the chemical conversion per time unit of the chemical reaction. The overall reaction is broken down into several subreactions, of which the slowest partial reaction determines the reaction rate for the entire CVD process, and thus also influences the actually achievable deposition rate (Figure 6.36).

When determining the deposition rate empirically, the idealized characteristic curve of a thermal CVD process is first obtained (Figure 6.37) which shows three

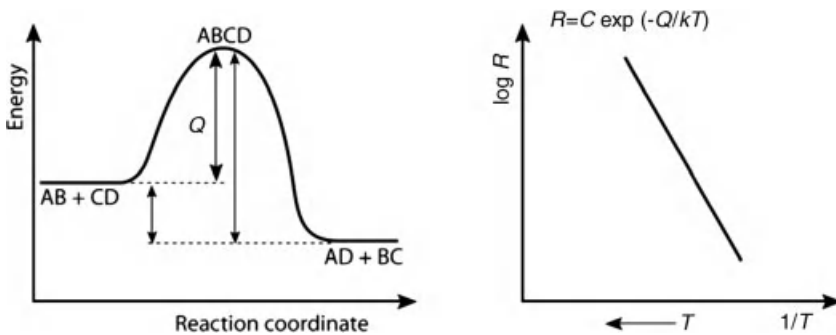


Figure 6.36 Reaction rate R of the chemical reaction as a function of the activation energy Q and substrate temperature T (Arrhenius' law).

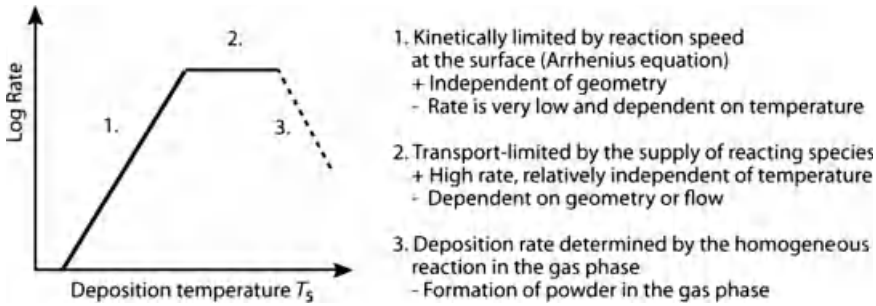


Figure 6.37 Idealized characteristic curve of a thermal CVD process.

characteristic regions. At low temperatures, the deposition process is determined by the reaction proceeding on the surface, and follows the Arrhenius law. This controlled reaction Region 1 is well suited for the uniform coating of complex geometries. At higher temperatures, the reaction rates become so high that the deposition process is limited by the transport of the species (Region 2). Still higher temperatures result in powder formation (Region 3). For economic reasons, most CVD reactors used are operated in the transport-limited Region 2.

The mass transport of the gases to the surface of the substrate determines the coating rate in Region 2. A CVD process is subject to a complex, fluid dynamical flow pattern. Typically, the gas mixture flows through pipelines, valves and chambers, whilst at the same time being subjected to a high temperature difference before coming into contact with, and reacting with, the substrate. Due to the phase transformation from gaseous to solid form, this is a heterogeneous reaction. The sub-steps during a CVD reaction are indicated in Figure 6.38, and can be summarized as follows [37, 39, 42]:

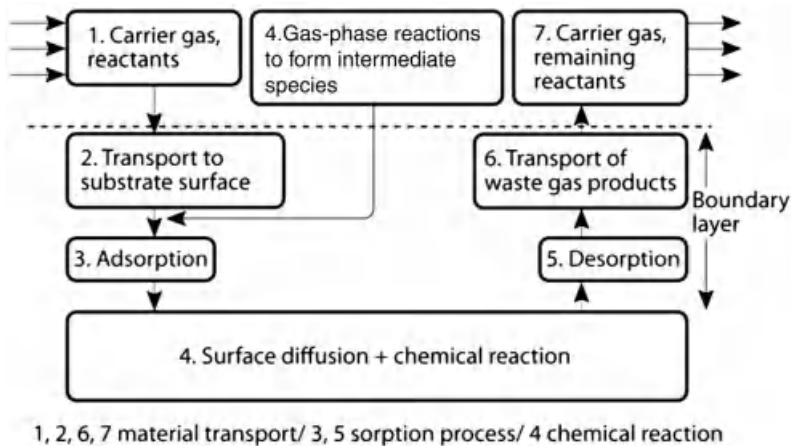


Figure 6.38 Sub-steps during CVD deposition onto the substrate surface [37].

- Convective transport of the educts to the boundary layer by the predominating forced flow (step 1)
- Diffusive transport of the precursors and gaseous-phase species through the boundary layer to the substrate surface (step 2)
- Adsorption of the reactants and the gaseous-phase species on the substrate surface (step 3)
- Upstream homogeneous equilibrium reactions in the gaseous phase to gaseous-phase species (step 4)
- Surface diffusion and chemical reactions (step 4)
- Desorption of gaseous byproducts (step 5)
- Diffusive transport of desorbed gaseous products through the boundary layer (step 6)
- Convective transport of the byproducts away from the boundary layer by the predominant forced flow (step 7)

With transport-limited deposition (Region 2 in Figure 6.37), depletion effects must be expected along the direction of flow on the surface of the component. In general, laminar flow over the substrate is desirable, although for higher pressures, larger chamber volumes or inhomogeneous temperature distributions, natural convection can perturb this situation. These phenomena can be countered in terms of the chamber design, the gas feed-in construction, and the charging.

When a uniform coating layer on complex geometries is of primary importance, industrial CVD processes are frequently operated in the kinetically controlled Region 1 of the chemical reaction (see Figure 6.37). Figure 6.39 illustrates the concept and the charging of a thermal CVD reactor for the coating of indexable inserts for 3-D coating. In such a reactor it is possible to carry out uniform coatings with complex geometries

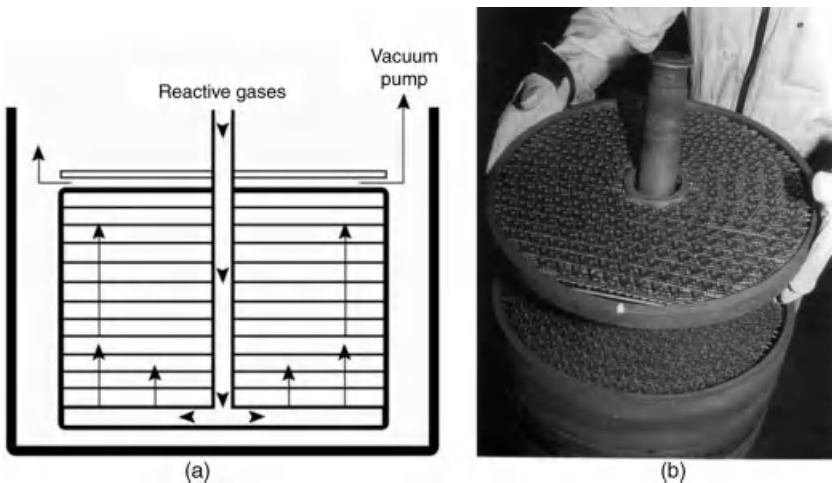


Figure 6.39 (a) Gas distribution in a thermal CVD reactor for 3-D coating; (b) Charging of indexable inserts for CVD coating [41].

Table 6.10 Different forms of excitation for CVD processes.

Thermal	Plasma	Photons
Substrate heating (cold wall reactor)	DC current	UV light
Furnace heating (hot wall reactor)	Medium-frequency pulses	Laser
Molecular beam (epitaxial)	High-frequency	
Hot filament	Microwave	
	Ion beam	

or very large batches reproducibly, with little technical effort and at favorable costs per piece. With this process, the dense charging over several levels of a hot wall reactor enables the production of piece numbers of several thousand indexable inserts.

6.2.3.4 CVD Processes

The classification of CVD processes is based on the type of activation energy that must be supplied (Table 6.10) in order to sustain the chemical reaction. Thus, it is possible to differentiate between thermally activated CVD (also known as high-temperature CVD, HT-CVD) processes, plasma-activated CVD (PA-CVD) processes (also referred to as plasma-enhanced CVD, PE-CVD), and photon-activated CVD processes (Photo-CVD or LI-CVD). From the technological point of view, thermal activation is most easily realized, and is employed typically for the uniform coating of large batches of indexable inserts in a hot wall reactor. For the coating of temperature-sensitive substrates, plasma-supported methods will be employed as a rule since, due to the significant lowering of temperature, these processes will enable the coating of a wide range of substrate materials. By using a laser it is possible to selectively initiate reactions on the surface of the substrate, enabling the growth of two-dimensional (2-D) and 3-D structures (rapid prototyping).

The different operating pressure has, furthermore, led to such designations as normal pressure CVD (atmospheric pressure CVD, AP-CVD), low-pressure CVD (LP-CVD) and ultra-high vacuum CVD (UHV-CVD, $p < 10^{-5}$ Pa) (Figure 6.40). Based on the type of activation, these processes can be further classified according to operating temperature into HT-CVD for deposition temperatures > 900 °C, middle-temperature CVD (MT-CVD) for the temperature range 600 °C $< T < 900$ °C, and low-temperature CVD (LT-CVD) for temperatures < 600 °C (for which the given temperatures are understood to be only approximate values).

For tool coating with hard materials, and particularly for the coating of cemented carbide cutting materials, thermally activated CVD processes continue to dominate the market. Temperature-sensitive steel substrates, for example for machine elements, are usually coated by using plasma-activated processes. With a view to the overall CVD coating market, plasma processes are employed in more than 50% of all cases (Figure 6.41).

High-Temperature CVD With thermally activated CVD processes, the chemical reactions are initiated by supplying thermal excitation energy to the inorganic

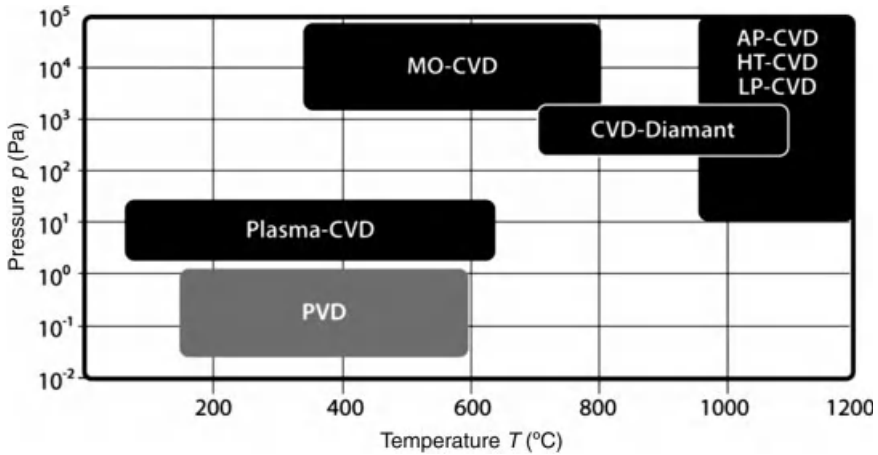


Figure 6.40 Classification of CVD processes according to coating pressure p and coating temperature T .

precursor in a hot wall or cold wall reactor. The thermal energy can be made available from different sources, such as RF heating, infrared radiation, or resistance heating. For the 3-D coating of tools and components, vertically arranged hot wall reactors are frequently used (Figure 6.42), where bubblers are generally employed to dose the liquid starting materials. In this case, the gas mixture flows into the reactor from above, while the residual gases are pumped off from below. This reactor type is suited for temperatures of 700–1000 °C, and is used primarily for the deposition of TiN, TiC, TiCN, and Al₂O₃.

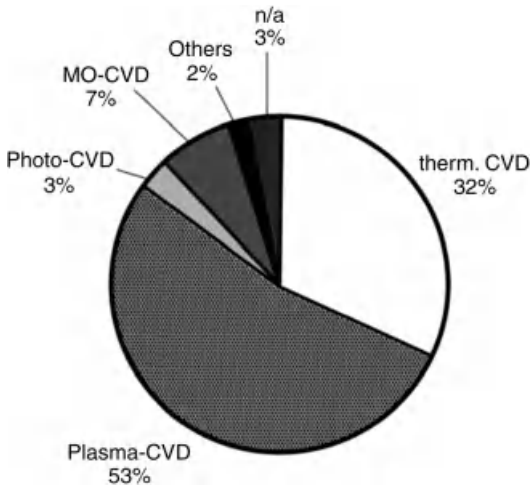


Figure 6.41 Percentage breakdown of industrially employed CVD processes [43].

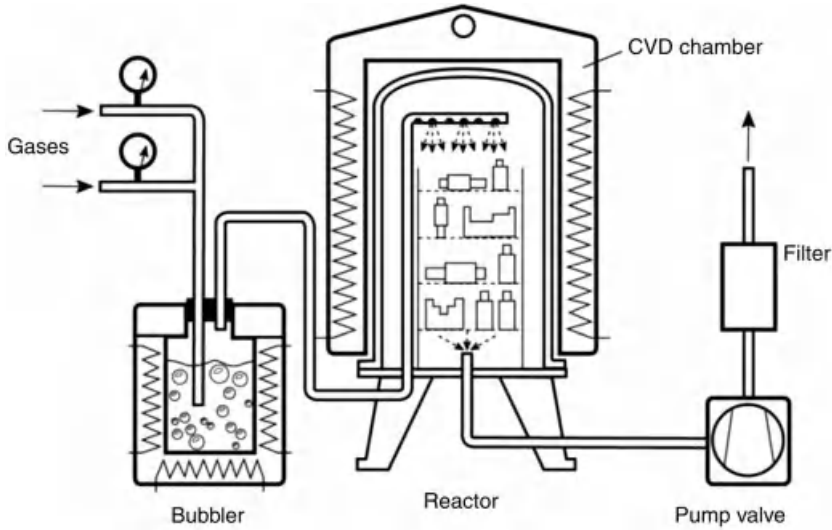


Figure 6.42 Design of a hot wall reactor for 3-D CVD coating (schematic representation).

Plasma-Activated CVD With PA-CVD or PE-CVD processes [37], the electron energy from a glow discharge is utilized to activate the chemical precursors. With this method, it is possible to operate well below the required thermal activation energy (Figure 6.43), so that the thermal loading of the materials to be coated is reduced to the range of 100–620 °C. When a gas is led under low pressure into an electric field, it will be decomposed and a glow discharge, comprised of electrons, ions and electrically excited species, is formed (Figure 6.44). The gaseous reactants are ionized, and decay as a result of collisions with electrons. Consequently, chemically active ions and radicals that form in the plasma will be deposited as a CVD layer onto the substrate.

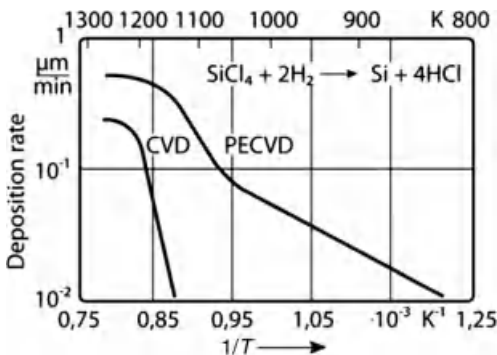


Figure 6.43 Comparison of the substrate temperature for the deposition of silicon in a thermal CVD process and a plasma CVD process.

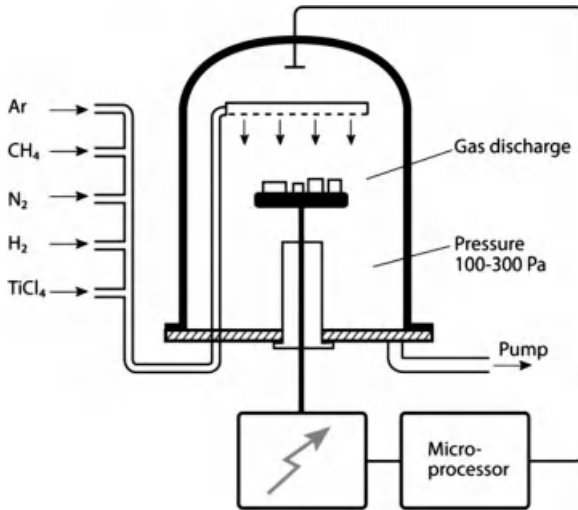


Figure 6.44 Plasma CVD reactor (schematic representation).

One advantage compared to the processes of PVD technology is the relatively high operating pressure ($p \sim 2\text{--}20\text{ Pa}$), which enables the homogeneous coating of complex geometric forms. One disadvantage which must be mentioned here is that, at the edges and in the bores of the substrate, an inhomogeneous distribution of the layer thickness can result from the inhomogeneous current density [44]. Nevertheless, the plasma effect on the substrate surface enables relatively good bonding properties to be achieved, even at low substrate temperatures. The plasma can be generated in different ways:

- DC glow discharge (DC discharge)
- Pulsed middle-frequency glow discharge (MF discharge)
- Radiofrequency glow discharge (RF discharge)
- Microwave discharge (MW discharge)

The simple DC glow discharge is the most widely used method for generating plasma in CVD processes, and it is also technically the least complicated. The pulsed DC glow discharge is particularly well suited to the coating of temperature-sensitive components and tools. RF discharges are used when higher ion energies are required for the coating process. Here, due to the different velocities of electrons and ions, the nonconducting surfaces become negatively charged, which results in an ionic current to the surface [45]; the typical frequency for RF generators is 13.56 MHz. Microwave plasmas represent special cases of RF discharge; this type of excitation is becoming increasingly common in industry because, with increasing frequency, the plasma density – and thus the density of the free radicals – increases [46]. The typical microwave frequency for CVD plasmas is 2.45 GHz.

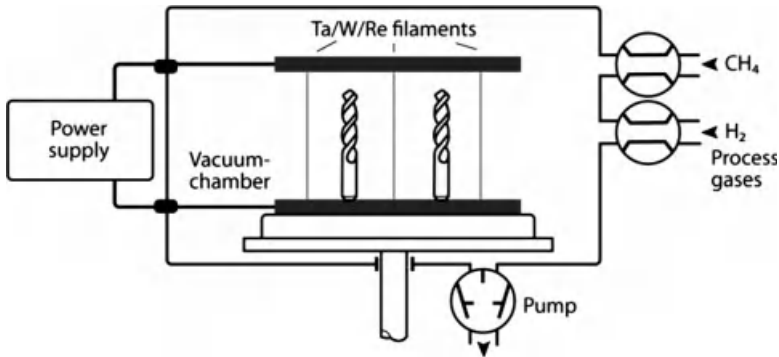


Figure 6.45 Schematic representation of the hot-filament CVD process [47].

Hot-Filament CVD Processes Hot-filament CVD processes are well suited for the deposition of diamond layers [47]. When synthesizing diamond, hydrogen and hydrocarbon carrier gases (methane: CH₄, ethyne C₂H₂) are employed as the process gases, while activation of the reactions is achieved by using electrically heated high-temperature stable filaments of tungsten (W), tantalum (Ta), or rhenium (Re). In a vacuum chamber at about 1000–10 000 Pa, the required atomic hydrogen is generated with the filaments at temperatures of >2000 °C (Figure 6.45). The filaments are distributed throughout the chamber in the vicinity of the substrate in order to guarantee a uniform distribution of the species required for the synthesis.

Figure 6.46 provides a detailed description of the processes taking place during hot-filament CVD diamond deposition. The excitation source splits part of the hydrogen molecules, and the resultant very reactive hydrogen atoms diffuse from the source into the coating space. The methyl radical (CH₃^{*}) which, according to prevailing opinion, represents the only growth species for diamond, can then form by reacting with the carbohydrate molecules. As the lifetime of the methyl radical is only very short, only those radicals formed immediately before the substrate can contribute to this growth. The distance between the wire and the surface of the substrate should therefore be around 0.5–1 cm [37, 48]. The process parameters must be chosen so as to prevent the undesired formation of graphite, or the graphite must be removed by etching with hydrogen. The atomic hydrogen also has the function of forming free growth positions at the growth front, and preventing the transformation of diamond-bound carbon back to the gaseous phase. Only in this way is it possible to prevent the formation of the normally thermodynamically more stable graphite under the given conditions [49]. In order to ensure sufficient mobility of the absorbed species on the substrate surface, a temperature of at least 650 °C is required [47].

Above a substrate temperature of 1000 °C the absorption of the layer-forming species is too low. On the other hand, for the formation of sufficient amounts of atomic hydrogen, temperatures of at least 2000 °C are required, so that the CVD diamond process cannot be carried out isothermally. In principle, this is a so-called “remote process”, in which the compounds for the CVD reactions themselves must first be produced and then transported to the substrate surface. The necessary correct

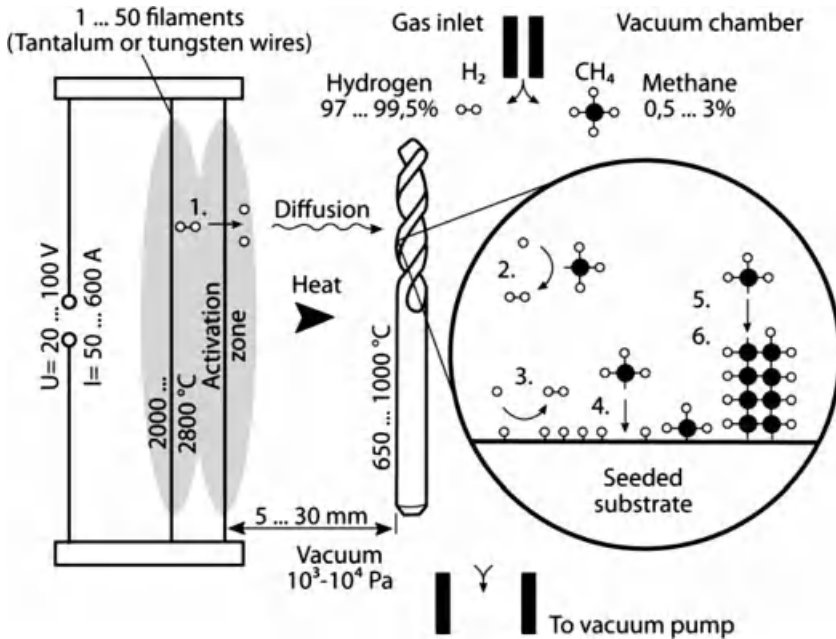


Figure 6.46 Layer formation during diamond synthesis with the hot-filament CVD process. 1, split up: $\text{H}_2 \rightarrow \text{H} + \text{H}$; 2, catching H from CH_4 : $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$; 3, catching H from surface: $\text{H} + \text{H} \rightarrow \text{H}_2$; 4, CH_3 fills open space on the surface; 5, step 4 continues on nucleus \rightarrow nucleus growth; 6, layer growth.

sequence of generation, transport, and absorption of the relevant species and, finally, of the required surface reaction, must be carefully matched to each other and, compared to other CVD processes, results in a relatively slow deposition rate of about $0.5 \mu\text{m h}^{-1}$.

The growth of diamond layers on the surface of the substrate takes place at the start of the process, by crystallization to small nuclei. Initially, these form tiny islands and, during the further course of the process, grow to a dense, contiguous diamond layer. For a suitable choice of the process parameters, the resulting layer structures can be varied over a wide range and matched to specific requirements. Thus, for example, besides standard rough microcrystalline coatings, it is also possible to obtain particularly smooth, nanocrystalline coatings (Figure 6.47).

6.2.3.5 CVD Tool Coating

For CVD tool-coating processes, the HT-CVD and MT-CVD processes in particular compete with PVD coating processes. When compared to PVD processes, CVD processes exhibit certain differences that make them interesting for industrial applications. For example, it is possible to deposit coatings either with a high growth rate or with excellent uniformity onto complex component forms. The most important advantages here are the better adhesion of the coatings that results from

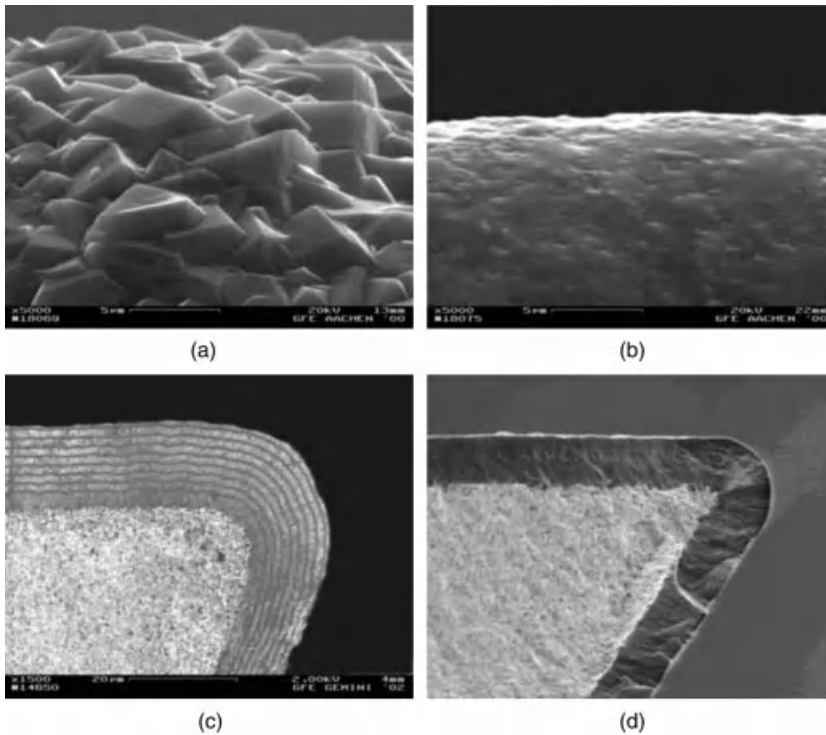


Figure 6.47 Topography and fracture structure of different diamond layers. Illustration courtesy of CemeCon AG.

inter-diffusion between the coating and the substrate, the good coating capability, and the simpler coating of large batches with low technical effort and at favorable piece costs. However, one distinct disadvantage of the CVD processes is that they are restricted to thermodynamically stable systems, such as TiN, TiCN, and Al_2O_3 , which severely limits the choice of coating materials. A further disadvantage of CVD processes involves restrictions in respect of the choice of substrate, as the temperatures required for HT-CVD processes are too high for tool steels. Although the relatively thick CVD coatings cause pronounced rounding of the tool edges, as a result they also exhibit a higher wear volume. In contrast to PVD coatings, for CVD coatings the tensile stresses exist in the coatings themselves. Although, at present, a greater proportion of cemented carbide tools are CVD-coated, market growth is expected shortly for the PVD coating processes (Figure 6.48).

Over the past twenty-five years, many more intensive developmental studies have been undertaken in the field of CVD processes than in any other area of thin film technology (Table 6.11) and, indeed, such studies are being intensively pursued to the present day. Thus, the favorable properties of individually deposited TiC and TiN coatings have been combined in multilayer coatings or mixed crystals such as TiCN. Other improvements relating to greater oxidation stability and elevated hot hardness

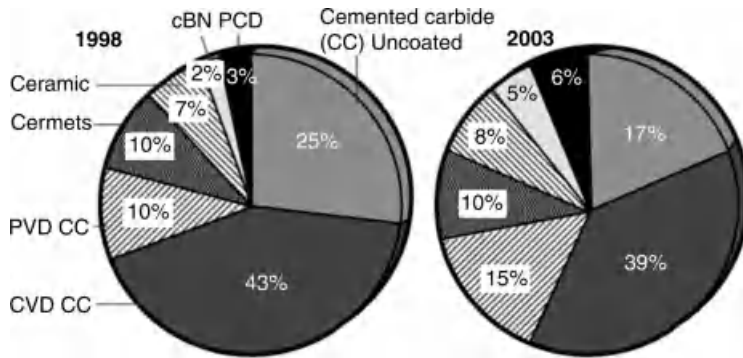


Figure 6.48 Market shares for metal cutting materials. Illustration courtesy of Kennametal Inc.

Table 6.11 Historical development of CVD hard-material coatings for metal cutting tools.

1969	TiC	Titanium carbide	1985	Al ₂ O ₃	Alternating multilayers
1974	TiCN	Titanium carbonitride	1985	TiCN	MO-CVD titanium carbonitride
1974	TiN	Titanium nitride	1986	Al ₂ O ₃	Thick aluminum oxide
1975	TiC-TiCN-TiN	Multilayer	1988	ZrN	Zirconium nitride
1979	Al ₂ O ₃	Aluminum oxide	1988		Post-treatment
1979	TiC-Al ₂ O ₃	Multilayer	1990	C _{Diamond}	Diamond synthesis
1982	HfN	Hafnium nitride	1998	C _{Diamond}	Nanocrystalline diamond

have been achieved with the CVD deposition of Al₂O₃, and also as multilayer coatings (Figure 6.49 and Figure 6.50). Both, diamond and DLC coatings, exhibit not only a very high degree of hardness but also good frictional behavior.

6.2.3.6 CVD Component Coating

The coating of components and machine elements using plasma CVD processes was first achieved at about the same time as PVD component coatings, during the mid-1990s. With plasma CVD processes, however, predominantly amorphous carbohydrate coatings (DLC) of the systems a-C:H are deposited. In terms of their properties, carbon coatings can be varied over a wide range, from very hard systems with a high fraction of sp³ bonding (diamond) to very soft, almost polymer-like coatings. Systems with high sp² bonding fractions (graphite) function as solid lubricants. Carbon coatings greatly reduce the coefficients of friction, and thus often contribute to improved efficiencies and, consequently, to a reduction of CO₂ emissions, notably in the automotive industry. They also offer excellent protection against wear and corrosion. Since pure a-C:H coatings are known to bond poorly, due to their high internal stresses, metallic bond coats are normally used together with these. The metallic layers are generated partly via PVD processes (mostly MSIP). One advantage here is that coatings can be deposited in the plant with PE-CVD and MSIP processes,

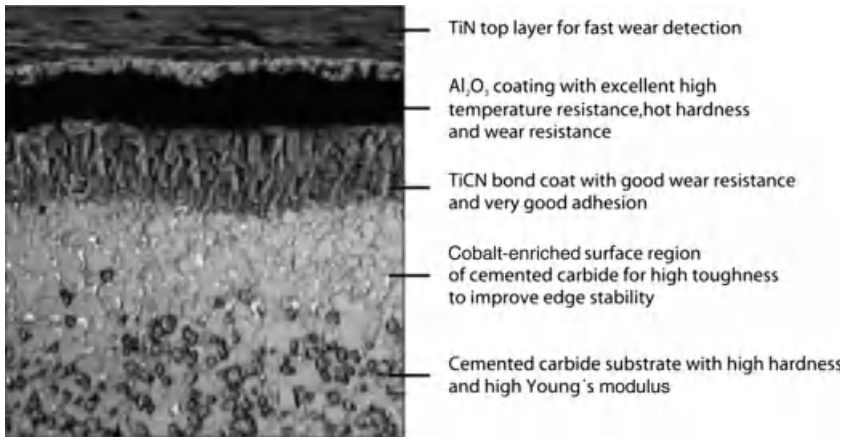


Figure 6.49 Multilayer coating ($\text{TiCN} + \text{Al}_2\text{O}_3 + \text{TiN}$) of a cemented carbide indexable insert. Illustration courtesy of Sandvik AB.

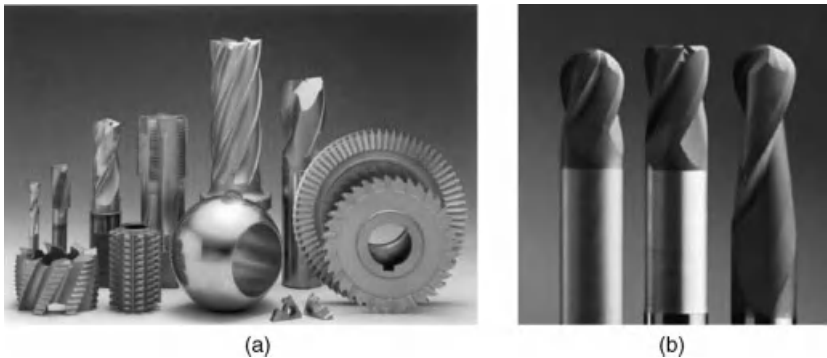


Figure 6.50 Examples of CVD tool coating applications. (a) $\text{TiCN} + \text{Al}_2\text{O}_3 + \text{TiN}$ (Illustration courtesy of Machine & Tools Vietnam); (b) Diamond (Illustration courtesy of Jablo Tools b.v., NL.)

such that the transition from substrate to bond coat, and then to the a-C:H outer layer proper, can be varied over a wide range.

Today, plasma CVD processes are employed typically for rocker arms, plain bearings, intake valves, tappets and gudgeon pins for the construction of motors. DLC coatings are also found on gearwheels and camshafts (Figure 6.51). Besides the automotive industry, carbon coatings are of interest to all areas in which tribological systems rule out the use of lubricating agents.

6.2.4

Sol-Gel Deposition

The sol-gel method is concerned with processes for the manufacture of ceramic or ceramic-organic materials in the form of bulk materials, nanopowders and fibers, as well as for the deposition of homogeneous nanocrystalline coatings. The starting



Figure 6.51 Examples of applications for diamond-like carbon (DLC)-coated components in the automotive industry. Illustrations courtesy of Kexel GmbH.

materials, mostly alcoholates/alkoxides or nanoparticles, are initially in a solution, the so-called *sol*. As a result of aggregation and condensation processes, the sol solidifies to a *gel*, whereby spatially crosslinked chains are formed. Different drying, aging, and heat treatment processes then determine the form and structure of the solid materials resulting. The resulting microstructures are, as a rule, more homogeneous than with other conventional manufacturing processes. Besides the high degree of purity of the products and the relatively low costs of the technology, the low process temperatures also represent an important advantage, so that coatings of sensitive materials, such as plastics, are also possible. The operational sequence and process variants are summarized in Figure 6.52 [50].

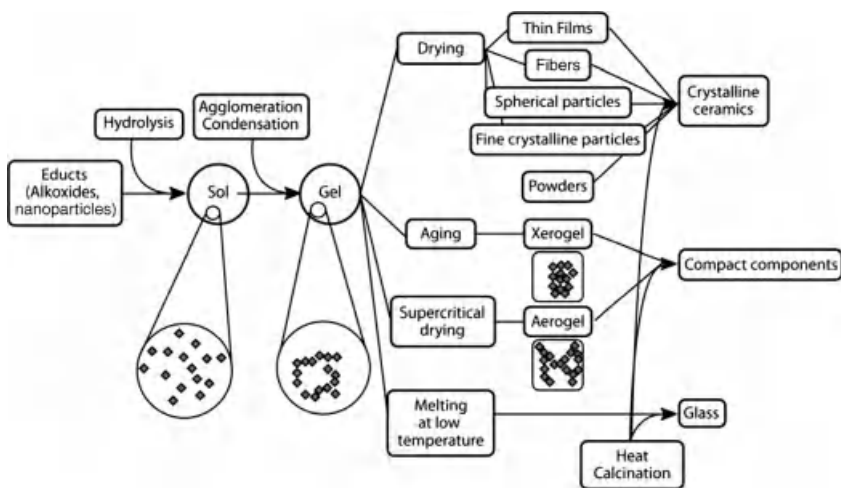


Figure 6.52 Operational sequence and process variants of the sol-gel process [50].

6.2.4.1 The Sol as Starting Material

A sol (Latin: solution) is a stable solution of colloids, that is, very finely distributed particles in a liquid. The diameter of these particles is in the range of 1 nm to 0.5 μm . As the density of the particles is greater than that of the solvent, sedimentation would normally be expected to take place; however, due to the dynamic equilibrium between the forces of attraction and repulsion acting on the particles, this occurs only to a limited extent or not at all. The forces of attraction derive from the influence of the free surface energy, the electrostatic force of attraction, and the van der Waals forces. The repulsive forces can be selectively influenced by the addition of emulsifying agents or a change of pH value, so that no unintentional agglomeration occurs [51].

6.2.4.2 The Sol–Gel Transition

While the individual particles can move freely in the sol, spatially crosslinked chains exist in the gel. Both, the solvent and liquid reaction products are incorporated in this structure, giving the gel its characteristic gelatinous structure. The transition from sol to gel is possible with every sol, and is referred to as *coagulation*. The reverse reaction (*peptization*) from gel to sol is possible only with so-called “reversible colloidal” solutions [52]. Different variants exist for the sol–gel transition, according to the structure of the (mostly metal-based) starting systems. Wet-chemical synthesis systems and particle-form sols and gels represent the most widely used of these.

Particle-Form Sols and Gels Particle-form sols and gels consist of fine particles ranging from 1 to 500 nm in size, that are dispersed in a solvent. The particles can be prepared for example, by ball-milling, flame oxidation, or spark erosion. Typical products are SiO_2 particles, produced by blowing SiCl_4 salt into a 1800 °C hot $\text{H}_2\text{-O}_2$ -flame; this material is sold under the commercial name of Aerosil or Cab-O-Sil [53]. The particle size is a function of the duration of exposure to the flame, whereby the size increases with increasing time. During the process, the particles are partly hydrolyzed (formation of OH groups); mixing the particles with a suitable solvent then forms the sol. When the equilibrium of forces (which stabilizes the sol) is then destabilized by stirring, heating, by the addition of ions or the removal of part of the solvent, this causes the formation of the gel. This process is shown schematically in Figure 6.53, where the larger particles are seen to agglomerate while the interstitial regions are filled with smaller particles. This explains why a large scattering width of the particle diameter leads to a more stable particle complex. With increasing growth, the branching of the chain structures becomes more pronounced [53].

6.2.4.3 Wet-Chemical Synthesis Systems

The starting materials for wet-chemical synthesis systems are alcoholates (also referred to as alkoxides), which can in general be described by the chemical formula $\text{M}(\text{OR})_n$, where M represents a metal, R an aliphatic chain, and n is the valence of the metal. One of the best-known examples of an alcoholate is tetraethyl orthosilicate (TEOS, $\text{Si}(\text{O-C}_2\text{H}_5)_4$). As a rule, alcoholates are liquids at room temperature, though exceptions to this are the alcoholates of the alkaline and alkaline earth elements. As these solid alcoholates are characterized by poor solubility, mostly TEOS solutions are

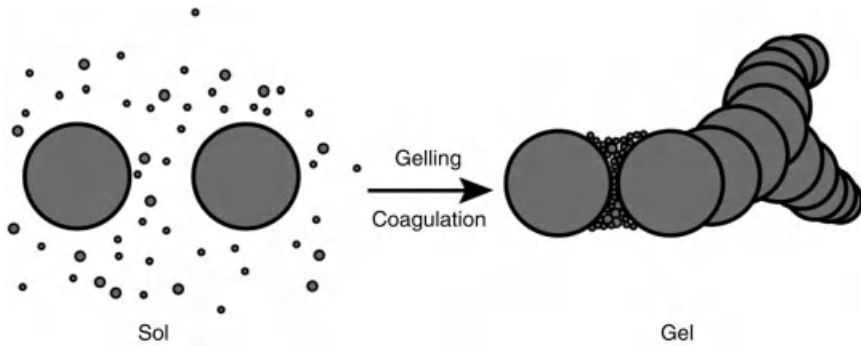


Figure 6.53 Sol-gel transition of a particle-form sol.

used, to which the relevant alkaline or alkaline earth metals are added in the form of salts, frequently as acetates and less frequently as nitrates.

When alcoholates are used, they are dissolved in alcohol prior to the sol-gel reaction itself. The first reaction step is then hydrolysis. With the addition of n parts of water to the alcoholate solution, the bond between the metal atom M and the aliphatic chain R is cleaved, with the formation of a metal hydroxide $M(OH)_n$ and n monovalent alcohols $nR-OH$ (Figure 6.54).

In the second reaction step, with the addition of catalytically acting acids or bases OH^- ions or H^+ ions, respectively, metal hydroxide ions are split off, with the formation of water. The splitting off of water leads to this process being referred to as *condensation*. The resulting free valences of Si or O atoms can then react with other metal hydroxides, ultimately to form polymer molecular structures (Figure 6.55).

Adjusting the pH value can influence the type of polymerization; for example, in acids (at $pH < 5$), hydrolysis takes place more rapidly than condensation. Due to the long diffusion paths, the condensed molecules have a relatively long time to arrange themselves and form long chains with little branching. In the basic region ($pH > 7$), however, condensation takes place considerably more rapidly than hydrolysis, so that the metal hydroxides formed will condense quasi-immediately; this results in the formation of short molecules, referred to as *clusters*. For pH values > 8.5 , the

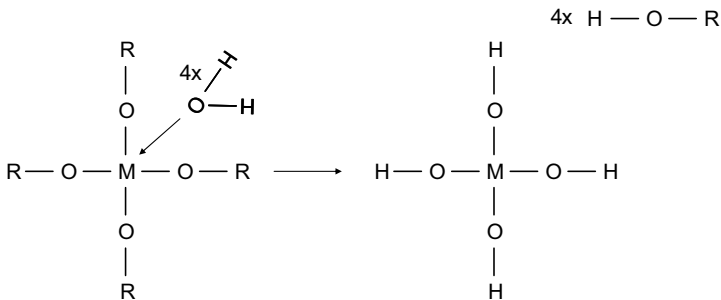


Figure 6.54 Hydrolysis of an alcoholate with the formula $M(OR)_4$.

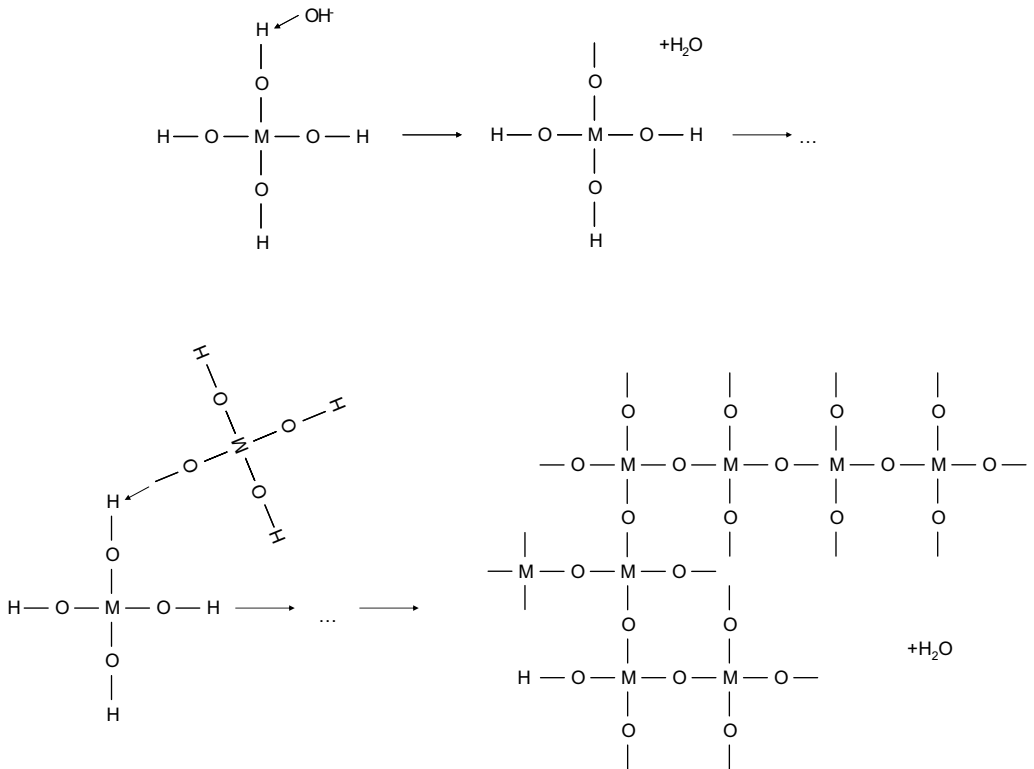


Figure 6.55 Base-catalyzed condensation.

preferential dissolution of long, thin molecules also takes place, leading to the formation of individual agglomerations. These relationships are depicted schematically in simplified form in Figure 6.56 [54].

The structure which forms in this way is important, especially for the further processing capability and the properties of products resulting from the follow-on drying process. The greater the degree of crosslinking, the better the structural strength. Whereas, long chains are particularly well suited for the processing of fibers, short molecules are required for the production of powders [51].

6.2.4.4 Coatings With the Sol-Gel Process

Coatings represent one of the most widely used applications of sol-gel processes, and are employed for a broad field of corrosion and wear protection, through heat insulation, to special optical and electro-sensory tasks. Typical coating thicknesses are in the range of 0.05 to 15 μm [55]. For the production of coatings, a sol film is applied to the component, thickened, and then thermally treated. Besides spray processes, which have disadvantages in respect of controlling the film thicknesses, dip processes and rotation coating processes are also employed.

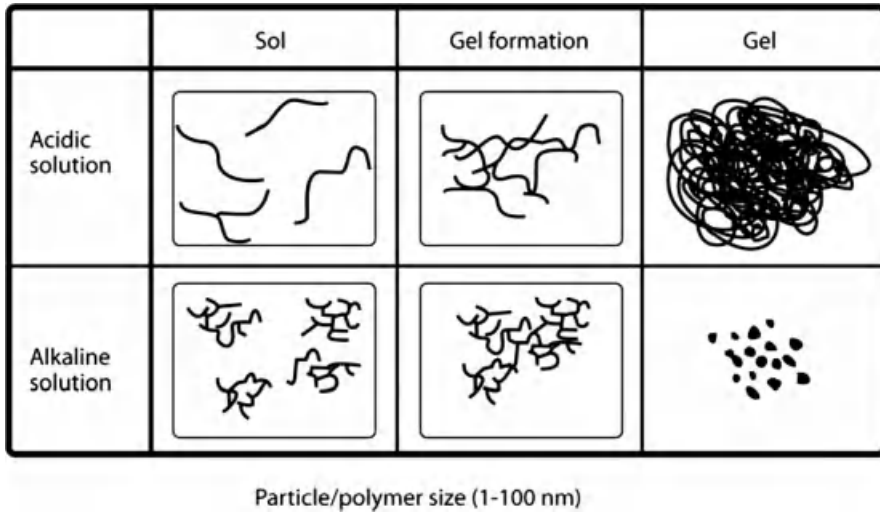


Figure 6.56 Influence of acidic and basic media on polymerization. Illustration courtesy of Stiftung Institut für Werkstofftechnik, IWT Bremen.

With the *dip process*, the component is immersed in the sol and removed at a defined speed, whereby a thin film remains bonded to the surface. This process finds application, for example, in the coating of architectural glass [53]. Here, the thickness of the sol film is proportional to the viscosity of the sol and the speed of removal, and inversely proportional to the density of the sol. The coating thickness is also influenced by the angle of immersion, so that it is possible to obtain different coating thicknesses on the two sides of the substrate [56].

Alternatively, for rotationally symmetric components, the *rotation process* – in which a definite amount of the sol is applied to the center of the component – can be employed. Due to the rotation, a uniform distribution of the sol over the entire component results, while any excess sol is spun away. In contrast to the dip process, one-sided coatings can be applied with the rotation process. The decisive parameters are the acceleration, final velocity of rotation, time, and the viscosity of the sol. The prerequisite for all processes is a sufficient wetting of the substrate by the sol.

With wet-chemical synthesis systems (e.g., TEOS), nanocrystalline coatings can be applied to glass, ceramics, plastics, and metals. Covalent bonds with the base material ensure good bonding. Inorganic coatings with good scratch resistance can be produced, on the surfaces of which organic molecular chains are chemically bound (Figure 6.57). The hydrophobic surfaces then offer self-cleaning properties, which imitate the “lotus blossom” effect (Figure 6.58). With sol–gel processes, flat products can be coated on one side or on both sides, while complex geometries, as well as cannulas and tubes, can be coated both inside and outside by utilizing the dip process.

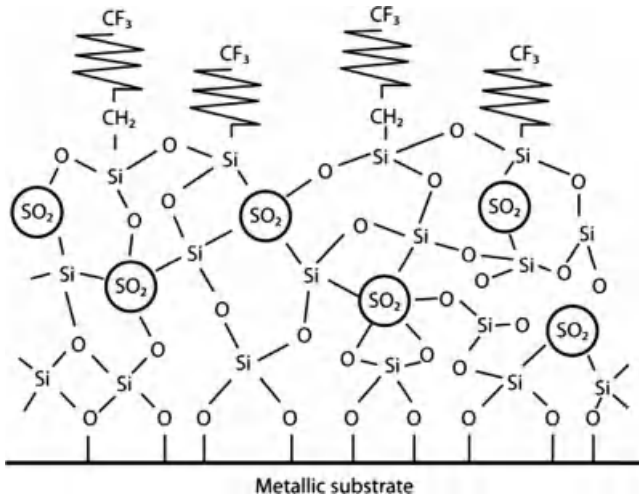


Figure 6.57 Schematic structure of an organic sol-gel coating with inorganic molecular chains on a metallic surface.

6.2.4.5 Examples of Applications for Sol-Gel Coatings

One of the most widespread applications is the production of scratch-resistant, transparent coatings on plastic substrates, mostly utilizing TEOS as the starting material. These coatings find application for example, as lenses, mirrors, light fibers and eyeglass lenses as protection against mechanical damage, along with numerous optical functions [53]. On metals, sol-gel coatings, often in combination with a self-cleaning effect, serve for corrosion protection and wear protection (Figure 6.59).

Window glass is treated with titanium-palladium-based sol-gel coatings in order to ensure thermal insulation by definite absorption and reflection behavior [53]. With the use of electro-chromatic coatings, it is possible to shift the transmission region of

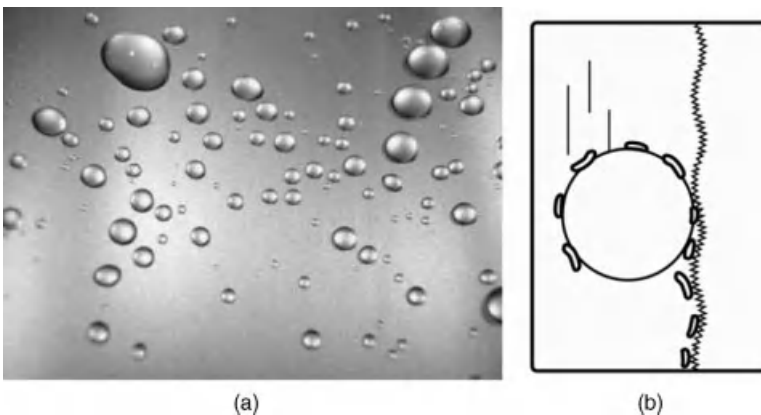


Figure 6.58 (a) Water droplets on a sol-gel-coated stainless steel surface; (b) Sketch illustrating the self-cleaning lotus blossom.



Figure 6.59 Aluminum wheel rim and petrol tank cap with sol-gel coating for corrosion protection and self-cleaning effect. Illustrations courtesy of Nano Tech Coatings GmbH, Tholey.

the coatings by applying a voltage; that is, to discolor the glass coated in this way. Tungsten oxide coatings are used in automotive rear-view mirrors which, in the event of strong incident light, such as from another car traveling behind, causes the mirror to darken [57]. Other possible applications for sol-gel coatings can be found in micro-system engineering, where ferromagnetic (e.g., $Y_3Fe_5O_{12}$), superconducting ($YBa_2Cu_3O_{7-x}$) or piezoelectric properties can be utilized ($Pb(Zr,Ti)O_3$) [58].

6.2.5

Electrochemical Metal Deposition

Electrochemical metal deposition onto the surface of a substrate is based on the redox reactions which take place in an electrolytic solution. These processes therefore follow the laws of electrochemistry, and may be classified as (Table 6.12):

- metal deposition processes *with* an external current (electroplating); and
- metal deposition processes *without* an external current (chemical metal deposition).

Generally speaking, the term “galvanotechnics” is often understood to refer to both deposition processes. While for electroplating the necessary electrons are made available from a current source, with chemical deposition the electrons derive either from a reducing agent added to the electrolyte, or from the potential drops between the work piece and the noble metal coating. In all cases, metallic cations are reduced by the acceptance of electrons ($Me^{z+} + z e^- \rightarrow Me$), and precipitate as a layer onto the surface; that is, the work piece to be coated is always cathodic.

The term “galvanotechnics” stems from the Italian physician and natural scientist Luigi Galvani (1737–1789), who first described the phenomena of electrochemical voltage sources in 1789.

On the basis of these investigations, in 1800 the physicist Alessandro Volta (1745–1827) developed the first battery (“Voltaic column”) and shortly thereafter, in

Table 6.12 Essential differences between electrolytic and chemical metal deposition in practical application.

	Electroplating	Chemical deposition
Rate	Faster by a factor of about 10	
Coating thickness	Irregular at edges and corners	More homogeneous distribution at edges, cavities can also be coated
Variation possibilities	Multilayer, gradient layers, dispersion layers can be produced	Coating thickness can be adjusted within limits, dispersion layers can be produced
Regulation	Can be controlled on the basis of current–voltage curves	
Materials	Great variety of coating material	Non-conductive materials can also be coated
Electrolyte baths	Lifetime several times longer	Low storage life, more sensitive, more expensive
System technology	Requires external current source	

1801, introduced the electrochemical series for metals. At the beginning of the nineteenth century, as a result of the work of Humphrey Davy (1778–1829) and Michael Faraday (1791–1867) the mutual relationship between electrical and chemical processes, which represents the basis of electrochemistry, became known. It was shown that, by way of electric charges and later electric current, substances can be combined and separated (so called “electrolysis”) while, conversely, chemical processes can be employed to generate electricity. Of particular interest was the realization that aqueous solutions of heavy metal salts can be deposited with the aid of an electric current in any thickness required, and with good adhesion properties, onto metallic substrates or substrates made electrically conductive. In 1833, Faraday recognized that chemical processes take place in proportion to the quantities of electricity present. In 1887, Svante Arrhenius (1859–1927) laid the foundation for the scientific basis of electrochemical processes with his “theory of electrolytic dissociation” [5]. The essential parameters for the characterization of electrolytes, such as the degree of dissociation, the dissociation constant and the activity coefficient, derive from Arrhenius’ work. At the beginning of the twentieth century, Walter Nernst (1864–1941) investigated electrochemical processes more exactly, and formulated quantitative relationships expressed in particular in the Nernst equation [5].

Viewed historically, galvanotechnic belongs to the oldest methods of metal deposition. In 1838, Moritz Hermann von Jacobi, on the basis of the observation of John Frederic Daniell (1790–1845) that copper undergoing deposition represents a true image of the electrode, further developed this technically. This led to the invention of “galvanoplasty,” which can be described as a process for the molding of different objects (e.g., medals) by means of a galvanic current. During the course of further development, it was found that all metallic objects could be furnished with metal coatings in suitable metallic solutions. Initially, this knowledge was utilized principally

for decorative purposes, such as for silver plating, gold plating, and copper plating (after 1840). The invention of the dynamo by Werner von Siemens in 1867 formed the basis for the large-scale technical utilization of electroplating, as only then were sufficiently large quantities of electricity made available. With the possibility of nickel plating for the corrosion protection of iron parts, the areas of application shifted from purely decorative purposes to technical utilization. As a result of the increasing use of iron materials, the need for galvanic corrosion protection coatings of cyanidic copper, acidic copper, nickel and chromium arose [5]. Only somewhat later, hard chromium coatings became established for many tribological applications.

In part, under the electrochemical deposition of metals, only electroplating is considered – that is, deposition making use of an external current. However, in practice there are very important processes which function without the application of current [5]. In 1835, Justus von Liebig (1803–1873) described for the first time the reduction of silver salts with aldehydes. An important advantage of deposition without current is the possibility of coating electrically nonconductive materials, such as glass, porcelain or polymers, with metal. Important also was the introduction in 1944 of hypophosphite by H. Brenner and G. Riddell, as a reducing agent for the deposition of nickel.

The electrochemical deposition of metals still belongs to the most frequently used surface-finishing processes. Besides the automotive industry, one of the largest customers for galvanized surfaces, other areas responsible for the high turnover and intensive development of galvanotechnic are the electrotechnical and electronics industries, the consumer goods industry, the building industry, the machine manufacturing industry, the aviation and space industry, the jewelry industry, and medical engineering (e.g., dental prostheses). The most important functions which the galvanized coatings assume are:

- Decoration
- Corrosion protection
- Wear protection
- Reduction of friction
- Enabling electrical contacts (printed circuit boards, PCBs).

Although the value of galvanized coatings is only around 5–15% of the total value, these coatings play a central role in the implementation of innovative concepts in both traditional and newly arising industries. In the Federal Republic of Germany, more than 3000 plating shops, sub-supplier, and service industries with around 100 000 employees achieve an annual turnover of €3.3 billion. With around 40% of overall turnover, the German plating industry is the leader within the European Union (Figure 6.60), and therefore represents an important part of middle-sized European industry [59].

6.2.5.1 Thermodynamic Principles of Electrochemistry

With the help of thermodynamic considerations, it can be determined under what thermodynamic conditions (chemistry, temperature, pressure) a reaction takes place. The most important terms used in electrochemistry will first be explained.

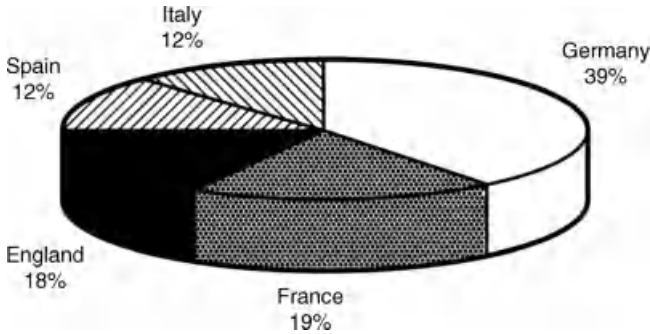


Figure 6.60 Distribution of turnover for plating industry in 1998 within the European Union [59].

An *electrode* is a conductor of electrons (e.g., every metal or graphite), surrounded by an electrolyte. An *electrolyte* is an electrically conductive material in which the charge carriers are in the form of ions. Usually, electrolytes are liquids, in which ions are freely mobile due to the solubility of many molecules (dissociation), for example, aqueous media ($\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$) as well as all acids and bases. There are, however, also solid electrolytes, such as yttria-stabilized zirconia, which is used to generate current in fuel cells. Electrolytes are not capable of conducting electrons, so that the exchange of electrons must take place by their conduction between the electrodes.

Electrochemical metal deposition is based on the *redox reaction*; that is, the total reaction consisting of oxidation (delivery of electrons) and reduction (acceptance of electrons), in which a charge exchange takes place in the form of electrons between the reaction partners. The driving force of the electrochemical reaction is the striving of the reactants to achieve a thermodynamically more stable state, on the basis of the equalization of potential differences. The assessment of the probability of a chemical reaction is based on the free molar reaction enthalpy ΔG_{R} , also known as the Gibbs enthalpy. When $\Delta G_{\text{R}} < 0$, the chemical reaction takes place spontaneously (see also Section 6.2.3.1). The free molar enthalpy G of a mixed-phase component can also be regarded as its molar thermodynamic potential, for which the term chemical μ has been introduced [60].

$$\text{Chemical potential } \mu : G_i \equiv \mu_i$$

The chemical potential μ_1 for a component of a mixed phase is given by the partial differential quotient of the thermodynamic potential (of the free molar enthalpy) G according to the amount of substance n of this particle type, at constant pressure, constant temperature, and constant amount of substance of all other components:

$$\mu_1 = \left(\frac{\partial G_1}{\partial n_1} \right)_{p, T, n_2, \dots}$$

The free molar reaction enthalpy ΔG_{R} then results as the stoichiometric sum of the chemical potentials of all components of the mixed phase:

$$\text{Gibbs enthalpy } \Delta G_{\text{R}} : \Delta G_{\text{R}} = \sum v_i \cdot \mu_i$$

v : stoichiometric numbers of the reaction equation; those for the end products have a positive sign, and those for the starting materials have a negative sign.

The free molar reaction enthalpy ΔG_R is calculated from the chemical potentials alone, as the contributions of the electrical work are not required. For the overall equations of a reaction, this is always the case. These reactions are characterized by the fact that the electrostatic charges of the phases remain unchanged in relation to each other. The behavior with so-called “electrode reactions” which, as partial reactions of the overall metal deposition process are of particular interest, is different [61].

At the phase boundaries of the electrodes (metal/electrolyte), a difference in the electrochemical potentials μ^* [J mol^{-1}] exists, as the different phases do not have the same electrochemical potential. This potential difference results in electrochemical reactions at the phase boundary. The electrochemical potential μ^* is comprised of the chemical potential μ (of the partial free molar enthalpy) and the electrical potential ϕ (Galvani potential):

$$\text{Electrochemical potential } \mu^* : \quad \mu^* = \mu + z \cdot F \cdot \phi$$

$$\text{where :} \quad F = N_A \cdot e$$

z : reaction valence; that is, the number of electrons exchanged in the atomic form of the equation for the chemical reaction, for example, for $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$, $z = 2$

F : Faraday constant = 9.4648×10^4 (A s mol^{-1})

N_A : Avogadro's number = 6.0221367×10^{23} (atoms mol^{-1}), the number of particles per mole

e : elementary electron charge = $1.6021773 \cdot 10^{-19}$ (A s^{-1})

The factor ($z \cdot e \cdot \phi$) is the reversible work which would be required for the transport from the “charge-free infinity” to within the phase for a single particle with z elementary electron charges, or for $N_A = 6.023 \times 10^{23}$, that is for 1 mole. The chemical potential μ is understood as the microscopic short-range effect to which charged particles are subjected. In respect of the terms used, the classification into chemical and electrical potential is not entirely clear, as the theory of chemical bonding indicates that the short-range effects are also of an electrical nature [61]. The calculation of the Gibbs enthalpy ΔG_R for electrode reactions then follows from the:

$$\text{Gibbs enthalpy } \Delta G_R : \quad \Delta G_R = \sum v_i \cdot \mu_i + z_i \cdot F \cdot \phi$$

All charged particles with the index i migrate in a gradient of μ_i^* , that is, the velocity w of these particles can be given in the form:

$$w \sim -\text{grad } \mu_i^* = -\text{grad } \mu_i - z_{ig} \cdot F \cdot \text{grad } \phi$$

For a constant μ_i^* (i.e., $\text{grad } \mu_i^* = 0$), electrochemical equilibrium exists. Then, for the equilibrium between two phases:

$$0 \equiv \Delta \mu_i^{*'} = \Delta \mu_i' + z_i \cdot F \cdot \Delta \phi'$$

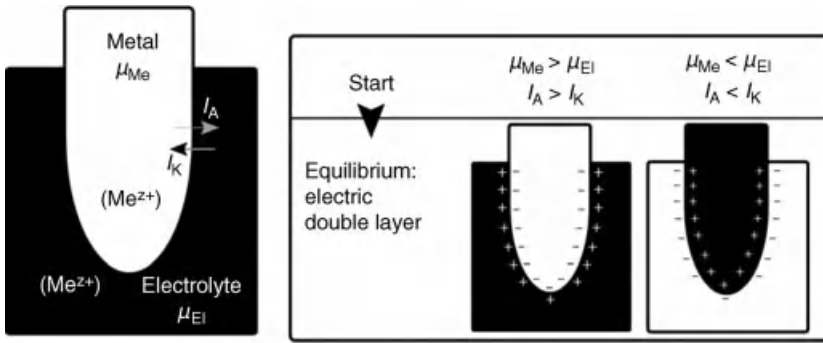


Figure 6.61 Formation of an electrical double layer on simple electrodes. μ : chemical potential; I_A : anodic partial current $\text{Me} \rightarrow \text{Me}^{z+} + z e^-$; I_K : cathodic partial current $\text{Me}^{z+} + z e^- \rightarrow \text{Me}$.

Here, the Δ symbol describes the difference between the respective values of the phases under consideration (metal/electrolyte), while the index “ i ” indicates that electrochemical equilibrium exists. The equation makes clear that, for electrochemical equilibrium, finite values of $\Delta\mu_i'$ and $\Delta\phi'$ exist, and therefore that chemical and electrical nonequilibria exist between the two phases (metal/electrolyte). The electrode potential E' , corresponding to the potential difference $\Delta\phi'$, is referred to as the “equilibrium state.” From the last equation, it follows that the anodic and cathodic partial reactions take place with a finite velocity only when $\Delta\phi$ is more positive or more negative than $\Delta\phi'$.

As a result of the potential difference at the metal/electrolyte phase boundary, an exchange of charges sets in. Here, the anodic partial current I_A describes the release of positively charged metal ions to the electrolyte, while the electrons set free at the same time (oxidation) remain in the metal. On the other hand, a charge exchange takes place in the form of a cathodic partial current I_K , using the electrons from the metal to reduce metal ions on the surface of the metal. Depending upon which partial current is initially larger, the metal becomes positively (here: cathode) or negatively (here: anode) charged. For simple electrodes, the current stops flowing as soon as the potential differences are equalized by the formation of an electrical double layer at the phase boundary (Figure 6.61).

Only with the electrical connection between the two different electrodes and the resulting flow of electrons from anode to cathode can the reactions continue. Two electrodes, when electrically connected to each other so that an electron current can flow, and simultaneously immersed in an electrolyte in which ion exchange takes place in the form of an ionic current, constitute an electrochemical (voltaic) cell. In voltaic cells, oxidation takes place on the anodic solid-state surface, and reduction on the cathodic solid-state surface of the electron conductor. The best-known example of a voltaic cell is the Zn–Cu battery, the so-called Daniell element (Figure 6.62).

The electron current between the anode and the electrode, which ultimately is responsible for ensuring that the anodic and cathodic partial currents are maintained, is produced by the potential difference ΔE between the two electrode

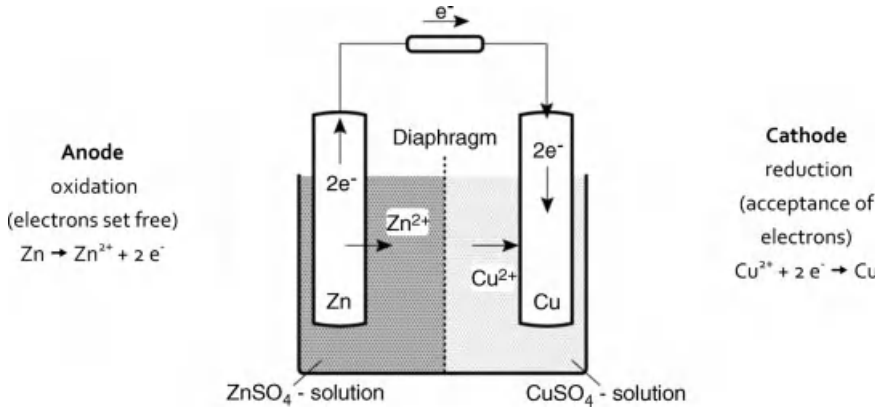


Figure 6.62 Daniell element as an example of a voltaic cell.

potentials of the cathode $\Delta\phi_K'$ and the anode $\Delta\phi_A'$ (Figure 6.63). The electrode potentials cannot be individually measured; hence, for their determination a second (reference) electrode is required.

In the “ideal” electrochemical series (Table 6.13), the electrode potentials are referred to the standard hydrogen electrode (SHE), arbitrarily defined as the zero point. The electrode potentials, referred to the SHE, of homogeneous metal electrodes in a solution of its own salts with the metal ion activity 1 at a temperature of 298 K and a hydrogen partial pressure of 1.013 bar are referred to as the “normal potentials” $E^0_{Me/MeZ+}$ (or standard potentials).

The Gibbs enthalpy ΔG_R of a redox reaction is calculated as the difference of the standard potentials of the electrode pair employed:

$$\text{Gibb enthalpy } \Delta G_R \text{ of a redox reaction : } \Delta G_R = (E^0_{H,A} - E^0_{H,K}) \cdot z \cdot F$$

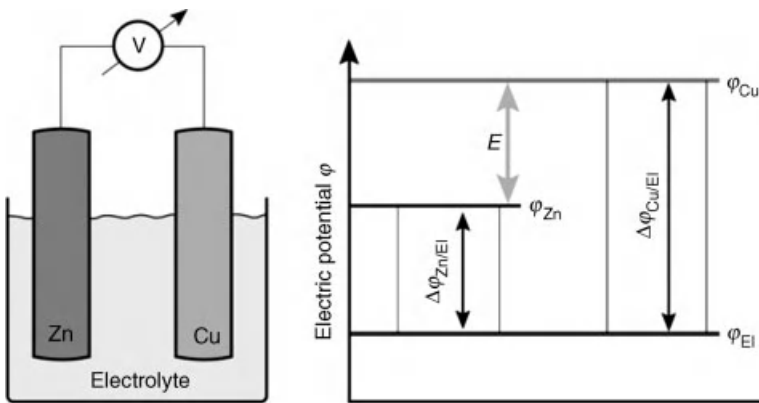


Figure 6.63 Potential difference E of a voltaic cell.

Table 6.13 Ideal electrochemical electromotive series (standard potentials).

Metals	Potential-determining process	Normal potential (in mV)
Magnesium	$\text{Mg} \rightleftharpoons \text{Mg}^{2+}$	-2380
Aluminium	$\text{Al} \rightleftharpoons \text{Al}^{3+}$	-1660
Manganese	$\text{Mn} \rightleftharpoons \text{Mn}^{2+}$	-1050
Zinc	$\text{Zn} \rightleftharpoons \text{Zn}^{2+}$	-760
Chromium	$\text{Cr} \rightleftharpoons \text{Cr}^{2+}$	-560
Iron	$\text{Fe} \rightleftharpoons \text{Fe}^{2+}$	-440
Indium	$\text{In} \rightleftharpoons \text{In}^{3+}$	-336
Thallium	$\text{Tl} \rightleftharpoons \text{Tl}^{1+}$	-336
Cobalt	$\text{Co} \rightleftharpoons \text{Co}^{2+}$	-270
Nickel	$\text{Ni} \rightleftharpoons \text{Ni}^{2+}$	-230
Tin	$\text{Sn} \rightleftharpoons \text{Sn}^{2+}$	-140
Hydrogen	$\text{H}_2 \rightleftharpoons 2\text{H}^{1+}$	± 0
Tin	$\text{Sn} \rightleftharpoons \text{Sn}^{4+}$	+ 50
Copper	$\text{Cu} \rightleftharpoons \text{Cu}^{2+}$	+ 345
Silver	$\text{Ag} \rightleftharpoons \text{Ag}^{1+}$	+ 799
Lead	$\text{Pb} \rightleftharpoons \text{Pb}^{4+}$	+ 800
Mercury	$\text{Hg} \rightleftharpoons \text{Hg}^{2+}$	+ 854
Platinum	$\text{Pt} \rightleftharpoons \text{Pt}^{4+}$	+ 900
Gold	$\text{Au} \rightleftharpoons \text{Au}^{1+}$	+ 1700

E_{H}^0 : standard anode and cathode potentials

z : valence

F : Faraday constant = 9.4648×10^4 [A s mol⁻¹]

For the calculation of the equilibrium potentials E_{H} for other concentrations, the Nernst equation is required:

$$\text{Nernst equation : } E_{\text{H}} = E_{\text{H}}^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln a_{\text{Me}^{z+}}$$

R : universal gas constant = 8.314 472 (J K mol⁻¹)

T : temperature (K)

z : charge number of the particles (valence of the ions determining the potential)

F : Faraday constant

$a_{\text{Me}^{z+}}$: activity/concentration of the soluted metal ions determining the potential.

The change E_{H} in E_{H}^0 during redox reactions is a function of the activities of the reduced and oxidized species, so that the:

Equilibrium potential of a redox reaction is given by:

$$E_{\text{H}} = E_{\text{H}}^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{a_{\text{ox}}}{a_{\text{red}}}$$

6.2.5.2 Kinetic Principles of Electrochemistry

The greater the potential difference ΔE between two electrodes, the greater the reducing (electron acceptance) or oxidizing (electron release) effect. The velocity for the course of the reaction in an electrochemical element therefore depends upon the potential ΔE between the two electrodes; the potential difference is consequently often referred to as the electromotive force (EMF) [62]. The potential difference is a function of temperature, which therefore also represents an important parameter for the kinetics. According to Faraday, the deposited metal Δm [g] is proportional to the transported charge, as the corresponding number of electrons is required for the reduction of the metallic cations on the surface.

$$\text{Faraday's law: } \Delta m = \frac{M \cdot Q}{z \cdot F}$$

Q : transported charge, $Q = I \cdot t$ (A s)

z : charge number of the metallic cation

F : Faraday constant

M : atomic weight of the coating metal

In other words, the current density i is a direct measure of the deposition rate, and a first approximation to the deposition rates can be made from this value. Real deposition rates are, however, reduced for example, by heat losses and/or secondary reactions [5]. In the interest of a better understanding, a first examination should be made of the processes that take place on simple electrodes (metal/electrolyte). For the electrochemical equilibrium potential E_H of a simple electrode, the cathodic partial current I_K for the metal deposition ($\text{Me} \rightarrow \text{Me}^{z+} + z e^-$) and the anodic partial current for the dissolution of the metal I_A ($\text{Me}^{z+} + z e^- \rightarrow \text{Me}$) are equal. In relation to the surface A , they correspond to the exchange current density $i_0 = i_A = i_K$.

$$\text{Exchange current density } i_0: \quad i_0 = \frac{Q}{A \cdot t} = \frac{\Delta m}{A \cdot t} \cdot \frac{z \cdot F}{M} = \frac{\Delta h}{t} \cdot \frac{z \cdot F \cdot \rho}{M}$$

A : coated area (cm^2)

t : duration of deposition (s)

m : mass of the deposited coating metal

Δh : coating thickness (mm)

ρ : density of the coating metal (g cm^{-3})

In a current-bearing electrode, the equilibrium potential E_H changes as a function of the current density i to the work potential E . The difference is referred to as the overpotential η :

$$\text{Overpotential } \eta \quad \eta = E - E_H$$

The overpotential η is the result of reaction inhibition at the metal/electrolyte phase boundary. This reaction inhibition can be described as a resistance to the exchange of charge carriers (polarization resistance). The equilibrium of the double

layer is disturbed by the fact that one of the partial reactions I_A or I_K is inhibited. The causes of this are:

- **Cross-over overpotential:** The reaction inhibition due to the cross-over of charge carriers arises as a consequence of the field present on the surface of the metal.
- **Diffusion overpotential:** The transport of ions or molecules in the electrolyte to or from the electrode determines the velocity, that is, the availability of the reactants and the conductivity of the electrolyte.
- **Concentration overpotential:** Due to the consumption of a reaction partner, changes in concentration result before the electrode.

For $\eta > 0$, the anodic partial current will predominate, and for $\eta < 0$ the cathodic partial current will predominate. The cathodic and anodic partial reactions therefore take place with finite velocity only when E is more positive or more negative than E_H (Figure 6.64). Assuming a cross-over overpotential η_D , the anodic dissolution of the metal (anodic partial current density i_A) and the cathodic metal deposition (cathodic partial current density i_K) can then be mathematically described in terms of the following exponential function [64]:

$$\text{Partial current densities } i_A, i_K : i_A = i_0 \cdot e^{\frac{\alpha \cdot z \cdot F}{R \cdot T} \eta_D} \quad \text{and} \quad i_K = i_0 \cdot e^{-\frac{(1-\alpha) \cdot z \cdot F}{R \cdot T} \eta_D}$$

i_0 : exchange current density at the equilibrium potential

η_D : cross-over overpotential (V)

α : symmetry factor, between 0 and 1

z : charge number

F : Faraday constant

R : universal gas constant

T : temperature (K)

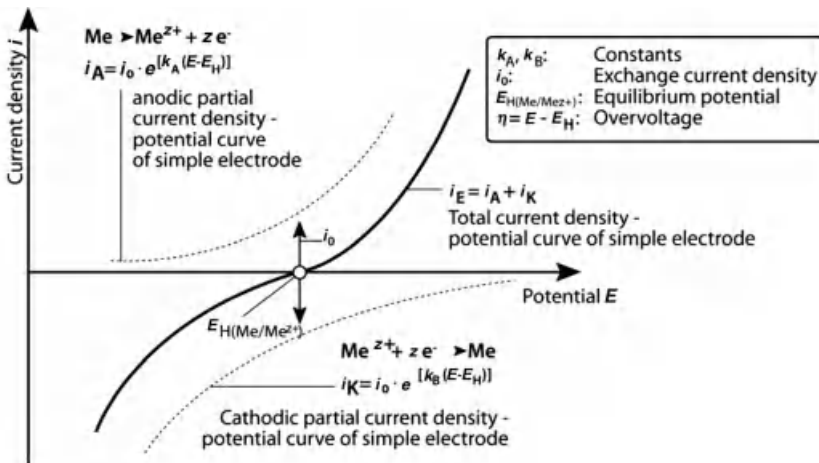


Figure 6.64 Current density–potential curve for a simple electrode.

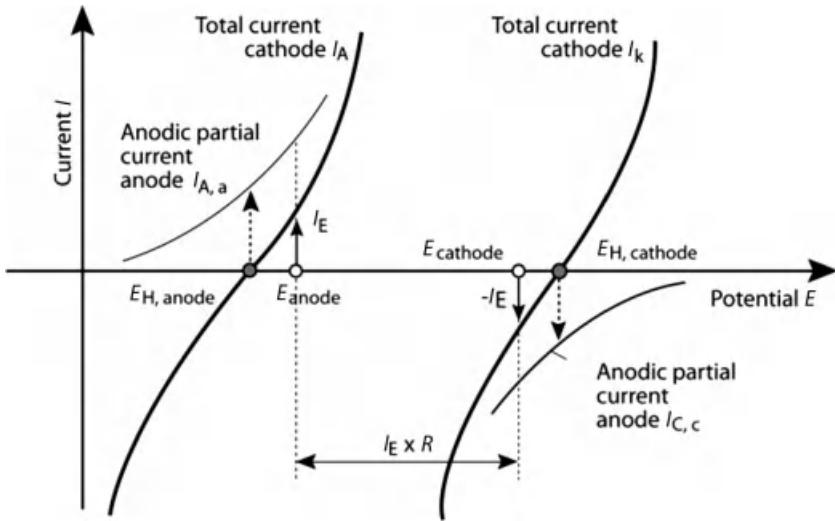


Figure 6.65 Current–potential relationship for an electrochemical element [62].

In a voltaic cell with two electrodes connected by a conductive path, the overpotentials of the simple electrodes are superimposed to a summed effect, referred to as *polarization*. The current intensity of the voltaic cell I_E is then a function of the potential differences and the polarization resistances of the simple electrodes (reaction inhibition) and the resistance of the electron conductor and the electrolyte. As a result of the potential difference ΔE between the anode and the cathode, the elementary current I_E flows via the resistance R of the electrolyte and polarizes the anode and cathode (Figure 6.65). With additional externally applied polarization, it is possible to regulate I_E . I_E can be measured.

$$\text{Polarization resistances : } R_A \equiv \frac{E_{\text{Anode}}(I_E) - E_{H,\text{Anode}}}{I_E}$$

$$\text{and } R_K \equiv \frac{E_{\text{Cathode}}(-I_E) - E_{H,\text{Cathode}}}{-I_E}$$

$$\text{Elementary current } I_E : I_E = \frac{E_{H,\text{Cathode}} - E_{H,\text{Anode}}}{R + R_A + R_K}$$

As a rule, theoretical predictions of the current density value for a given polarization are not possible. Altogether impossible is the determination of the expected current densities, which represent a direct measure of the metal deposition rate, from the equilibrium potentials [61, 62]. The relationship between potential and current density can be only empirically determined. The measured current density–potential curves represent the sum of the curves for the anodic and cathodic partial reactions taking place in an electrochemical element (Figure 6.66).

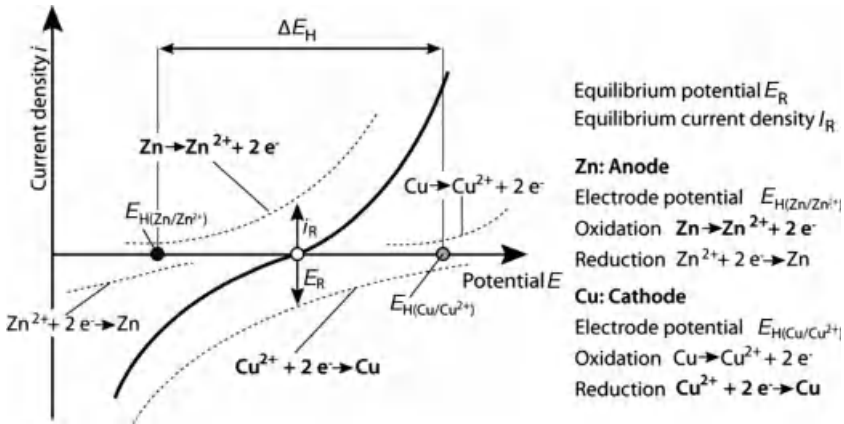


Figure 6.66 Partial current density–potential curve and total current density–potential curve for the Daniell element.

6.2.5.3 Electroplating

For electrochemical metal deposition with an externally applied current, the electron current is additionally supplied from an external current source, permitting influence over the direction of the reaction and thus over the required metal deposition [4, 53]. The growth of the coating layer can be predetermined in respect of rate, nucleation, morphology, and composition. Besides DC current sources, pulsed current techniques are also employed. With unipolar pulses, the current is switched cathodically, and consists of simple or DC-superimposed square-wave pulses. Alternate switching of the current to the cathodic or anodic region (bipolar pulsing) causes the layer to be deposited periodically, while in-between the coating is partly soluted again at the anode. With pulsed processes, it is possible to deposit multilayer coatings with different layer properties, graded coatings, and also multilayer coatings of different materials from an electrolyte. The metal ions for the formation of the coating are made available either by the dissolution of an anode or by the electrolyte [5]. The component to be coated is switched as the cathode, and the reduction of the metal ions takes place here. The required electrons are produced by oxidation at the anode (Figure 6.67).

A distinction can be made between oxidation processes taking place on:

- *Soluble anodes* : Cu, Zn, Ni, Ag
oxidation of the metal $Me \rightarrow Me^{z+} + ze^-$
- *Inert anodes* : Pt, stainless steel, Pb, graphite
- evolution of oxygen $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$
- oxidation of non-complex anions $2Cl^- \rightarrow Cl_2 + 2e^-$
- oxidation of complex anions $[Sn(OH)_4]^{2-} + 2OH^- \rightarrow [Sn(OH)_6]^{2-} + 2e^-$

Due to the process technological characteristics of electroplating, the following prerequisites must be satisfied in order to obtain coatings of optimal quality. The

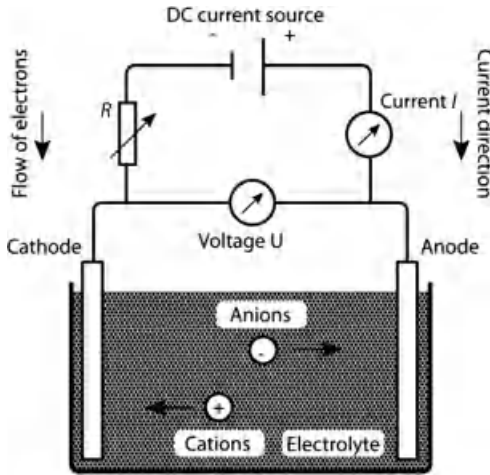


Figure 6.67 Principle of the electrochemical metal deposition process with external DC current source.

first prerequisite requires that the surfaces to be electroplated must be electrically conductive. When this is not the case, they can then be rendered electrically conductive by applying a finish coating containing silver or graphite or by the prior chemical deposition of a metal layer. The second prerequisite requires that the geometry of the components to be coated is amenable to coating. Here, the shape of the tools is important, as the scattering power of the electrolyte imposes certain limits (Figure 6.68). An unusually prominent profiling or overlapping and turn-downs result in only very thin and irregular coatings or, under certain conditions, deposition may be entirely prevented, even when auxiliary anodes are used. A design of the component to be coated which is suitable for electroplating can influence the success and the quality of the coating process [4].

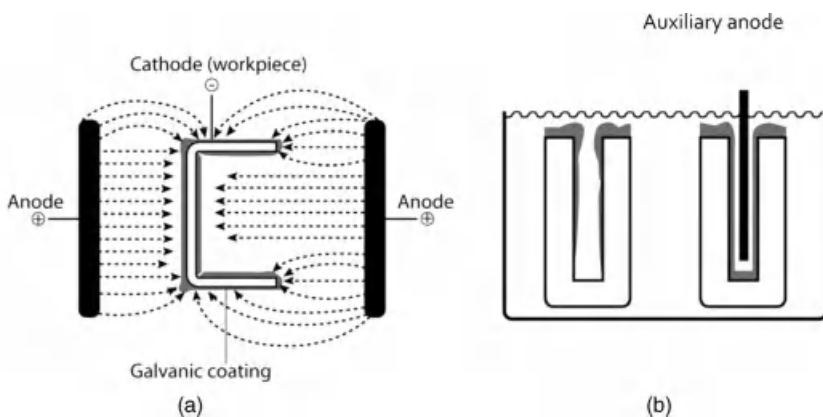


Figure 6.68 (a) Influence of the current density distribution on the coating thickness of electroplated coatings; (b) Counter-measure utilizing auxiliary anodes [64].

As a rule, electroplating plants is comprised of a series of several baths, in which the process steps for coating are carried out sequentially (Figure 6.70). This can include the following process steps:

- cleaning
- etching
- activating
- pre-coating (without externally applied current)
- electrolytic coating
- post-processing

The work piece to be coated passes through all of the process steps in a carrier container, through which the current is simultaneously fed to the tool. Most types of electroplating plants can be distinguished in terms of their degree of automation and their suitability for mass production. The different designs of electroplating systems are illustrated in Figure 6.69.

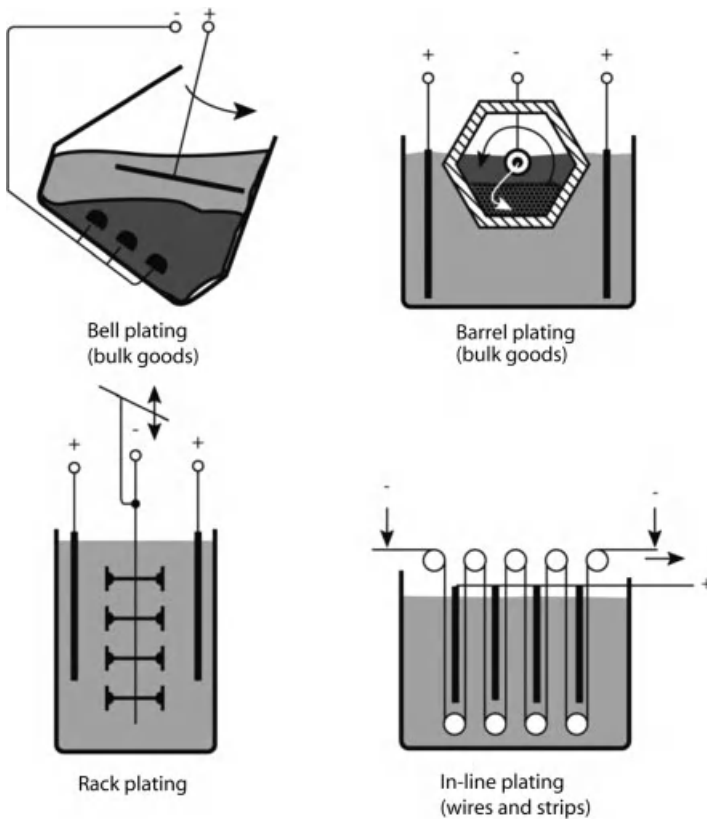


Figure 6.69 Designs of electroplating equipment [5].



Figure 6.70 Fully automated electroplating unit for rack parts or barrel goods with continuous bath analysis and treatment steps, such as filtration. Illustration courtesy of Carl Dittmann GmbH & Co KG.

6.2.5.4 Chemical Deposition

With chemical metal deposition (metal deposition without an external current source), both oxidation and reduction take place on the work piece surface [4]. With chemical coating processes, metal deposition is made possible by ion-exchange processes, by contact of the base metal with a less-noble contact metal (contact process), or by the reduction process. With dipping and contact processes, electrically conductive, non-noble base metals are coated with more noble metals; the driving force for this reaction is the difference in standard potentials of the metals. As deposition of the coating can take place only until the work piece is completely coated, the possibilities for varying the coating thickness are severely limited. However, unfavorable geometries, such as bores and sharp edges, can be coated using this approach. In addition, with help from the reduction process, electrically non-conductive substrates can also be coated or, by utilizing autocatalytic reactions, metals can be coated with layers of the same metal.

Ion-Exchange Processes (Dipping Processes) The prerequisite for the formation of a coating on a component with the ion-exchange process is that the metal to be coated possesses a lower potential in the metal electrochemical series, and is therefore a less-noble metal than the metal to be deposited (more-noble metal). The metal to be deposited must be present in ionized form in the electrolyte. The driving force for this process is the potential difference between the electrolyte solution and the soluting metal. Figure 6.71 shows the example of copper plating iron with the dipping process, with the relevant reaction equations. Dipping the iron rod into the electrolyte (here, the copper(II) sulfate solution) initiates the anodic dissolution (oxidation) of the iron rod. The more-noble metal ions (Cu^{2+}) present in the electrolyte are reduced on the

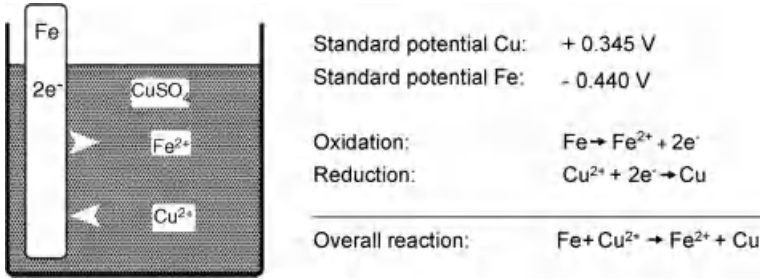


Figure 6.71 Deposition by the dipping process: Iron rod in a copper(II) sulfate solution.

surface of the work piece by the electrons that are set free. The reaction occurring will stop as soon as a fully contiguous copper layer has formed on the iron rod, and no further Fe^{2+} metal ions can enter the solution; hence, no further electrons are produced for the reduction of the Cu^{2+} ions. Consequently, the coating thickness which can be achieved is severely limited.

Contact Processes The contact process, which is an extension of the ion-exchange process, is used when the work piece to be coated is not sufficiently less-noble than the coating metal; this means that the anodic partial reaction cannot take place autonomously, and deposition cannot take place. The arrangement of the equipment is shown schematically in Figure 6.72. In addition to the work piece to be coated, another metal – the contact metal – is suspended in the electrolyte solution and connected electrically to the work piece (the contact metal must be less-noble than the work piece). During the deposition process, both the work piece and the contact metal are dissolved, the anodic partial reaction taking place more intensively with the latter. The contact metal supplies electrons to the work piece to be coated via external contact, thus enhancing the excess of electrons on the work piece. The ions of the metal to be deposited are reduced on both the work piece and the contact metal, so as

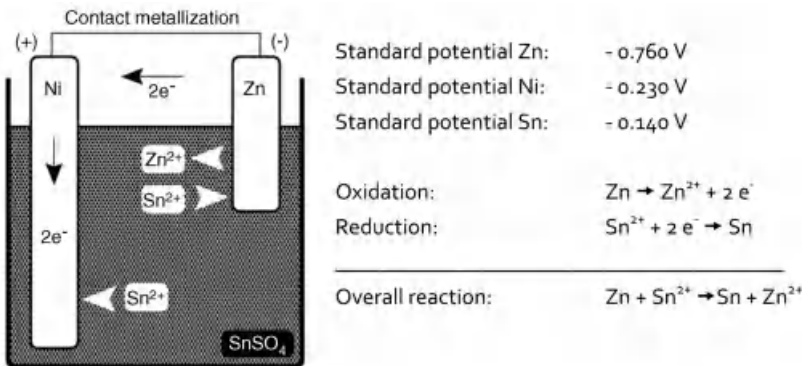


Figure 6.72 Contact deposition: Nickel rod in a tin sulfate solution with zinc contact metal.

to produce a metallic coating. The pronounced excess of electrons on the work piece brings about a vastly greater deposition rate, and also leads to thicker coatings on the work piece. The metal deposition process ceases as soon as both metals are contiguously coated.

Reduction Processes For metal deposition using a reducing agent, an alternative electrochemical process takes place, other than the ion-exchange and contact processes described above. In this case, a suitable reducing agent is added to the electrolyte solution in order to make the electrons available that are needed for the reduction of the metal ions in the electrolyte solution. As a prerequisite, the potential of the reducing agent must be less noble than that of the metal to be deposited. In order to prevent electron exchange between the metal ions and the reducing agent in the liquid phase, complexing agents are added to the electrolyte. The reducing agent sets the electrons free to the surface of the work piece, and these are then taken up by the cations of the metal to be deposited. The work piece surface thus has the function of an electron-transfer medium, and also functions as a catalyzer for the electrochemical process (Figure 6.73). In order that the deposition process is maintained, the coating being formed must also be catalytically effective. In fact, the deposition process will be maintained as long as the reducing agent and the other required electrolyte components are present in sufficient amounts [65]. Electrically non-conductive substrates can be activated by seeding with catalytically effective metals (e.g., Pd). Examples of the reducing agents used include sodium hypophosphite (NaH_2PO_2) or sodium borohydride (NaBH_4), for the deposition of nickel and cobalt, or formaldehyde (HCHO) for the deposition of copper and silver [65].

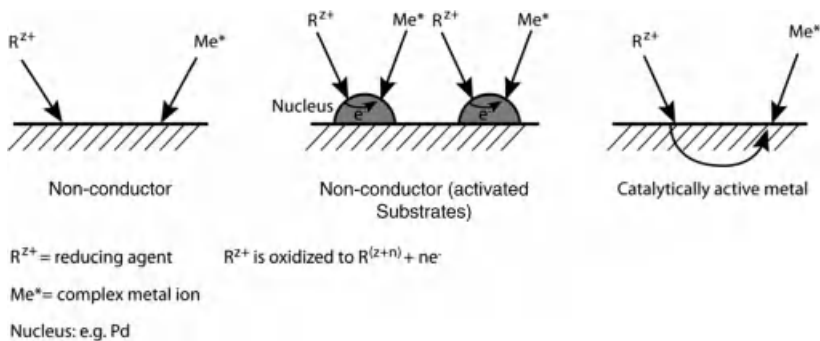
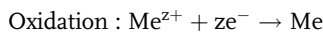
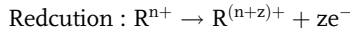


Figure 6.73 Variants for the transfer of electrons to substrate surfaces [5].

Table 6.14 Typical electrochemical metal deposition coating systems for surface protection.

Wear protection	Reduction of friction	Corrosion protection
Hard chromium plating	Silver plating	Zinc plating
Chemical nickel plating	Nickel dispersion plating	Zn alloys (ZnNi, ZnCo, ZnFe)
Dispersion plating (Hard nickel plating)		Nickel plating Chemical nickel plating

6.2.5.5 Coating Systems for Electrochemical Metal Deposition

Although electrochemical metal deposition enables the deposition of a great number of metals, these systems are of technological importance only for the following metals: aluminum, chromium, cobalt, nickel, copper, zinc, silver, cadmium, nickel-cadmium, tin, and lead. The most important coating systems for surface protection are listed in Table 6.14.

Chromium Plating Chromium platings are deposited electrochemically, by employing an external current source. Pretreatment of the components to be coated consists of degreasing and, if required, etching, and the aid of a wrinkling bath, the composition of which is identical to that of the electrolytes for electroplating (Table 6.15). The substrates are poled as the anode, and then wrinkled by dissolution of the surface. Plating takes place after transfer to the chromium plating bath, in which the component is cathodically plated (Figure 6.74).

The “classical” chromium bath is based on the patent [66] of 1920, which was further developed for the Elektro-Chrom-GmbH in Berlin. This second patent [67], from 1924, is regarded as the key patent for chromium plating. Accordingly, a chromium electrolyte is comprised of about 250 g CrO₃ with the addition of 1% (2.5 g l⁻¹) sulfuric acid as catalyzer. Chromium(VI) oxide, and also chromium

Table 6.15 Technologically important chromium electrolytes for electroplating [5].

Electrolyte components	Temperature deposition rate	Anode material	Typical electrolytic feature
H ₂ CrO ₄ : 250–400 g l ⁻¹ H ₂ SO ₄ : 3.5–4 g l ⁻¹ (conc.)	38–42 °C 10–20 A dm ⁻²		Plating quality depends strongly on temperature and current density, cooling required! Hard chromium: Microcracks
H ₂ CrO ₄ : 200–450 g l ⁻¹ HF: 0.8–1.6 g l ⁻¹ (or corresponding NaF mass)	30–50 °C ca. 3 A dm ⁻²	Hard lead	Typical cold chromium plating electrolyte
H ₂ CrO ₄ : 150–450 g l ⁻¹ H ₂ SiF ₆ : 0.3–3 g l ⁻¹ H ₂ SO ₄ : 0.35–1 g l ⁻¹ (conc.)	20–22 °C ca. 3 A dm ⁻²	Hard lead	Hard chromium plating electrolyte

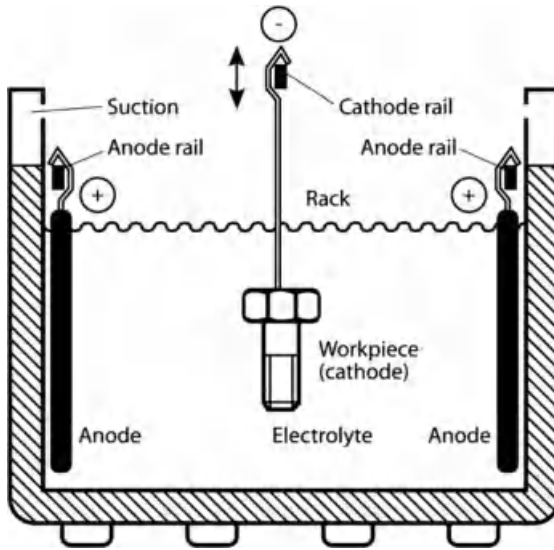


Figure 6.74 Sketch illustrating the principle of electrochemical metal deposition [5].

trioxide (CrO_3), easily dissolves in water to form chromic acid, H_2CrO_4 . For a current density of $i = 50 \text{ A dm}^{-2}$, the efficiency is around $\eta = 18\%$; that is, 82% of the current produces hydrogen. With the same electrolyte, in high-speed processes, a greater than 50% current yield is achieved, although the electrolyte must be quickly moved. Piston rods for shock absorbers in the automotive industry are, for example, coated in platinum tubes at more than 1000 A dm^{-2} in only a few seconds. In spite of the further development of electrolytes, chromium deposition rarely achieves efficiencies in excess of 30%.

Whilst the mechanism of chromium deposition has not yet been entirely explained, the process can be described in terms of its principal features [68, 69]:

- Following the dissolution of CrO_3 , a state of equilibrium develops in the electrolyte between chromate ions and condensed higher polychromate ions, such as di-, tri-, and tetrachromate. For the usual concentrations of $250 \text{ g l}^{-1} \text{ CrO}_3$ and a pH value of 0, the equilibrium favors the polychromates. When the tool is dipped in the electrolyte, a passive layer of different chromium oxides is initially formed which is both electron- and ion-conductive, acts as an ion-exchange mechanism, and also represents a diaphragm. The reduction of polychromates to Cr^{3+} takes place on the surface of this passive layer. In this case, a multistage mechanism must be assumed. The resulting trivalent chromium is not present in the form of a hydrated complex, the dehydration of which would represent an energy-consuming step, but instead forms a complex with the anions of the foreign acid. The deposition of chromium without foreign acid is not possible. The Cr(III) complex formed is transported by the electrolyte and oxidized at the anode to Cr(VI) , resulting in a state of equilibrium in the electrolyte.

- The passive layer then transports the Cr(III) to the cathode surface, where the multistage reduction to chromium takes place with the evolution of hydrogen, which is also taken up by the coating. This is an important reason why the properties of chromium electroplatings differ from those of metallurgically produced coatings. If the passive layer did not function as a diaphragm, only hydrogen would evolve at the cathode, and Cr(VI) would be reduced to Cr(III).

Insoluble lead alloys serve as anodes, although in modern systems platinum-plated titanium has replaced the lead anodes in order to prevent the creation of toxic lead slurries. The use of anodes of titanium-surrounded copper with platinum-plated titanium surfaces is particularly advantageous for chromium plating in sulfuric acid-based electrolytes. Increasingly strict environmental regulations and expensive waste disposal continue to demand processes that allow more environmentally compatible hard and gilded chromium plating in fluoride-free electrolytes.

The concept of “hard” chromium is misleading, as it gives the impression that hard chromium platings are harder than gilded chromium platings. In reality, both types of plating are equally hard, but differ in their thickness. Hard chromium [70] describes chromium platings with a thickness of $>1\ \mu\text{m}$ deposited directly onto the substrates [65]. Hard chromium platings can be machined to requirement using a follow-on grinding process [71]. Thinner coatings of $0.2\text{--}0.5\ \mu\text{m}$ are described as “gilded” chromium platings; these are preferable, for example, for steel substrates as a finishing layer following copper or nickel plating. In this case, the gloss of the chromium finishing will depend on the underlying nickel plating.

The coatings can be deposited with a thickness of up to several millimeters, with the usual coatings in the range of 1 to $300\ \mu\text{m}$ (Figure 6.75). Thicker hard chromium coatings of $\gg 1\ \text{mm}$ find application for example, on printing cylinders or feed rollers in the paper industry. As these coatings show a brittle behavior, a chromium coating which is not too thick is recommended, if the component is to be subjected to impact loads. According to the conditions for deposition, the hardness of the chromium coating is $800\text{--}1000\ \text{HV}$. Hard chromium coatings can be utilized at temperatures of up to $450\ ^\circ\text{C}$, without significantly impairing the coating properties, but from approximately $600\ ^\circ\text{C}$ oxidation begins to take place. Electroplated hard chromium coatings show a characteristic micro-crack structure (Figure 6.76). The formation of these cracks is closely related to out-gassing of the hydrogen evolved during the deposition process, as a proportion of the hydrogen is temporarily incorporated in the form of chromium hydride in the chromium coating. The subsequent decomposition of the chromium hydride causes a shrinking of the chromium plating, and the resulting stresses lead to the cracking. The cracking of chromium coatings makes it clear that, in spite of the excellent properties of chromium, a gilded chromium plating alone does not provide good corrosion protection. Rather, corrosion protection is provided only in conjunction with suitable intermediate layers (mostly nickel or copper and nickel). Hard chromium platings without an intermediate layer should possess a thickness of at least $25\text{--}50\ \mu\text{m}$, in order to ensure that any cracks that arise do not reach the base metal [65, 70]. For certain special cases, however, such a crack structure may be advantageous, for example by improving the adhesion of an oil film.

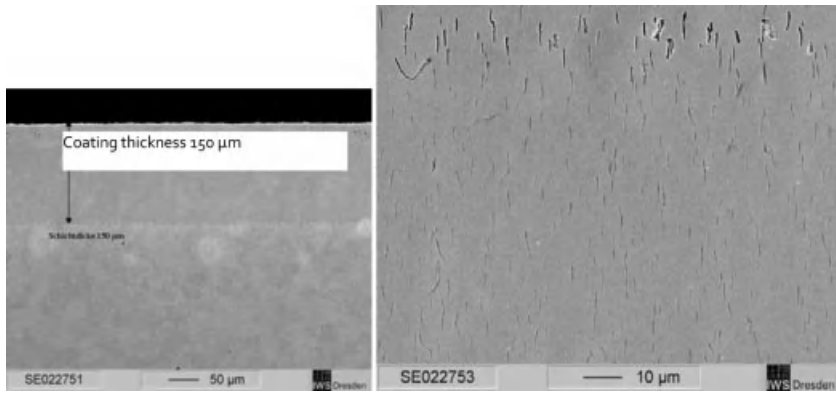


Figure 6.75 Hard chromium-plating for corrosion protection. REM images of polished cross-sections. Illustration courtesy of Pallas GmbH, Würselen.

Nickel Plating Nickel plating is employed preferentially for deposition onto components of steel, zinc die casting, brass, or aluminum. Most nickel electrolytes achieve an efficiency of $\eta > 95\%$, which means that 95% of the current applied is used for deposition of the metal. Nickel can be deposited either electroplating or in the

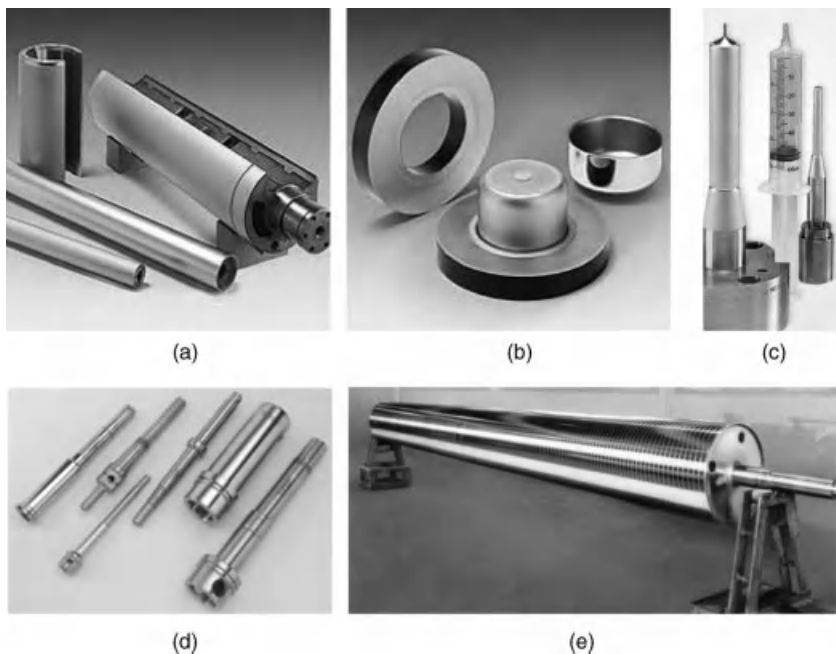


Figure 6.76 Examples of applications for hard chromium plating. (a) Printing cylinders; (b) Forming tools; (c) Injection-molding forms; (d) Drive shafts; (e) Paper roll. Illustrations courtesy of: panels (a–c) Topochrom GmbH; panel (d) JFD Pumps Rotors Oy, FI; panel (e) Strötzel Oberflächentechnik GmbH & Co. KG.

Table 6.16 Technologically important nickel electrolytes for electro plating [5].

Electrolyte component		Temperature (°C)	pH value	Anode material
NiSO ₄ :	300–350 g l ⁻¹	20–70	pH 4.0–4.5	Ni ribbon
NaCl:	20–25 g l ⁻¹ (conducting salt)			
H ₃ BO ₃ :	30–40 g l ⁻¹ (buffer)			
Ni[H ₂ N-SO ₃] ₂ :	300–400 g l ⁻¹	30–50	pH 3.0–4.0	Sulfur-depolarized electrolyte
NiCl ₂ :	10 g l ⁻¹			
H ₃ BO ₃ :	30–40 g l ⁻¹			

absence of an external current source. Nickel is resistant to atmospheric corrosion, to many dilute acids (e.g., nitric acid), and also to concentrated sulfuric acid as well as many bases and ammonia. Often, nickel platings are partly combined with copper plating and applied as an additional corrosion protection under chromium coatings.

Electroplated nickel coatings are among the most frequently produced, and serve mainly for corrosion protection and decorative purposes. For tribological applications, thick nickel plating (hard nickel plating) and nickel dispersion plating find application, although for this purpose nickel coatings of about 200–3000 μm are required. The first report of electrolytes for nickel plating on the basis of nickel sulfate was made in 1840, although these electrolytes were unsuitable for surface finishing. Some years later, in 1916, O.P. Watts invented the Watts nickel electrolyte which, to this day, still serves as the basis for most nickel electrolytes. The principal supplier of metal is nickel sulfate (NiSO₄), while nickel chloride, due to its chloride content, enhances dissolution of the anode. Boric acid (H₃BO₃) may serve as a buffer material, maintaining the pH value within a certain range. Two typical nickel electrolytes, together with their relevant process parameters, are detailed in Table 6.16.

Chemical nickel coatings represent the best-known examples of chemical deposition, with nickel–phosphorus alloys typically being deposited at the catalytically effective surfaces. The main reaction partner for chemical nickel deposition is sodium hypophosphite, NaH₂PO₂ (less frequently, NaBH₄) (Table 6.17). Secondary reactions lead to the formation of phosphorus (or boron), which is incorporated into the coating as a phosphide (or boride) and thus also contributes to determining the coating properties. Chemical nickel coatings are essentially NiP coatings containing 2–15 wt% phosphorus, while amorphous coatings have a P content of >10 wt%, and crystalline coatings a P content of <8 wt%. The hardness of the deposited coatings can be greatly improved by heat treatment, such that hardnesses of around 1000 HV can be achieved. The usual coating thicknesses are in the range of 0.5 to 50 μm. Similar to the situation with electrolytically deposited nickel coatings, dispersion coatings are also possible with this type of deposition. Nickel dispersion coatings can achieve hardnesses of up to 1200 HV following heat treatment, and they also demonstrate good wear behavior [65].

Table 6.17 Technologically important nickel electrolytes for chemical deposition [5].

Electrolyte component	Temperature	Reaction
	deposition rate	
NiSO ₄ ·7 H ₂ O: 20–30 g l ⁻¹	82–84 °C	Ni ²⁺ + 2 e ⁻ → Ni
NaH ₂ PO ₂ ·H ₂ O: 10–20 g l ⁻¹	ca. 15 μm h ⁻¹	[H ₂ PO ₂] ⁻ + H ₂ O → [H ₂ PO ₃] ₋ + 2 H ⁺ + 2 e ⁻
Acetic acid: (with NaOH to pH 4.5)	10 g l ⁻¹	Secondary reaction: 2 H ⁺ + 2 e ⁻ → H ₂
Thiourea: 0.7 mg l ⁻¹		[H ₂ PO ₂] ⁻ + e ⁻ → P + 2 OH ⁻ Incorporation of about 10 wt% P into the coating (NiP)
NiSO ₄ ·7 H ₂ O: 20 g l ⁻¹	75–78 °C	Ni ²⁺ + 2 e ⁻ → Ni
NaH ₂ PO ₂ ·H ₂ O: 15 g l ⁻¹	ca. 3–5 μm h ⁻¹	[H ₂ PO ₂] ⁻ + H ₂ O → [H ₂ PO ₃] ₋ + 2 H ⁺ + 2 e ⁻
Lactic acid: 30 g l ⁻¹		Secondary reaction: 2 H ⁺ + 2 e ⁻ → H ₂
Propionic acid: 3 g l ⁻¹		[H ₂ PO ₂] ⁻ + e ⁻ → P + 2 OH ⁻
Pb(NO ₃) ₂ : 1 mg l ⁻¹ (with Na acetate to pH 4.0–5.0)		
NiSO ₄ ·7 H ₂ O: 20 g l ⁻¹	50–60 °C	Ni ²⁺ + 2 e ⁻ → Ni
NaH ₂ PO ₂ ·H ₂ O: 15 g l ⁻¹	ca. 5–8 μm h ⁻¹	[H ₂ PO ₂] ⁻ + H ₂ O → [H ₂ PO ₃] ₋ + 2 H ⁺ + 2 e ⁻
Citric acid: 15 g l ⁻¹		Secondary reaction: 2 H ⁺ + 2 e ⁻ → H ₂
Na ₂ B ₄ O ₇ ·10 H ₂ O: 15 g l ⁻¹ (with NaOH to pH 9.5)		[H ₂ PO ₂] ⁻ + e ⁻ → P + 2 OH ⁻ Incorporation of about 7 wt% P into the coating (NiP)

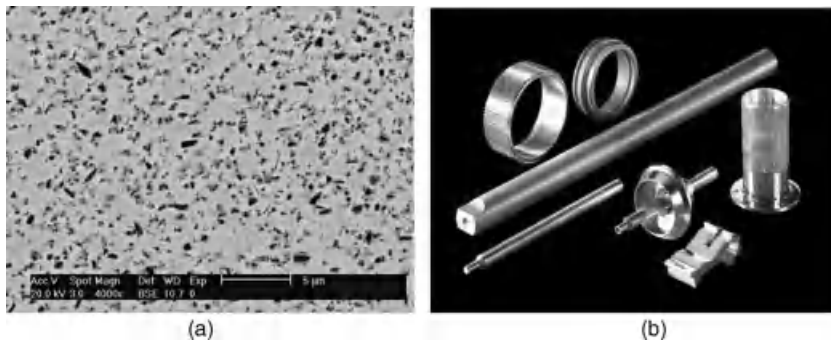


Figure 6.77 Dispersion coatings. (a) Au matrix with embedded diamond particles materials; (b) NiP matrix with embedded hard SiC, Si₃N₄, B₄C on components for the textile industry. Illustrations courtesy of: panel (a) Echem GmbH; panel (b) Gramm Technik GmbH.

Dispersion Coatings Due to the incorporation of hard material or solid lubricant particles, dispersion coatings are manufactured to a defined thickness (ca. 0.1–3 μm). The dispersant may be in the form of carbides (SiC, WC), nitrides (e.g., cubic BN), oxides (e.g., Al₂O₃), or even diamond (Table 6.18) (Figure 6.77). The fraction of the incorporated dispersant in electrolytically or chemically deposited metal coatings is 5–10 wt% or 20–30 vol%. The incorporation of particles into the

Table 6.18 Deposition by electrochemical dispersion coatings [64].

Matrix	Oxide	Carbide	Sulfide	Sulfate	Other
Ag	Al ₂ O ₃	SiC			
Au	Al ₂ O ₃	SiC			Diamond, TiN
Cd	Fe oxides	SiC, WC			
Co	Different oxides				Mica
Cr	Al ₂ O ₃				
Cu	Al ₂ O ₃ , CeO ₂ , TiO ₂ , ZrO ₂	SiC, WC, ZrC	MoS ₂	BaSO ₄ , SrSO ₄	Mica, graphite
Fe	Al ₂ O ₃ , Fe oxides	SiC, WC	MoS ₂		Mica
Brass		SiC			
Ni	Al ₂ O ₃ , BeO ₂ , CdO, CeO ₂ , Fe oxides, MgO, SiO ₂ , ThO ₂ , TiO ₂ , ZrO ₂	SiC, VC, WC	MoS ₂	BaSO ₄	c-BN, PTFE, mica

metal matrix takes place during deposition of the metal from solutions of the metal salt, in which the solid substances are distributed in suspension form as homogeneously as possible by stirring, flow, pump transfer, or the injection of air. The positively charged particles migrate to the surface of the component as a result of electrophoretic motion. Due to van der Waals forces, the particles are adsorbed and enclosed in the growing layer, with the metal assuming the function of the matrix material. The dispersant, on the other hand, determines the tribological properties of the compound layer. In terms of bonding strength, it has been shown advantageous to first deposit pure nickel [4, 71].

Among the possible carbides, oxides, nitrides, and borides used as dispersants for nickel coatings, SiC has gained industrial importance. Nickel dispersion coatings can be deposited in uniform thicknesses, as with pure nickel coatings. The use of sulfamate electrolytes allows coating thicknesses of >1 mm, while the hardness of Ni + SiC dispersion coatings is about 550 HV.

6.2.6

Thermal Spraying

According to DIN EN 657, thermal spraying encompasses "...processes in which spray admixtures are supplied within or outside of the spray pistol and heated to the plastic or melted state" [72]. The initial attempts at applying metallic coating materials onto different substrate materials were carried out in 1880, at which time the liquid metal was propelled with the aid of a rotating drum onto the component surface. In 1882, the first patent application for lead spraying followed. This type of coating, however, bears little resemblance to the thermal spraying employed today. The first patent application for a thermal spraying process was made in 1909, under the number 49 278, by the Swiss engineer Max Ulrich Schoop with the Swiss Office of Intellectual Property, and can be viewed as the basis for today's thermal spraying

processes. In 1911, Schoop produced the first coating of lead and tin for corrosion protection, and shortly thereafter constructed the first wire flame-spraying system. Instrumental in this research into metal spraying and the development of wire and powder systems was an observation made while shooting with lead bullets. When lead bullets were fired in succession at a wall, they were pressed flat and not only adhered to the wall but also formed weld-like bonds with each other. On the basis of this observation, Schoop first developed stationary systems to manufacture such coatings and, consequently, spray pistols to make the process more flexible [73].

Since Schoop's first investigations, thermal spraying has been developed into a highly innovative and flexible coating technology, used in a wide range of applications. The properties of this technology also enable the use of either shaping processes or powder treatment, although with thermal spraying processes predominantly protective surface finishes are produced. Important areas of thermal spraying application include:

- Wear-resistant protective coatings and friction-reducing coatings for tribological systems in nearly all producing sectors.
- Corrosion protection coatings in the offshore area, for pumps, valves, and building constructions.
- High-temperature corrosion protection coatings and thermal barrier coatings for combustion engines (aircraft turbines, stationary gas turbines for power engineering, motor technology in the automotive industry).
- Biocompatible coatings for medical implants.
- Seal coatings in aircraft engines.

In 2007, the global market for thermal spraying totaled €6.1 billion, with the European Union, in second place, accounting for a turnover of €1.77 billion, behind North America (USA and Canada, €2.28 billion) [74]. In North America, the aviation and space sector dominates the thermal spraying area, whereas in Europe a vastly more uniform distribution among other industrial sectors (printing and paper industry, vehicle and ship building, general machine building, medical technology, etc.) is found. Among German-speaking countries there is a clear focus on tribological applications in almost all technical areas (Figure 6.78).

6.2.6.1 Principle of Thermal Spraying Processes

A number of different process variants exist for thermal spraying, all of which have a concentrated, high-energy heat source in common, into which the material to be sprayed is introduced, melted, surface-fused or heated and then, in the form of sprayed particles, propelled at high speed onto the surface of the substrate (Figure 6.79). On impacting on the surface, the particles are flattened and rapidly cooled, while their superposition results in the formation of a coating.

All thermal spraying processes require the availability of two types of energy to produce sprayed coatings, namely thermal and kinetic energy. Depending on the process variant, different process temperatures and particle velocities are achieved, which decisively characterize not only the coating process but also the properties of the coating. Accordingly, the coating material may be heated in a flame, a plasma, or

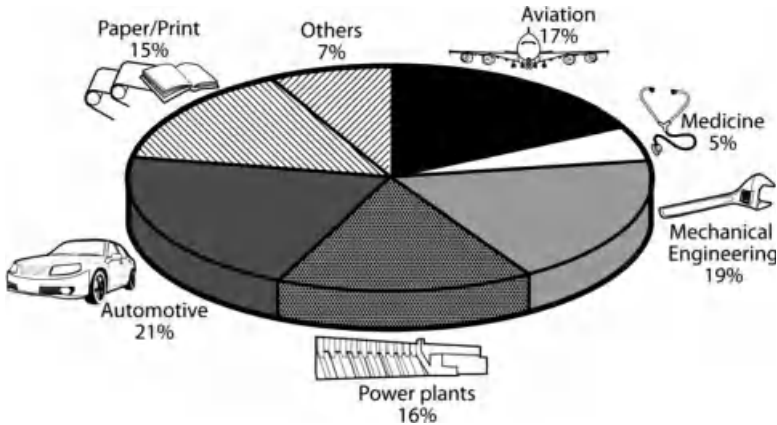


Figure 6.78 Market shares of thermal spraying processes in the German-speaking countries [74].

an electric arc or, in the case of metallic coatings, it may also be heated electrically. This results in the formation of fine droplets, which are initially accelerated in a gas flow and then propelled against the surface of the component to be coated. In general, the spray material is introduced as a wire or powder, and less frequently as a strand or rod. The kinetic energy that the process gas flow imparts to the powder particles is directly coupled to the particle velocity, and influences the density of the coating, the bonding strength itself, and the adhesive pull strength of the coating to the base material [75, 76].

Typical coating thicknesses for thermal-sprayed functional coatings range between 100 and 400 μm , but in individual cases may be up to 3 mm. It is important that the material to be coated (the feedstock) does not change significantly during the coating process – that is, no structural transformation takes place in the base material. A robot-guided spray device will enable a wide range of geometries to be created under minimal thermal loading of the work piece, with uniformly thick coatings [77]. Classical spraying processes have been designed for externally applied coatings whereas, for internal coatings, special rotating internal coating processes are currently available for cylinder diameters of $D \geq 40$ mm. In principle, virtually any

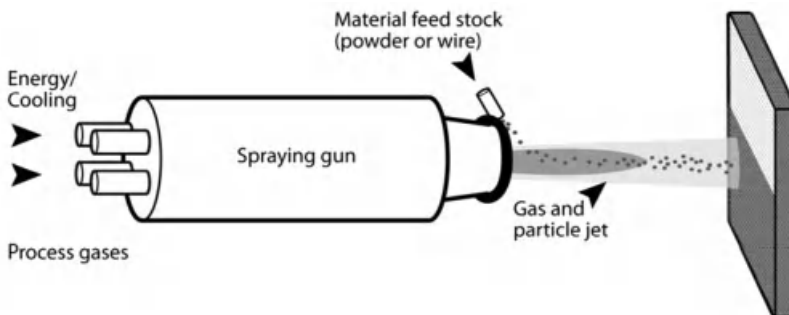


Figure 6.79 Sketch illustrating the principle of thermal spraying.

material that can be transformed by thermal coupling to a molten or ductile state can be utilized as the feedstock. Many different spraying processes have permitted the coating of virtually all technically interesting base materials with polymers, ceramics, and metals, as well as with mixtures thereof [73].

When the spraying is completed, the surface of the coating will be comparatively rough. Likewise, according to the process variant, the coatings may also be somewhat porous. The roughness values depend essentially on the size of the sprayed particles and their deformation behavior on impact; consequently, by using finer powder particle fractions the roughness values can be reduced. For most technical applications, the coatings are post-processed; in order to manufacture smooth surfaces, various cutting processes may be employed (primarily grinding and polishing), in addition to other processes such as turning or honing. Heat treatment can then be applied to improve the coating's properties, to improve its toughness values, and to compress and smooth the surfaces. Depending on the heat treatment process used, a metallurgical bond between the coating and the substrate material may lead to improved adhesion. For applications in corrosive media, sealing materials are used which ensure the sealing of porosities.

6.2.6.2 Formation of Coatings with Thermal Spraying

The process of coating formation with thermal spraying is determined by the successive build-up of the coating as a result of the impact and superposition of individual particles on the substrate surface. On impact, the molten or semi-molten particles are flattened, solidify, and form individual splats (plaques), the superposition of which leads to the formation of a laminar-structured, closed layer. An understanding of the flattening and solidifying process is essential when assessing the particle adhesion, the state of internal stress, and the physical properties of the resultant compound material. The flattening behavior of the particles is dependent on several factors [76, 78, 79]:

- The temperature, velocity, and angle of incidence of the particles, resulting from the spray parameters.
- The type of spray material (composition, form, size).
- The chemical, thermal, and topographical state of the substrate surface.
- The interaction between particles and base material, such as wetting behavior or heat transfer.

On impact with the substrate, the kinetic energy of the particles is transformed into deformation energy and thermal energy (Figure 6.80); this is followed by a sudden dissipation of heat to the substrate and the atmosphere. According to the material present in the spray admixture, the particle size and the thermo-physical properties, solidification times of between 10^{-8} and 10^{-4} s can be achieved [80]. These enormous cooling rates of the spray particles leads to the concept of a "rapid solidification process," but this frequently results in the formation of meta-stable phases. Metallic materials may be present in amorphous form, while ceramic materials may be present in typical high-temperature modifications of the phases [81, 82].

Depending on the viscosity and impact velocity, the tiny particles become detached and solidify in a corona surrounding the splats. The dependence of the thermal and

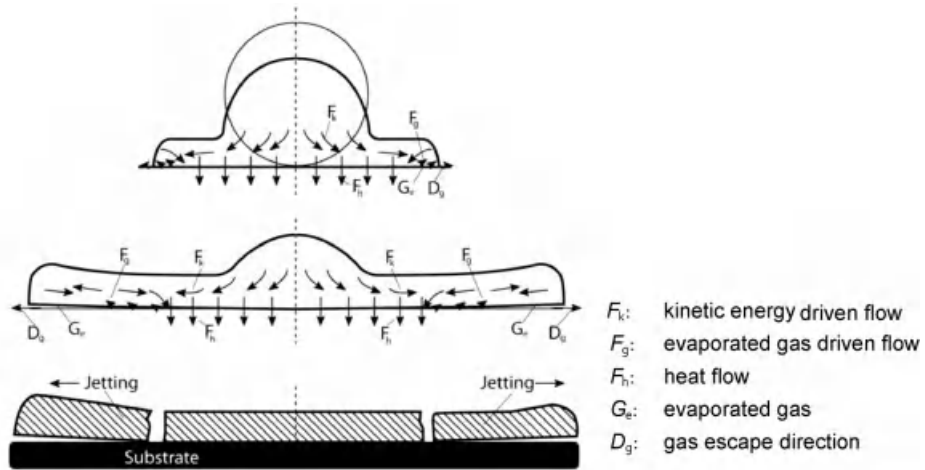


Figure 6.80 Schematic representation of the flattening behavior of an incident ceramic spray particle (here with ring formation) [83].

kinetic energy on the flattening behavior of the particles (after Voggenreiter) is shown schematically in Figure 6.81; this has a decisive influence on the microstructure of the resultant coating. Generally, the solidification process has already occurred before the next particle strikes; however, as the particles cool on the substrate surface, internal stresses develop due to the different thermo-mechanical behaviors of the superimposed lamella in the solidified spray particles. In ceramic coating systems, these stresses are relieved by the formation of micro-cracks, which run predominantly along the grain boundaries perpendicular to the surface of the substrate. In certain applications the micro-cracks are introduced intentionally, for example, to

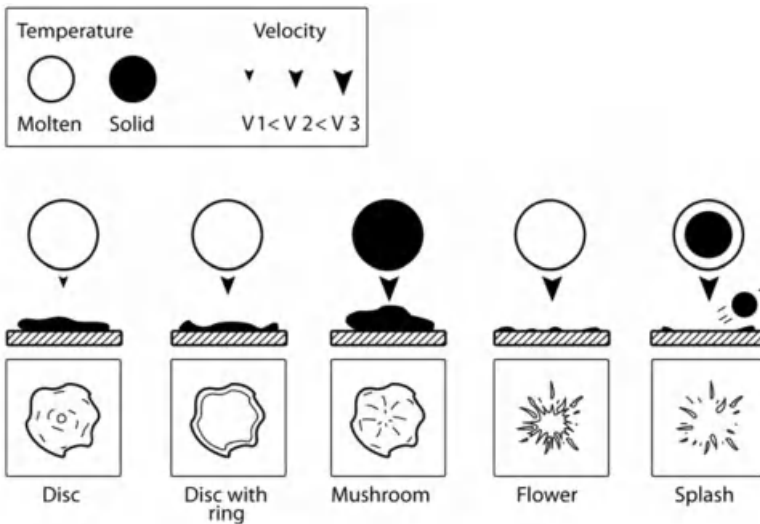


Figure 6.81 Dependence of particle flattening behavior on kinetic and thermal energy [84].

improve the thermal cycling behavior of coated turbine blades. In metallic coating systems, however, these stresses can usually be relieved by elasto-plastic forming processes.

Another phenomenon to be considered in the process of coating formation is the oxidation of metallic materials, and the reduction of ceramic materials. During the flight phase, due to their pronounced disposition to react in the molten state and the large surface-to-volume ratio of the particles, metallic particles (in particular) tend to oxidize. The point at which such oxidation occurs in spraying processes remains a matter of controversy in the literature, however; whereas some investigators have ruled out particle oxidation occurring during the airborne phase and have diagnosed and simulated oxidation phenomena only for the particle impact, others have found evidence for oxidation during the airborne phase also [85–88]. According to the size and path of flight of the particles, they may be either partly or completely oxidized, and incorporated into the coating with the impact of other particles. Any oxide skins present on the surface of the spray particles will be shattered on impact with the substrate and, with the radial propagation of the spray particles, incorporated into the coating as an inter-lamellar structure. The degree of oxidation of metallic particles influences not only the micro-hardness of the coating, but also its micro-structure. In addition to the vacuum spraying technique, a reduction of the process temperature and an increase in particle velocity have proved to comprise an effective method for the prevention of oxide inclusions. In particular, cold gas spraying yields excellent results in this situation.

According to application, widely different coating morphologies can be produced with thermal spraying (Figure 6.82). Thus, in combination with the virtually unlimited choice of material, thermal spraying offers the greatest variation range of all coating processes.

6.2.6.3 Bonding of Thermal Spraying Coatings

Bonding of the surface coating is of elementary importance for the fulfillment of technical requirements. With thermal spraying coatings, adhesion based on mechanical clamping is frequently described as the dominant bonding mechanism, but physical and metallurgical bonding mechanisms also play important roles here [89]. A model-based representation of the origin of coating adhesion for thermal spraying is shown in Figure 6.83, where the most important adhesion mechanisms are:

- **Mechanical clamping:** Owing to their momentum, the spray particles that strike the substrate surface, the molten particles, penetrate the uneven and undercut regions by capillary effects, where they are anchored form-locked following complete solidification. This mechanism can be further reinforced, when the molten material flows around roughness peaks on the surface; during solidification the clampings force-fit with these as a result of shrinkage stresses [77].
- **Welding:** Due to the heat transfer between the impinging particles and the base material, partial micro-welding can occur at the boundary layer.
- **Diffusion:** Bonding mechanisms based on the formation of a diffusion zone are found with thermal spraying coatings, particularly when follow-on heat treatment has been employed.

- **Adhesion:** With thermal spraying, the adhesion bonding mechanism (which is based on atomic interactions) is thought to play a far less important role. A distinction can be made here between *physisorption* and *chemisorption*.

Bonding is decisively influenced by the properties of the spray material and the substrate material, the condition of the substrate surface, and the spraying parameters [90–92]. Prior to the coating process, a mechanical pretreatment is usually performed whereby any grease and contamination residues are removed by shot-blasting. This also causes the surface to be roughened and freed from any firmly clinging contamination and oxide skins. This may lead, on the one hand, to a high surface energy, but on the other hand to a high lattice defect density (e.g., displacements, boundary layers, lattice deformations) and micro-cavities. Today, blasting with

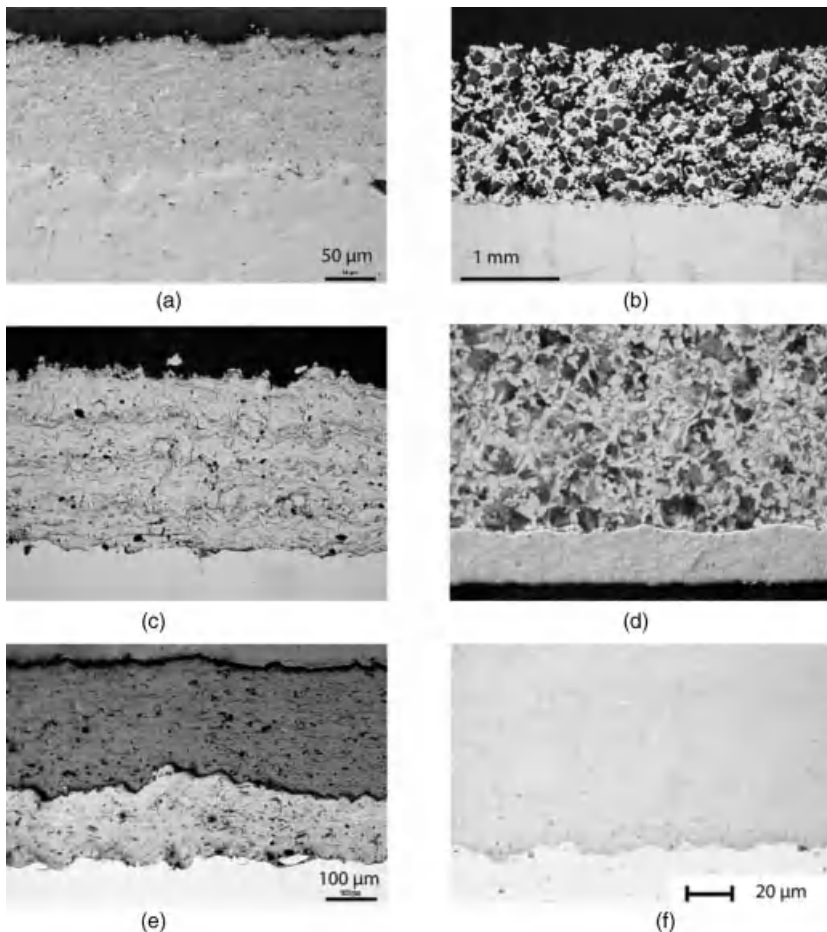


Figure 6.82 Selection of different coating morphologies for coatings produced with thermal spraying. (a) HVOF: hard-metal coating WC/Co; (b) APS: abrasion-resistant coating NiCrAl/bentonite; (c) LDS: Fe base core wire; (d) FS:

NiCrBSi inductively fused; (e) APS: Al bond coat + $\text{Al}_2\text{O}_3/\text{TiO}_2$; (f) CGS: Oxide-free copper coating. Illustrations courtesy of: panels (a)–(e) IOT, RWTH Aachen; panel (f) OBZ GmbH, Bad Krozingen.

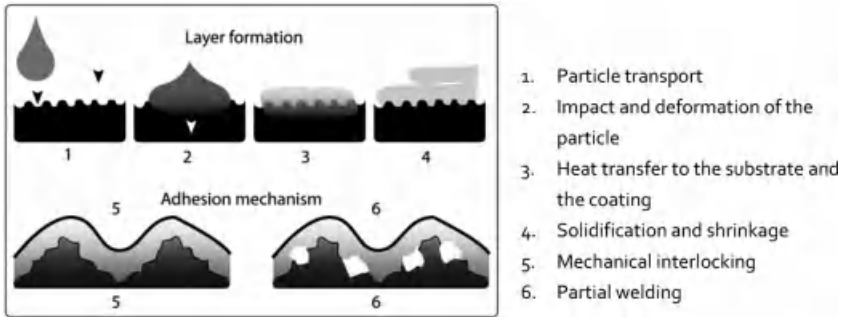


Figure 6.83 Model-based representation of the origin of coating adhesion for thermal spraying. Illustration courtesy of Advanced Coatings SA, Belgium.

either metallic (e.g., steel or cast iron) or ceramic (e.g., corundum or silicon carbide) shot is the most frequently used method for roughening. The effect of the shot on the substrate surface depends on several factors (such as the air pressure, nozzle size, blasting angle, hardness, and form, as well as the size and chemical composition of the steel casting), and must accordingly be matched to the required conditions. Following this process, it is necessary carefully to remove all shot residue from the surface of the substrate, in order not to impair the bonding between the coating and the substrate.

6.2.6.4 Thermal Spraying Processes

The classification of thermal spraying processes is in accordance with the method of introducing thermal energy (Figure 6.84). According to the particular process,

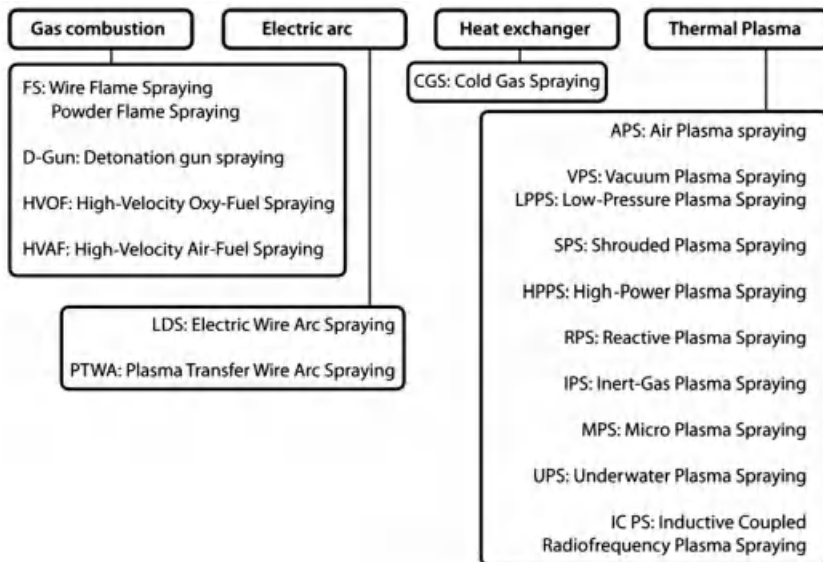


Figure 6.84 Thermal spraying processes.

Table 6.19 Gas supply for thermal spraying [93].

		Flame spraying	HVOF spraying	Plasma spraying	Cold gas spraying	Wire arc spraying
Acetylene, Ethine	C ₂ H ₂	•	•			
Ethene	C ₂ H ₄		•			
Propane	C ₃ H ₈	•	•			
Propylene	C ₃ H ₆	•	•			
Hydrogen	H ₂	•	•	•		
Carbon dioxide	CO ₂	•	•	•		
Oxygen	O ₂	•	•			
Helium	He			•	•	
Nitrogen	N ₂			•	•	•
Argon	Ar			•		
Kerosene			•			
Pressurized air		•	•	•	•	•

different process temperatures and particle velocities are obtained, which characterize the coating process and decisively influence the properties of the coating (structure, porosity, oxide content, etc.) The most widely used industrial processes are described in greater detail in the following subsections.

All thermal spraying processes require a supply of gas (Table 6.19), which assumes different functions depending on the particular process [93]:

- *Combustion gases* and *plasma gases* for the generation of the thermal energy required to produce molten or semi-molten spray material.
- *Coolant gases* for cooling the spray pistol, substrate and spray coating.
- *Carrier gases* for the transport of the spray particles.
- *Sputtering gases* for the sputtering of wires, rods or strands to be melted.
- *Shroud gases* for protecting the hot particle gas flow against the surrounding atmosphere.

Flame Spraying The utilization of a combustion gas flame as a source of thermal energy derives directly from the methods developed by Max Schoop. With flame spraying, the process energy is generated in the exothermic chemical reaction of a combustible gas (e.g., acetylene, hydrogen or propane) with oxygen. The feedstock can be in the form of either a wire or a powder, though rods or strands are also occasionally used. Due to the limited flame temperature (maximum 3160 °C for acetylene), the flame-spraying process is principally employed for metals, polymers and ceramics with low melting temperatures ($T_S < 2.500$ °C). The design of a flame-spraying burner is shown schematically in Figure 6.85. The comparatively low particle velocities attained (50 m s⁻¹ using powder materials and 200 m s⁻¹ using wire materials) at relatively high temperatures often lead to porous coatings, with a comparatively poor bonding of the coating. Furthermore, the long dwelling time of the particles in the flame due to the low particle velocities will result in a high degree

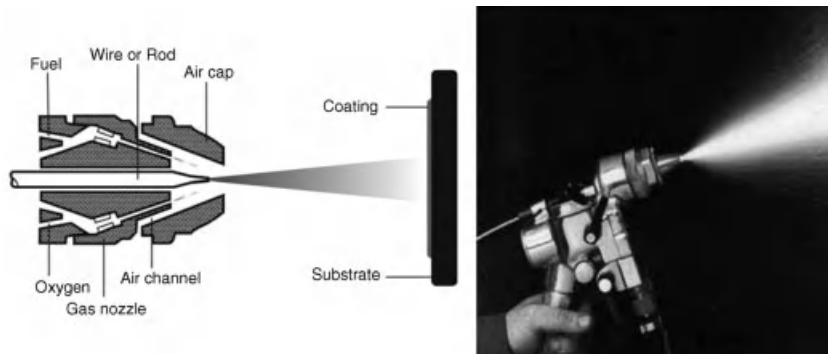


Figure 6.85 Schematic illustration of the design of a flame-spraying burner.

of oxidation. The advantage of flame spraying, on the other hand, is a high coating growth rate that enables the rapid coating of large surfaces. Moreover, coating can be performed on-site, using mobile, hand-held devices.

Among all spraying processes, flame spraying requires the least energy, and the consequent low investment costs for the system itself, the good mobility and the low operational costs have led to the widespread use of this process. However, when compared to the other processes described here, the use of flame spraying has declined considerably over the past 15–20 years, due mainly to the limited coating qualities that can be achieved. At present, the principal areas of use for flame spraying involve coatings that require a low hardness and a high degree of porosity (e.g., abrasible coatings in the compression stages of modern aircraft gas turbines), the processing of polymers, and coatings with self-flowing alloys. Of these applications, the latter represents the most widely used for flame spraying-produced coating systems. Typically, in a two-stage process, an alloy with self-flowing properties of type FeCrBSi or NiCrBSi is first sprayed onto the component, and then fused with an autogenous burner or inductive heating. The melting temperature is reached when the spraying alloy takes on a characteristic, mirror-like appearance (“wet shine”). As a result of the melting process, a particularly dense and homogeneous structure with excellent bonding is achieved. The self-flowing alloy can, in addition to borides precipitating from the alloy, be further reinforced with hard materials (e.g., Cr_3C_2 or WC) in order to obtain even better wear properties.

High-Velocity Flame Spraying The process-technical limits of classical flame spraying have led to the development of high-velocity oxy-fuel flame spraying (HVOF), a process in which a vastly higher level of kinetic energy is achieved with a low thermal energy. With high-velocity flame spraying, the combustion occurs at a higher pressure (5–15 bar), in an open combustion chamber.

The thermal energy of the combustion gases is transformed in a follow-on convergent-divergent nozzle (Laval nozzle), in part to kinetic energy (Figure 6.86). During the expansion of the gas flow in the Laval nozzle, a pronounced drop occurs in the gas flow pressure (in accordance with the laws of gas dynamics), resulting in a

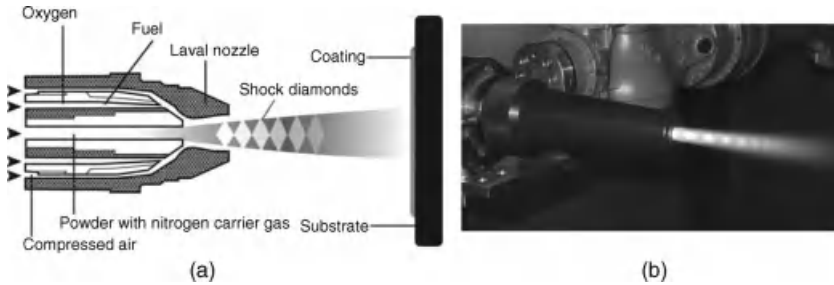


Figure 6.86 (a) Schematic representation of the high-velocity oxy-fuel flame-spraying (HVOF) burner design; (b) The unit in operation.

pressure of the order of the ambient pressure at the exit of the nozzle. Simultaneously, after passing the narrowest cross-section of the nozzle (the “critical cross-section”), the gas flow is accelerated to supersonic velocity, with the hot combustion gases reaching velocities of more than 2000 m s^{-1} on escape [94, 95]. The functional principle of an HVOF spraying system is thus similar to that of a liquid-fuel rocket drive. The supersonic gas flow is utilized here to impart sufficient thermal and kinetic energy to the spray material admixture, in order to ensure the formation of a dense coating with good bonding to the surface of the component. This leads to very high particle velocities of between 400 and 700 m s^{-1} , depending upon the material. When the first HVOF flame spraying system, the JetKote, was developed by Jim Browning in 1980, particle velocities of up to 450 m s^{-1} could be achieved. Yet, by 1990 Browning’s second system, the JP 5000, had already reached 600 m s^{-1} , and was therefore the first HVOF system based on the flame shock principle to achieve velocities in this range. Unfortunately, the high gas velocities with HVOF spraying give rise to high noise levels; indeed, according to the fuel used, noise levels of around 130 dB(A) must be expected, requiring extensive hearing protection measures to be taken. The wearing of personal hearing protection is therefore essential, as would be the operation of the unit from a sound-protected cabin [80].

As a result of heat losses, dissociation of the reactants, and incomplete combustion, the maximum process temperature lies below the adiabatic combustion temperature, which is a function of the type of combustible gas, the stoichiometry, and the pressure level. In the real process, the temperatures are of the order of magnitude of $2700\text{--}3000^\circ\text{C}$, and the usually powder-form, spray material is introduced to the process either axially in the combustion chamber, or radially in the divergent section of the combustion chamber. The heating and acceleration of the particles depend on the density, velocity, and temperature of the surrounding flow field. The acceleration of the particles within the Laval nozzle takes place very much more efficiently than in a free jet, which is strongly braked by the influence of the surrounding atmosphere. In order to ensure an optimal acceleration of the powder particles, the acceleration nozzle is designed to be much longer than would be favorable for reaching the maximum velocity. Occasionally, the nozzle may even be extended by a cylindrical tube attached to the divergent section.

The laws of supersonic flow in the Laval nozzle of modern HVOF systems result in a defined static pressure level at the exit of the nozzle, which depends largely on the nozzle contour and the static output pressure of the combustion chamber. With the simplified assumption of an adiabatic and frictionless gas flow, for the ratio of the exit cross-section A_E to the narrowest cross-section A^* of the Laval nozzle:

$$\frac{A_E}{A^*} = \frac{1}{Ma_E} \cdot \left[1 + \frac{\kappa - 1}{2} Ma_E^2 \right]^{\frac{\kappa + 1}{2(\kappa - 1)}}$$

Ma_E : Mach number for the flow at the nozzle exit

κ : Isentropic exponent of an ideal gas.

The Mach number for the flow at the exit of the nozzle, Ma_E , is consequently a function of the nozzle geometry alone, as the isentropic exponent κ represents a gas constant and therefore depends upon the composition of the gas. As the Mach number represents the ratio of the actual velocity of the gas flow v_E to the local velocity of sound a_E , the variation of the gas exit velocity is possible only by changing the local velocity of sound. Here, the velocity of sound is a function of the gas constants κ and R , and of the static gas temperature of the gases T_E at the exit of the nozzle. An increase in temperature thus leads to a higher velocity of sound and, for a constant Mach number determined by the defined nozzle geometry, also results in an increase in the flow velocity of the gas.

$$\text{Mach number for flow at the exit of the nozzle : } Ma_E = \frac{v_E}{a_E} = \frac{v_E}{\sqrt{\kappa \cdot R \cdot T_E}}$$

v_E : gas velocity at the exit of the nozzle

a_E : velocity of sound of the gas at the exit of the nozzle

R : specific gas constant of the gas

T_E : static temperature of the gas at the exit of the nozzle

The Mach number, as a function of the pressure p_0 in the combustion chamber, determines the exit pressure of the gas flow p_E . From the point of view of fluid mechanics, optimal exit flow is obtained when the pressure of the escaping gas flow at the exit of the nozzle is exactly identical with the ambient pressure.

$$\frac{p_0}{p_E} = \left(1 + \frac{\kappa - 1}{2} Ma_E^2 \right)^{\frac{\kappa}{\kappa - 1}}$$

p_0 : total pressure of the gas \approx static pressure in the combustion chamber

p_E : static pressure of the gas at the exit of the nozzle.

If this is the case, then a *matched nozzle flow* or a *matched nozzle* might be referred to. For a given operating point of the HVOF system, and thus of the combustion chamber, the optimal expansion of the flow can then be regulated. As, however, due to the required broad parameter field and the complex interaction between the gas flow

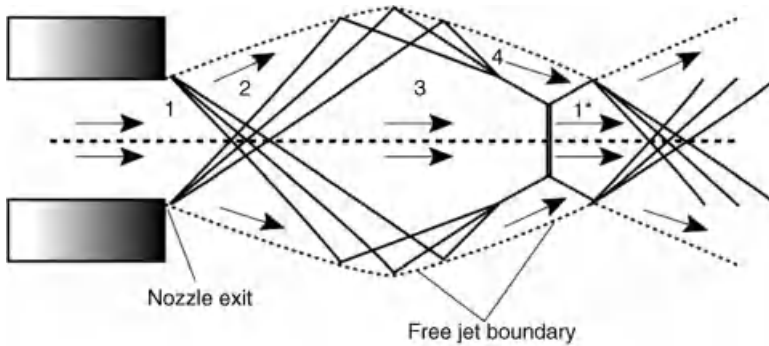


Figure 6.87 Expansion chambers for under-expanded flow at the exit of the nozzle ($p_1 > p_U$).

and varying particle loading, the nozzle cannot be optimally designed for every operating situation, so that the gas flow at the exit of the nozzle is, as a rule, not matched. This means that the flow achieved on exiting the nozzle is not exactly identical with the ambient pressure, and is either under- or over-expanded.

Viewed ideally, in this case, the matching of the pressure predominating in the exiting gas flow by a series of obliquely applied shock waves and Prandtl–Meyer expansion fans. This process is illustrated in simplified form in Figure 6.87, for the example of an under-expanded flow, whereby turbulence effects, friction, and mixing effects have been neglected.

At the exit of the nozzle, the under-expanded gas flow has a higher static pressure than the ambient gas ($p_1 > p_U$). On escaping from the nozzle, the velocity vectors for the regions in the vicinity of the central flow axes are oriented parallel to the axis. At the free jet boundary, the flow overpressure immediately surrounding the outlet of the nozzle gives rise to a widening of the jet; the reason for such widening is a deflection of the jet as a result of the expansion process. This is necessary, because at the free jet boundary no pressure discontinuity may occur, so that the static pressure of the flow must be identical with the ambient pressure. The expansion for the under-expanded jet ($p_1 > p_U$) takes place by means of Prandtl–Mayer expansion fans from region 1 to region 2, at which ambient pressure predominates ($p_2 = p_U$). The flow for passage through the expansion fan is simultaneously deflected, so that the velocity vectors of the gas flow, which previously were parallel, then diverge following expansion. The expansion fans proceeding from both sides of the nozzle outlet cross each other and continue up to the free jet boundary, where they are finally reflected. At the superimposed expansion fans, a further relaxation takes place and the flow is again deflected, leading to a pressure level in region 3 below the ambient pressure ($p_3 < p_U$). In this region, the velocity vectors for the flow are oriented parallel to the central axis. At the same time, the pressure reduction means a reduction of the potential energy and an increase in the kinetic energy of the flow, and therefore a reduction of the temperature and also an increase in the Mach number. In region 3, the flow is over-expanded; that is, the gas pressure lies above ambient pressure. In order that the ambient pressure can again be attained at the free jet boundary ($p_4 = p_U$), the flow must now be compressed; this is accomplished with the use of

lossy obliquely applied shock waves, with which kinetic energy of flow is again transformed into potential energy of flow. In region 1, the superimposed shock waves then generate a pressure higher than the ambient $p_{1^*} > p_U$, as well as a higher temperature $T_{1^*} > T_4 > T_3$ and a lower Mach number $Ma_{1^*} < Ma_4 < Ma_3$. The compression caused by the obliquely applied shock waves is also coupled with a deflection of the flow. In this idealized view, this results in the alternating widening and narrowing of the free jet boundary. The sequence of regions of higher and lower temperature through the expansion fans and shock waves is the reason for the development of the shock diamonds characteristic of the HVOF process. In the case of over-expanded nozzle flow, the same pattern can be recognized; however, in this case the adaptation of the flow to the ambient conditions begins with a compression by an obliquely applied shock wave immediately at the exit of the nozzle. Fundamentally, with the same nozzle configuration, both over- and under-expanded flows are possible, depending on the respective process parameters. Here, it should be pointed out again that, with a matched nozzle flow, no shock diamonds occur, so that this condition indicates whether the process parameters are matched to the nozzle geometry and no lossy flow occurs.

Today, essentially two different HVOF process variants are employed, namely liquid combustible liquid-driven and gas-driven. Typically, aliphatic carbohydrates with a flash point of $>50^\circ\text{C}$ (petroleum or kerosene) are used as combustible liquids, while the choice of combustible gas corresponds to that of conventional flame spraying (see Table 6.19). Besides safe handling, an important advantage of combustible liquids is their far better cost-effectiveness compared to gas. One disadvantage, however, is their unclean combustion, which can result in the formation of significant quantities of soot.

Due to the realizable and relatively low process temperatures, HVOF spraying is excellently suited to the processing of materials that tend to decompose at higher temperatures or undergo phase changes or oxidation, or which have a microstructure that imposes special requirements on the control of the degree of melting. The kinetic energy on impact with the substrate no longer requires the complete melting of the particles, yielding very dense and well-adhering coatings ($<1\%$ porosity). At the same time, the oxygen content of the coatings is comparatively low for a coating applied at atmospheric pressure. From a technological standpoint, high-velocity flame spraying belongs to the high-quality thermal spraying processes. Commonly found material systems manufactured using the HVOF process include carbidic metal-matrix materials of the type WC/Co or $\text{Cr}_3\text{C}_2/\text{NiCr}$, which are used predominantly for highly demanding corrosion and wear protection applications, as well as hard alloys on a Ni, Fe or Co basis for high-temperature applications or tribological loading.

Cold Gas Spraying A further development of high-velocity flame spraying can be found in the form of cold gas spraying (CGS). The schematic design of a cold gas spray pistol is shown in Figure 6.88. Here, a gas (pressurized air, He, or N_2) under pressure (15–35 bar), heated in a heat exchanger to a temperature of about 800°C , serves as the energy source. The high gas pressure is relaxed by using a Laval nozzle

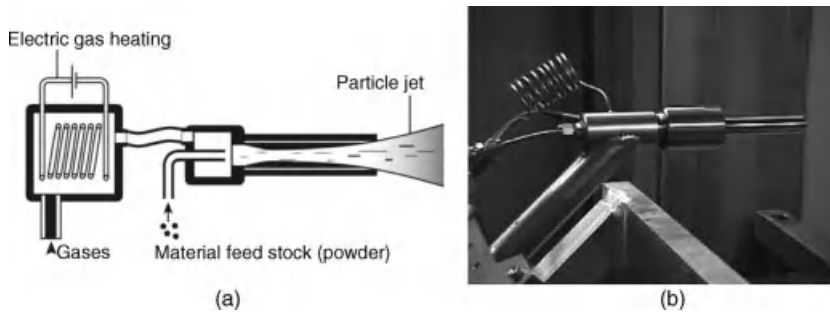


Figure 6.88 (a) Schematic representation of the cold gas-spraying (CHS) process; (b) The unit in operation.

and, according to the amount of gas and the nozzle geometry, produces very high kinetic energies. The powder material, previously injected into the nozzle, is accelerated to supersonic velocities of up to 1200 m s^{-1} . Based on the high gas velocities and resultant high particle velocities, CGS is the first process to have permitted the processing of materials without the spray material having to be in a molten or semi-molten form. Hence, the way was paved for applications that previously were accessible to thermal spraying only with great difficulty. In terms of their material properties, the coatings produced closely approximated those of the starting metals. As the spray material does need to be transformed to the molten state, and is shaped primarily by impact with the substrate, a certain ductility of the material would be required. Unfortunately, however, this limits the CGS process to mostly metallic and composite materials.

From a particle velocity which specifically depends upon the coating material, it is possible to produce dense and very pure coatings with good bonding. The bonding mechanisms of the particles, impacting in solid form, include mechanical clamping, friction welding processes and cold welding. Due to the high kinetic energy of the spray particles on impact, the regions of the substrate close to the surface will be deformed, enabling a good bonding between the substrate and the base material. Oxide layers (e.g., on aluminum substrates) are destroyed by impact, so that a shot-blasting pretreatment is not always required. The decisive advantage with the CGS process is the low thermal loading of the spray particles. Damage to the substrate as a result of imparted thermal energy can also be virtually excluded. Based on these low process temperatures, it is possible today for ductile materials such as aluminum, titanium or copper powder to be sprayed whereas, with other processes this is not possible or is possible only with a very high oxide content in the coating. The most recent process technology in the meantime has also enabled the processing of different types of steel, such as austenitic and ferritic stainless steels. Refractory materials can be processed as composite materials in a ductile matrix, and in this respect copper can be regarded as an ideal material. When copper coatings are produced with CGS, some 90% of the electrical and thermal conductivity of pure copper can be obtained. Notably, the basic prerequisite which materials must fulfill for application of the CGS process is that of adequate ductility.

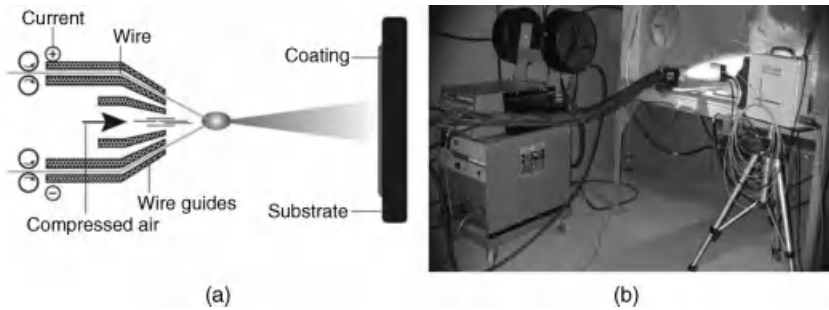


Figure 6.89 (a) Schematic representation of wire arc spraying; (b) The unit in operation.

Arc Spraying Electric arc wire spraying (which usually is referred to as “wire arc spraying”) is also based on methods developed by Max Ulrich Schoop. In order to melt the wire-form spray admixture material, an electrically generated arc is used, whereby two electrically conductive wires are led via a regulated infeed through contact tubes to the pistol, where they come together at an angle of about 30–60° (Figure 6.89). A potential difference is applied to the contact tubes, which usually are made from copper. This results in an electric arc being produced at the contact point between the tips of the wires; the high current density of more than 100 A mm^{-2} and the resulting temperatures of 4000–5000 K cause the wire material to melt. The molten material is atomized by a sputtering gas (usually pressurized air or nitrogen), accelerated by the flow, and then accelerated onto the substrate, with the particles typically attaining velocities in the range of $100\text{--}150 \text{ m s}^{-1}$. Due to the strongly diverging spray cone and partial vaporization of the spray material, the application efficiency is, however, very low compared to that of other spraying processes. Nevertheless, on the basis of its high melting capacity, more cost-effective electrical energy carrier, better machining properties of the coating materials, and simpler handling, arc spraying is – at least in principle – more economical than flame spraying.

As the use of wire arc spraying requires electrically conductive materials that can be processed to a wire form, the process is largely limited to ductile metallic materials. The spray wires used can be of the same or of different materials. When using cored wires, electrically nonconductive and refractory materials (e.g., tungsten carbide) which cannot be manufactured as (or processed to) solid wires can be incorporated into the coating. According to the device type, wires with diameters of 1.2–3.2 mm may be used, while the process parameters generally incorporate current strengths of 200–350 A and voltages of 25–45 V.

Due to the high temperatures, wire arc spraying causes the burn-off of different alloying elements. For most of these, the burn-off is relatively small, but for manganese and silicon it may rise to 25–40%, and for carbon to 40–60%, of the fraction originally in the wire material. This burn-off of alloying elements can be minimized by melting the two wire tips in the shortest possible electric arc. This also results in a better focusing of the spray jet, an improved melting performance, a very

fine spray structure, and a highly stable electric arc. The regulation of the voltage, wire feed, spray offset distance, and sputtering air pressure permit wide-ranging control over the coating quality, application efficiency, and process stability [80].

Compared to other spraying processes, the wire arc process offers considerable advantages. An essential characteristic worthy of mention here is an efficient introduction of the process energy, which is directly coupled to the wire material, whereas with the plasma and flame spraying processes the heat is first introduced to the plasma or gas flow, and then partially transferred to the spray material. As a result of the partial particle welding and acceleration of the spray particles to a high velocity, it is possible to achieve denser coating systems and around 50–100% greater bonding strengths with wire arc spraying than with conventional flame spraying. Based on the good bonding properties of coatings produced with wire arc spraying, it is also often possible to dispense with costly substrate pretreatments and the spraying of special bonding layers. Likewise, because less heat is introduced to the substrate (due to the lack of a flame cone), it is possible with wire arc spraying to produce far thicker coatings than with flame spraying, as the extent of thermally induced shrinkage stresses that arise during the coating process can be reduced.

The low consumption of process gases and the high coating performance make wire arc spraying a cost-effective process, to be used above all for coating large surfaces. Another advantage is the mobility of the process, which allows constructions such as bridges or ships to be coated on-site with minimal effort. The theoretical deposition rate with wire arc spraying (i.e., the amount of spray material melted per time unit) is typically $8\text{--}20\text{ kg h}^{-1}$, which is two- to threefold greater than for wire flame spraying ($6\text{--}8\text{ kg h}^{-1}$), and is primarily limited only by the available strength of the current source. Modern wire arc systems have a material hourly throughput of up to 8 kg aluminum and 20–30 kg zinc. However, for extensive spray work in serial production and for large constructions, wire arc spraying systems with more than 1200 A and rated capacities in excess of 36 kW are available, permitting the processing of more than 120 kg zinc per hour [80].

Wire arc spraying is employed for the deposition of zinc and aluminum for the purpose of corrosion protection. Due to the protective mechanism of cathodic corrosion protection, a dense coating system is no longer necessary against the aggressive electrolyte, which makes the use of a cost-effective wire arc process more attractive. Furthermore, wire arc spraying can also be used to apply wear-protection coatings, as well as coatings for frictional and gliding functions, thus enabling a cost-effective solution especially for large components. For wear-protection applications, both conventional solid wires and cored wires are used, allowing a considerably greater flexibility in the choice of material. Cored wires are composed of a thin metallic sheath that ensures both the form and electrical conductivity of the wire, together with a filling of any required powder-form material (Figure 6.90).

Wear-resistant cored-wire materials mostly have a powder filling with hard carbidic or boridic phases. The base alloys that also make up the metallic wire sheaths are mostly Ni or Fe alloys containing chromium. In order to employ wire arc spraying-produced coatings for corrosion protection applications, it is as a rule necessary to seal the surface in order to close the existing pores in the coating structure, and to

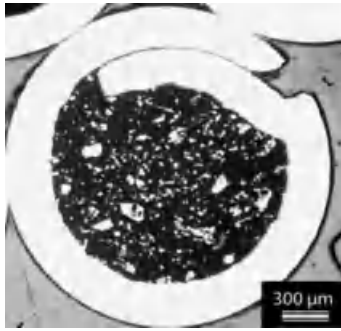


Figure 6.90 Optical microscopy image showing a cross-section through a grooved cored wire.

prevent the penetration of the corrosion medium. For this purpose, organic sealers (typically epoxy- or silicone-based) are mostly used.

Plasma Spraying Although, the use of a plasma as an energy source can be traced to developments of the 1920s and 1930s, the technique became suitable for industrial use only around 1950. The main characteristic of plasma spraying is a high process temperature, of up to 20 000 K, which enables the processing of any congruently melting material. Between 1960 and the late 1990s, there was an enormous growth phase in thermal spraying technology such that, as a result of the constantly growing demand for thermal barrier coatings for the aviation and space industry, plasma spraying finally became established, on the basis that its vastly higher process temperatures (12 000–15 000 K), when compared to the D-Gun process (3000 K), offered distinct advantages [96]. Plasma spraying processes are, as a rule, carried out under normal atmospheric pressure and, in this variant, are referred to as atmospheric plasma spraying (APS). The process can also be carried out for the processing of oxidation-critical materials in a vacuum chamber, as vacuum plasma spraying (VPS) or low-pressure plasma spraying (LPPS), or with the use of a protective gas as shrouded plasma spraying (SPS).

The term “plasma” was introduced in 1923 by the American physicist and chemist Irving Langmuir. Plasma is understood to mean a hot, ionized gas consisting of ions, electrons and neutral particles, in different energy states and state of excitation as a result of their continuous interaction with each other, and with photons. Plasmas thus possess a high electrical conductivity. As seen from the outside, a plasma is quasi-neutral; that is, overall it has equal numbers of positive and negative charges. Plasmas can be produced in different ways: by high temperatures or by electric and electromagnetic fields [97]. With plasma spraying, the plasma is produced by an electric arc discharge at atmospheric pressure. Thus, attention will be focused here on a thermal equilibrium plasma, for which the temperatures of the electrons T_e and ions T_i assume approximately equal values, and correspond to the plasma temperature T_p . Mention is also made of a local thermodynamic equilibrium (LTE), in which the particles are in equilibrium in certain spatial regions. The temperature thus represents a measure of the kinetic energy of the particles in the plasma:

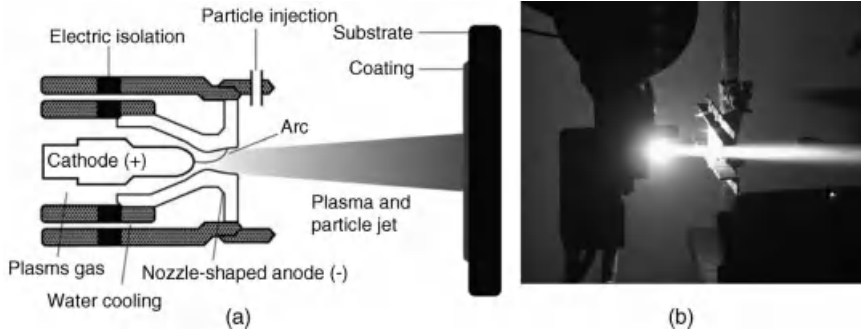


Figure 6.91 (a) Schematic design of a single-cathode plasma generator; (b) The unit in operation.

Temperatures of thermal plasmas $T_p \approx T_e \approx T_i \leq 20000 \text{ K}$

The DC plasma generator (Figure 6.91) is comprised of two basic components: (i) a pin-shaped copper cathode with a tungsten tip; and (ii) a copper anode in the form of a nozzle, with a corresponding tungsten inlet. Both, the cathode and the anode, are cooled with water by an external cooling circuit. Between the two electrodes a high-voltage discharge ignites an electric arc, after which electrons emitted from the cathode dissociate and ionize the plasma gas flowing past by collision processes. In order to reduce the work of emission of the electrons at the cathode, this is alloyed with 1–2% thorium, which improves the stability of the electric arc. In spite of this, due to the presence of hydrodynamic and electromagnetic forces, the electric arc is subject to a continuous effect, which results in a continuously changing length and continuous re-ignition.

At the nozzle outlet, the gas recombines as soon as it passes the electric arc and energy is no longer introduced. This sets free enormous quantities of energy, leading to an explosion-like expansion of the gas through the nozzle. The electric energy of the arc is consequently transformed into the thermal and kinetic energy of the plasma beam, and utilized for the melting and acceleration of the spray particles [80].

The high energies which the electric arc introduces to the process require the anodic base point of the electric arc to be moved in order to prevent local overheating and the resultant destruction of the copper anode [98]. For this reason, the gas flow is via a rotating gas distribution ring, forcing a rotational fluctuation of the electric arc in addition to the axial fluctuation. By using suitable cooling measures, the substrate temperature can be held in the range of 70 to 200 °C. Typical process parameters are in the range of 400–600 A current strength, 20–200 kW gross output, 15–25 kW heat dissipation by the cooling water, and 40–60 SLPM (standard liters per min) volume flow of the plasma mixture.

Argon, helium, nitrogen, and hydrogen are each utilized as plasma gases. The enthalpy (heat content) and temperature of the plasma depend on the plasma gas or gas mixture employed. Due to the lack of dissociation and the associated recombination step, the enthalpy of the monatomic gases argon and helium is substantially

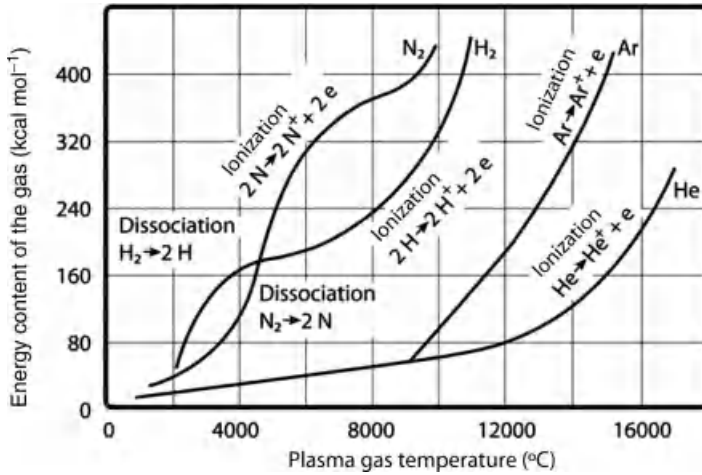


Figure 6.92 Enthalpy of a pure plasma gas.

less than that of the diatomic gases hydrogen and nitrogen. At the same time, the temperature of the monoatomic gases is much higher than for nitrogen or hydrogen (Figure 6.92), so that a mixture of diatomic and monoatomic gases enables optimal matching to the spray material. Thus, for example, as a result of its lower thermal capacity, an Ar/H₂ mixture contributes less than hydrogen to the melting of the powder. However, due to its higher atomic weight, argon positively influences momentum transfer and, therefore, the particle velocity. Hydrogen, on the other hand, as the lightest plasma gas, contributes only slightly to increasing the particle velocity; however, as a result of its high thermal capacity and good heat transfer characteristics, it imparts a great deal of heat to the powder particles [80].

The, as a rule, powder-form spray material is introduced to the process radially by an inert carrier gas at the exit of the nozzle. The positions of the powder injector and the carrier gas volume flow have a decisive influence on the trajectories of the injected particles in the hot zone of the plasma. Consequently, besides matching the plasma properties, the coating process can also be influenced by controlling the injection of material. In the case of refractory materials, temperatures in excess of 3000 °C can be achieved, with typical particle velocities in the range of 100–400 m s⁻¹ [99, 100].

In order to minimize the electric arc instabilities described for DC plasma spraying, in 1997 K. Landes developed a new type of plasma spraying system, based on the three-cathode technique [101]. The generation of multi-arc systems is the most recent ongoing development in plasma generators which, with three cathodes (Triplex Pro 200, Sulzer Metco Ltd, Axial III, Mettech) or three anodes (Axial III, Mettech/Delta Gun, GTV mbH), enables the formation of three constant electric arcs [102].

With the atmospheric plasma spraying process, in addition to a wide range of metals and alloys for moderate corrosion and wear loading, in particular ceramic materials can be processed. The most common ceramic material systems are oxide

ceramics, such as $\text{TiO}_2/\text{Al}_2\text{O}_3$ and Cr_2O_3 for wear and corrosion protection in the general area of machine and system construction, Y_2O_3 (partially) -stabilized ZrO_2 as a thermal barrier coating in stationary and aeronautical gas turbines, and Al_2O_3 and MgO_2 for electrical insulation. Abradable coatings, which serve on the rotor housings to reduce flow losses to the blade tips in aeronautical engines, and mixtures of materials (e.g., AlSi/polyester, NiCr/BN/polyester or NiCrAl/bentonite) are applied using plasma spray processes. Furthermore, certain medical engineering applications have been identified in which, for example, the ceramic material hydroxyl apatite is applied for the improvement of bone growth with implants.

6.2.6.5 Coating Materials and Examples of Thermal Spraying Applications

Spraying material admixtures are, corresponding to their form, classified as solid wires, rods, capillary tubes, cored wires, and powders. Among a total annual global consumption of 70 000 tonnes of spraying material, wire materials predominate with a fraction of about 65% [103]. The majority of solid wires utilized are steel, nonferrous metals, and their alloys. Powder materials cover the entire range of materials, and a wide range of methods exist for their manufacture, including spray aeration (metals and metal alloys), sintering (metal carbides and oxides), melting and crushing, as well as compound techniques (e.g., “abradables”). The details of more than 100 different materials that can be treated with thermal spraying processes, as summarized in DIN 32 529, are listed in Table 6.20, while details of frequently used spray material admixtures in relation to their coating function are classified in Table 6.21 (see also Figure 6.93).

Table 6.20 Overview of typical powder materials in thermal spraying.

Material	Example(s)
Pure metals	Mo, W, Ti, Nb, Ta, Cr, Ni, Cu, Al, Zn
Metal oxides	Al_2O_3 , TiO_2 , Cr_2O_3 , ZrO_2
Metal alloys	NiCr, NiAl, steels, CuAl, CoCrW
Self-flowing alloys	NiBSi, NiCrBSi, as well as nickel-based alloy with: 16 wt% Cr, 3.5 wt% B, 3.5 wt% Si, 4.5 wt% Fe, and 1 wt% C
Multi-material systems	Sheathed metals: e.g., NiAl, NiCrAl, NiAlMo, NiC Sheathed metal oxides: e.g., $\text{Al}_2\text{O}_3 + \text{TiO}_2$, $\text{Cr}_2\text{O}_3 + \text{TiO}_2$ Agglomerated metals and metal carbides: e.g., NiAl, WC-Co Agglomerated metal oxides: e.g., $\text{ZrO}_2 + \text{CaO}$, $\text{ZrO}_2 + \text{MgO}$, $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ Mixtures: e.g., self-flowing alloys + metals, self-flowing alloys + carbides
Other powders	Cu-W, bronze-steel, Al-Mo composites, MMC, polymers (e.g., polyester, polyethylene)

Table 6.21 Classification of typical spray material families according to function [104].

Coating function	Spray material admixture	Properties
High-temperature corrosion protection (+ surface preparation)	Mo NiAl 95/5 NiCr 80/20 NiCr-Al 95/5 NiCrAlY	↓ Increasing oxidation and temperature stability
Wear protection	Steels NiCrBSi Stellites CrC-Ni CrC-NiCr CrC-MCrAlY WC-CrC-Ni WC-Co WC-CoCr	↓ Increasing hardness ↓ CrC-containing materials stable for temperatures up to 850 °C
Corrosion protection (+ wear protection)	Al Zn X2CrNiMo 17 13 2 (1.4404, 316 L) NiCr 80/20 Al ₂ O ₃ Al ₂ O ₃ -TiO ₂ Cr ₂ O ₃	↓ Increasing additional wear protection
Thermal insulation	ZrO ₂ -CaO ZrO ₂ -MgO ZrO ₂ -Y ₂ O ₃	↓ Increasing thermal loading capacity and thermo-shock stability
Reduction of friction, gliding properties	Mo MoNiCrBSi WC-Co + NiCrBSi WC-Co	↓ Increasing wear protection and decreasing gliding properties
Biocompatibility	Ti Hydroxyapatite	Normally processed in vacuum plasma processes
Abradable coatings, mechanical seals	Al-Si-polyester Ni-graphite NiCrAl-bentonite ZrO-base material	↓ Increasing temperature stability



(a) Sealings, erosion and corrosions protection coatings, thermal barrier coatings in jet engines; hydraulic components in landing gears



(c) Transport rollers for steel industry



(f) Shaft sleeves



(b) Cylinder bore coatings of aluminium cylinder blocks



(d) Ball valves for petrochemistry



(e) Roller coatings for paper industry



(g) Pistons, piston rings, piston pins

Figure 6.93 Examples of applications for thermal spraying coatings for surface protection against wear and reduction of friction.

Illustrations courtesy of: (a) Boeing; (b) IOT

RWTH Aachen; (c) Salzgitter AG; (d) Praxair

Surface Technology GmbH; EVS valves Inc.;

(e) Voith Paper AG; (f, g) Sulzer Metco Ltd.

6.2.7

Deposition Welding

In DIN 1910, the different welding processes are classified, for example, in accordance with the welding purpose, whereby two fundamental distinctions are made in respect of the application (joint welding and deposition welding). Accordingly, deposition welding refers to the coating of a work piece by welding processes. With

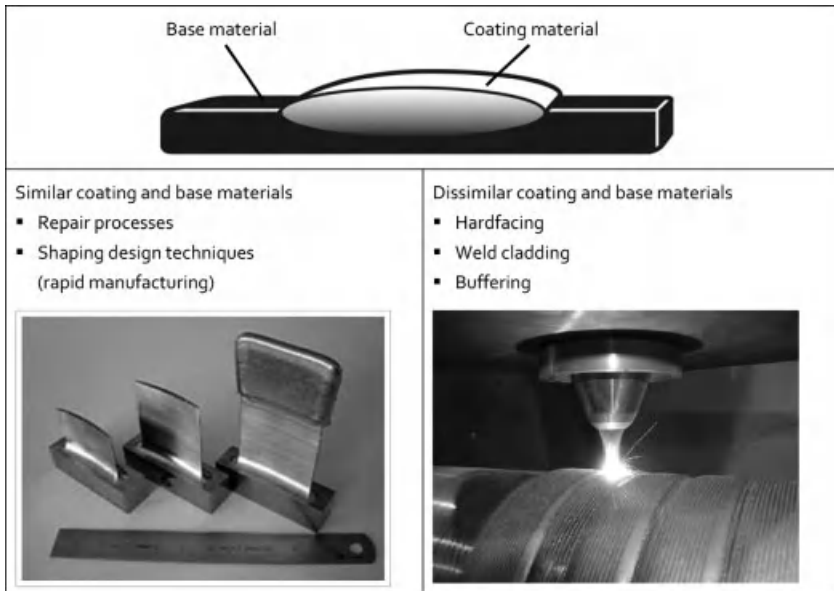


Figure 6.94 Classification of deposition welding processes. Illustration courtesy of Fraunhofer IWS, Dresden.

this technique, a coating is applied by a metal fusion process to a work piece, giving excellent bonding of the coating. The coating is applied by bringing welding layers next to or over one another onto the base material (Figure 6.94). As the coating material, two metal alloys of the same type as the base material can be used for repair purposes or structural design. For the use of other types of metal alloys as coating material, it is necessary to distinguish between hardfacing, weld cladding, and buffering.

In accordance with DIN 1910:

- *hardfacing* serves to improve wear resistance;
- *weld cladding* serves to improve corrosion resistance; and
- *buffering* serves to match different material properties of the coating and base materials by utilizing suitable intermediate layers.

Deposition welding produces very thick coating layers, from about 0.1 mm up to 20 mm. Although, the most commonly employed base material is inexpensive steel, other materials for which the surfaces can be melted are also suitable for deposition welding. For the extreme application of force expected, tempering steels or tool steels are chosen as substrate materials. Temperature-sensitive light metals, such as alloys of magnesium or aluminum can, however, also be coated by using deposition welding processes. According to the welding process employed, these are introduced in the form of wires, cored wires, ribbons, rods, or powder.

6.2.7.1 Material Composites Produced by Deposition welding

Deposition welding requires the introduction of energy (electrical, thermal, or mechanical) to melt a metallic welding filler on the work piece surface. The surface of the base material to be coated simultaneously melts, resulting in the formation of a compound material by metal fusion. In this way, particularly wear-resistant or corrosion-resistant materials can be applied to inexpensive base materials. The partially or completely fused compound material produced by deposition welding generally possess a higher bonding strength than that obtained with other coating processes. To the extent that brittle phases, resulting from unsuitable combinations of coating and base material, do not influence the bonding, the compound zone between the coating and the substrate never constitutes the weak point in the compound material [105]. Deposition welding is, therefore, particularly suitable for applications with severe wear stress and, furthermore, possess good edge-loading properties [105].

An important measure for the evaluation of a protective coating produced by deposition welding is the dilution factor, A . The dilution factor is the ratio of the penetration volume V_E to the deposition volume V_A . The penetration is responsible for the formation of the fused metal compound, and thus for the bonding between the coating and the base material. The protective effect depends upon the deposition volume and the choice of welding filler. With increasing dilution factor, the composition of the welded compound material changes due to alloying with the base material. The optimal utilization of the properties of the welding filler chosen is achieved for sufficient bonding of the coating with minimum dilution (Figure 6.95).

$$\text{Dilution factor } A : A (\%) = \frac{V_E}{V_E + V_A} \cdot 100$$

V_E : penetration volume

V_A : deposition volume

$$\text{or dilution factor } A : A (\%) = \frac{\frac{\rho_{FM}}{\rho_{BM}} \left(\frac{m_{FM}}{m_{DA}} - 1 \right)}{\frac{\rho_{FM}}{\rho_{BM}} \left(\frac{m_{FM}}{m_{DA}} - 1 \right) + 1} \cdot 100$$

ρ : density

m : mass

FM: filler material

BM: base material

DA: dilution alloy

6.2.7.2 Deposition welding Processes

In general, deposition welding can utilize the same welding process as for joining (Figure 6.96). For deposition welding, variants have been developed for nearly all metal fusion processes, only a few of which are of major importance in practice [106, 107].

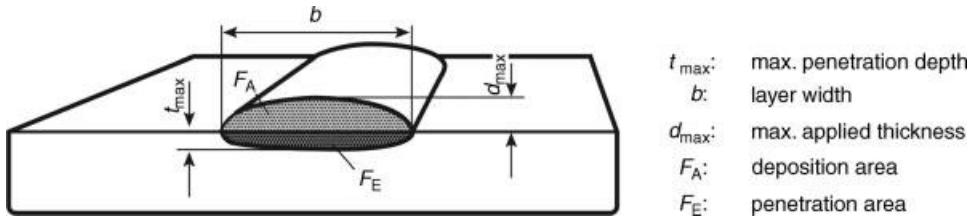


Figure 6.95 Schematic representation of the degree of dilution.

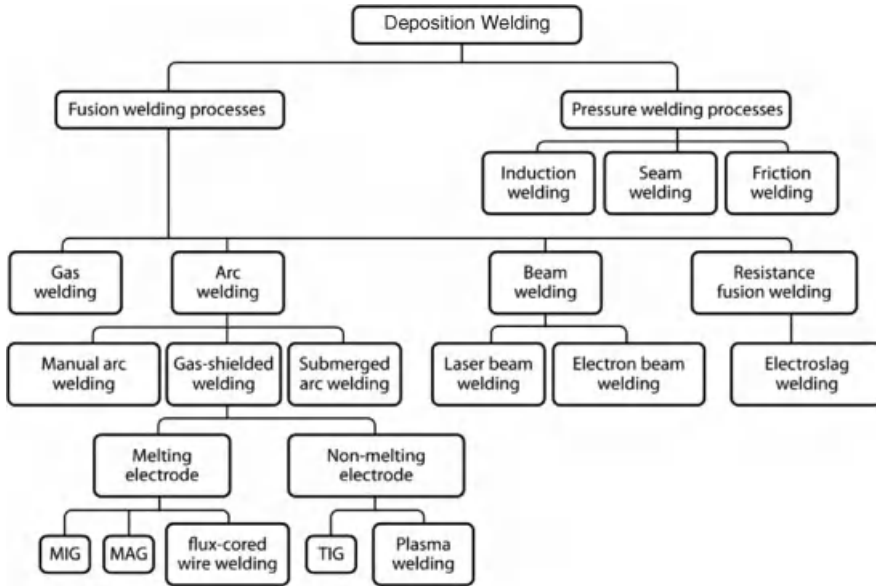


Figure 6.96 Classification of welding processes [105].

It is possible also to classify welding processes according to the degree of protection of the hot deposition welding zone from the environment, as open processes (gas flame), processes with covered glaze [shielded metal arc welding, electroslag welding (ESW), submerged arc welding], and inert gas welding [metal inert gas (MIG), tungsten inert gas (TIG), plasma]. This criterion is of particular importance with filler materials in which hard materials tend to decompose when exposed as a hot molten mass to oxygen. For high-quality coatings, in order to prevent the formation of pores, the melt should always be covered or protected by an inert gas against contact with oxygen [105]. The most important welding processes employed for deposition welding are compared in Table 6.22. The functional principles of deposition welding processes are represented schematically in Figures 6.97 and 6.98, for the examples of gas deposition welding, which belongs to the gas welding processes, submerged arc

Table 6.22 Characterization of deposition welding processes [105].

Welding process	Shielded metal arc, gas welding	TIG	MIG/MAG	SAW	Plasma welding	Beam welding	ESW welding
Welding filler Technique	Electrode/rod Manual	Rod/wire Manual	Wire/cored wire Manual, mechanized, automated	Ribbon/wire Mechanized, automated	Powder (wire) (Manual) mechanized, automated	Powder (Manual) automated	Ribbon/wire Mechanized, automated
Deposition rate	1 kg h ^{-1a)}	2 kg h ^{-1a)}	8–9 kg h ⁻¹	10–40 kg h ⁻¹	2–30 kg h ⁻¹	1–2 kg h ⁻¹	18 kg h ⁻¹
System costs	Low	Low	Relatively high	Relatively high	Relatively high	High	Relatively high
Applications	Small areas, Edges, Repair	Small to medium-sized areas, Edges,	Small to large areas, New manufacture, repair	Large areas New manufacture	Small to large areas New manufacture	Very small to small areas New manufacture	Large areas New manufacture
Dilution factor	15–30%	10–30%	15–25%	13–40%	5–20%		10–30%
Coating thickness (single-layer)	Difficult to control 2–4 mm ^{a)}	High 1.6–5 mm ^{a)}	High 4–8 mm	High 5–8 mm	Low 1–6 mm	Low 0.1–2 mm	High 4–5 mm

a) According to Wahl (specialist conference on deposition welding, 4/5.6.1996 Halle/Saale).

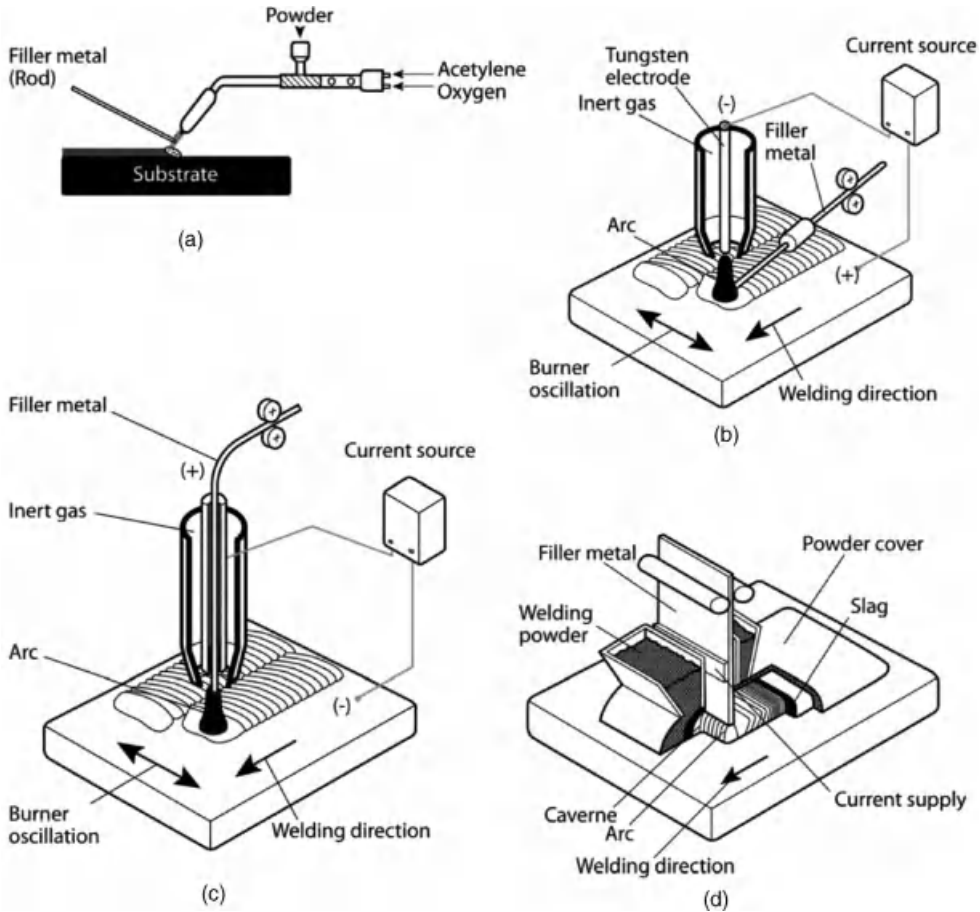


Figure 6.97 Deposition welding processes. (a) Gas deposition welding; (b) Tungsten inert gas deposition welding (TIG); (c) Metal inert gas deposition welding (MIG) and metal active gas deposition welding (MAG); (d) Electroslag welding (ESW) and submerged arc welding (SAW).

welding (SAW), which belongs to group of metal arc welding processes, and the TIG welding, MIG/MAG (metal inert/active gas) welding, plasma powder deposition welding and hot wire plasma deposition welding processes, as well as laser deposition welding, which belong to the group of beam welding processes.

With SAW, as a process variant from the group of metal arc welding processes, welding filler materials in the form of ribbons up to a width of 200 mm are employed. The relatively wide ribbon form enables high coating efficiencies, and the ribbon is fed continuously via suitable drive rollers to the process. The slag-producing welding powder, which serves to protect the welding joint from atmospheric air, is applied to the work piece in front of the ribbon by means of a powder support fixture, and then extracted by suction. The slag forming on the welding layer must (to the extent that it does not become detached by itself) be removed by mechanical methods in order to

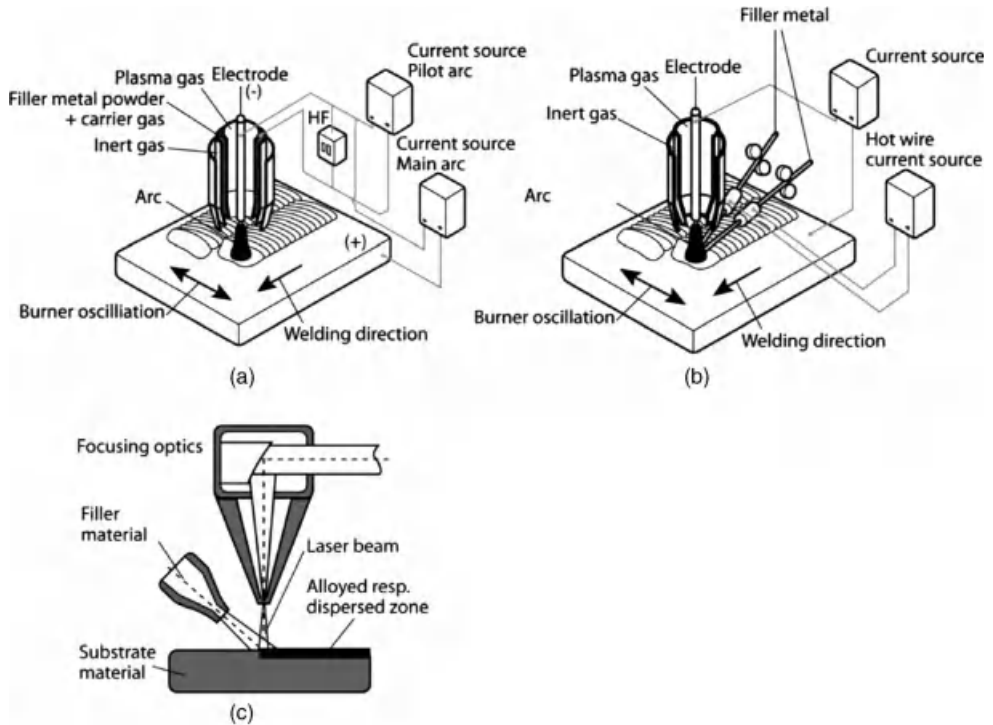


Figure 6.98 Deposition welding processes. (a) Plasma powder deposition welding and plasma-transferred arc (PTA-wire) welding; (b) Hot wire plasma deposition welding and plasma-transferred arc (PTA-powder) welding; (c) Laser deposition welding.

prevent its inclusion during the ongoing welding process. The arc then moves to the lower edge of the ribbon, so that the ribbon is uniformly melted.

The inert gas welding processes are characterized by the use of an inert gas (e.g., argon), which serves to protect the arc, electrode, and molten pool from the influence of hydrogen, nitrogen, and oxygen present in the atmosphere. This ensures that the inert gas is applied in a sufficient amount and purity to the welding position. Of the different inert gas welding process variants, the example of plasma powder deposition welding – which is distinguished by excellent surface quality, low dilution factors, and the formation of a homogeneous structure – will be described here. In this process, a pilot arc is ignited between a tungsten electrode and a copper nozzle with the help of a superimposed radiofrequency. The electrode is flushed by a plasma gas, which dissociates and ionizes in the pilot arc. In this way, the plasma (as in plasma spraying) is generated. However, in contrast to plasma spraying, in the case of plasma powder deposition welding a transferred electric arc is ignited between the tungsten electrode and the work piece, which is fed from a second current source. This transferred arc melts the base material and produces a molten bath. The powder, which is contained in a carrier gas, is then injected via bores in the burner into the arc,

and melted onto the base material. A protective gas flows through a further rig gap in the burner, in order to protect the arc, molten bath and applied welding layer from the ambient atmosphere.

Laser coating enables the specific local improvement of the material properties by the laser-guided provision of welding filler. It is defined as the volume deposition of a material onto a base material, with the partial mixing of both components. The achievable degree of mixing of the coating and base material is virtually unavoidable for laser processing. Typical of laser processing is the formation of a fine structure, resulting from a rapid dissipation of the heat applied by the material processed. With laser deposition welding utilizing powder-form welding fillers, the powder feed to the molten bath plays a decisive role, as it may greatly influence the powder utilization ratio, oxidation by the surrounding atmosphere, and the roughness of the coating.

6.2.7.3 Coating Materials and Examples of Applications for Deposition welding

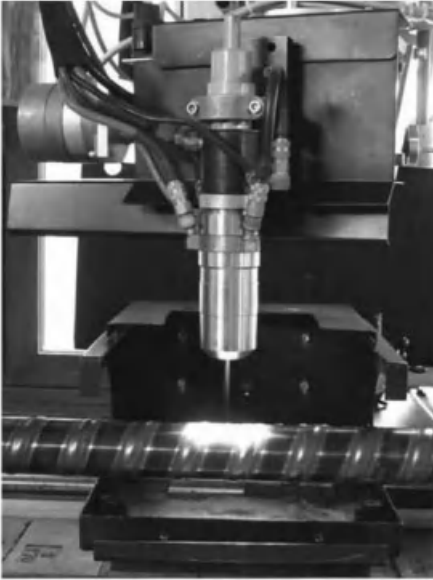
Deposition welding is a recognized industrial method, with which protective coatings for applications with extremely demanding wear and corrosion protection demands can be applied (Table 6.23; Figure 6.99). The method finds application for example, in:

- power engineering and waste incineration plants;
- the cement industry, brick, clay and ceramic industries and porcelain industry;
- mining, strip mining and construction machinery;
- the steel industry;
- mold-making for glass, polymer and metal processing;
- agricultural engineering and agricultural machines;
- rail vehicle construction;
- combustion engines for the automotive industry and aircraft engines;
- cutting tools; and
- extruder or centrifuge construction.

Table 6.23 Application-oriented selection of coating materials for deposition welding.

	Hardfacing	Weld cladding	Buffering
Purpose	Wear protection	Corrosion protection	Property gradient between coating and substrate
Examples of typical coating materials	<ul style="list-style-type: none"> • Hard alloys on the basis of iron, nickel or cobalt (stellite) • Pseudo-alloys (matrix of hard alloys with additional hard phases) 	<ul style="list-style-type: none"> • Ferritic to martensitic Cr steels • Soft martensitic Cr–Ni steels • Austenitic-ferritic Cr–Ni duplex steels • Austenitic Cr–Ni steels 	<ul style="list-style-type: none"> • Multilayer coatings • For the prevention of bonding problems, for example, due to the formation of hard phases • For the prevention of excessively high internal stresses, due to different coefficients of thermal expansion

(a)



Plasma powder deposition welding
of an extruder screw
(Source: Kjellberg Finsterwalde, Essen)

(b)



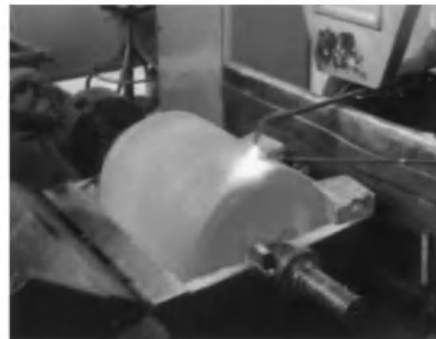
Laser deposition welding.
Stellite coating of a valve seat
(Source: Fraunhofer IWS, Dresden)

(c)



Laser deposition welding.
Tool and mold making.
(Source: Fraunhofer IPT, Aachen)

(d)



Gas deposition welding of a
stellite coating.
(Source: Colombo, France)

Figure 6.99 Examples of applications for deposition welding for surface protection against wear and corrosion.

Deposition welding is a comparatively cost-effective process, as large amounts of material can be deposited within a relatively short time. In particular, the local heating of the base material and the possibility of working on location with mobile systems are major advantages.

Deposition welding has been used successfully for many years for wear protection, with hard alloys on the basis of cobalt, nickel and iron having become firmly established as welding filler materials [108]. With these alloys, the wear resistance derives from the formation of characteristic hard phases during solidification. The structure is comprised of a relatively tough matrix with 15–45 vol% embedded hard phases, the type, size, fraction and distribution of which determine the wear resistance. The metal matrix serves for protection against mechanical and chemical stressing [109]. With the addition of dissimilar hard materials in the form of carbides, and partly also borides and silicides, the wear properties of these alloys can be significantly improved. These alloys are described as hard material-reinforced alloys or “pseudo-alloys” [110]. Tungsten carbide, due to its very good wear resistance, has gained great importance, while chromium, titanium, niobium, and vanadium carbides are also widely employed.

6.2.8

Brazing

Brazing is a thermal process for the bonding of joints and material-locking coating of materials, whereby a liquid phase is produced as a result of the melting of a brazing filler metal (fusion brazing) or diffusion at the boundary surfaces (diffusion brazing). By contrast with welding, the solidus temperature of the base materials is not exceeded. The principal advantage of the brazing process compared to welding is, along with the lower thermal loading of the base material, that dissimilar materials (e.g., metal/ceramic) can be bonded in a material-locking manner. In the area of wear protection, brazing is employed in the form of:

- **deposition brazing:** the deposition of brazing materials in a suspension process or fleece process
- **fusion joint brazing:** the surface mounting of armoring, for example, of stellite (CoCrWC), cemented carbide (WC-Co), Si_3N_4 , polycrystalline diamond (PCD), cubic boron nitride (CBN), and so on.

In accordance with ISO 857-2, these processes can be divided into *soldering* and *brazing* processes. The concept of high-temperature brazing, although no longer found in national and international standards, is however still used in German-speaking countries. Soldering refers to filler metals having liquidus temperatures below 450 °C, while brazing refers to filler metals having liquidus temperatures above 450 °C. High-temperature brazing refers to flux-free brazing in the absence of air (vacuum, shroud gas) with filler metals having liquidus temperatures above 900 °C. Compared to brazing and high-temperature brazing, soldering exhibits a lower strength, and is used primarily in electrotechnology and electronics, as well as in household installations. Soldering will not be further considered in the following subsections.

While brazing has become indispensable as a joining process in important industrial sectors, until now it has received very little attention as a coating process.

Nevertheless, deposition brazing opens up new possibilities for wear protection which cannot be realized in the same way by utilizing alternative processes, such as thermal spraying or deposition welding [111]. For such processes, special hard material filler metal compound systems have been developed which primarily serve for protection against abrasive and erosive wear.

Brazing is suited to different tasks, such as wear protection and corrosion correction and the repair of worn or fault-ridden work pieces. The most important areas of the application of deposition brazing and fusion joint brazing for surface protection include:

- machine and system construction
- tool construction; and
- aircraft engine and motor construction.

6.2.8.1 Principles of Brazing

During brazing, reactions must take place between the base material and at least one element of the brazing filler material. This requires the mutual solubility of at least one filler component and the base material. As filler materials, pure metals or metal alloys are employed, for which the liquidus temperature lies below the solidus temperature of the base material.

A special form of brazing is the so-called *diffusion brazing*, or transient liquid phase (TLP) bonding. In this case, the filler metal melts at the brazing temperature, in part supported by diffusion processes. Because the melting point-lowering elements diffuse into the base material, in contrast to fusion brazing, an isothermal solidification results. The brazing temperature is maintained until a joint zone completely free of residual filler metal is obtained by complete diffusion (up to 48 h). As a rule, the result is a structure with the same strength properties as the base material. This procedure finds use for example, in the repair brazing of nickel-based super-alloys on turbine blades. The brazing processes described below for tribological applications belong to the fusion brazing processes.

In conventional *fusion brazing*, the bond is formed by wetting of the base material with molten filler metal. During the wetting process, an alloy is formed initially at the boundary surface between the base material and the filler metal in the region of fewer atomic layers. The brazing temperature at which wetting begins is maintained until the brazing gap and the surface to be brazed are completely wetted (about 5–30 min). As a result of the ensuing solidification, a metallurgical bond is formed between the filler metal and the base material, yielding strength values comparable with those of the base material.

In brazing and high-temperature brazing processes, various dissolution processes of the solid base material in the filler metal take place. This gives rise to alterations in the composition of the liquid phase (filler metal) as a result of shifts in concentration or dispersion effects. Although, during the dissolution process, diffusion effects of the atoms from the liquid phase onto the solid phase occur simultaneously, the rate of dissolution of the solid metal into the liquid filler

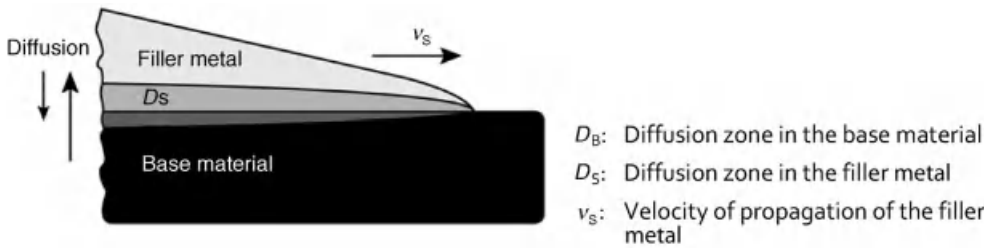


Figure 6.100 Wetting process during brazing.

material is vastly greater than the rate of diffusion of the atoms from the liquid phase into the solid base material. For this reason, brazing and high-temperature brazing processes as a rule yield only relatively narrow diffusion zones in the base material (Figure 6.100).

The adhesion of deposits such as impurities or the incorporation of water, hydroxides or oxides can disturb the interfacial reactions between the filler metal and the base material (Figure 6.101). Due to the dissimilar atomic structure of metallic oxides, characterized by very stable ionic or covalent bonding types, the wetting is hindered by the molten filler metal. The filler metal–base material oxide compound possibly forming will then have a very limited adhesion strength.

In order that the base material and filler metal may come into contact with each other, the outer boundary layers must be removed from the base material. This can

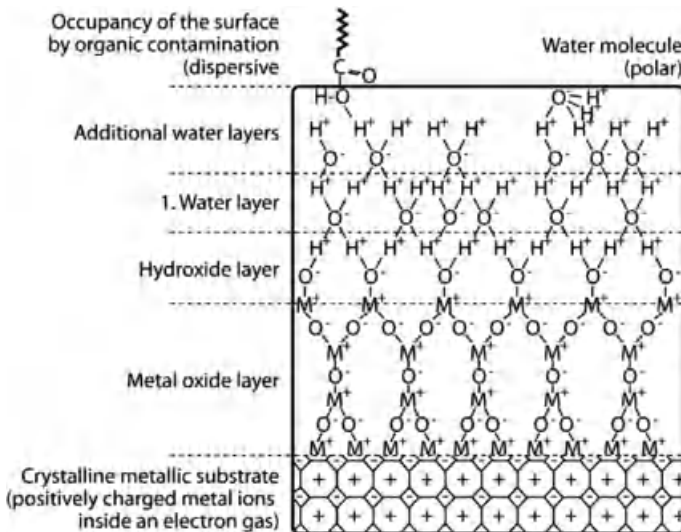


Figure 6.101 Structure of the outer boundary layers on metallic materials.

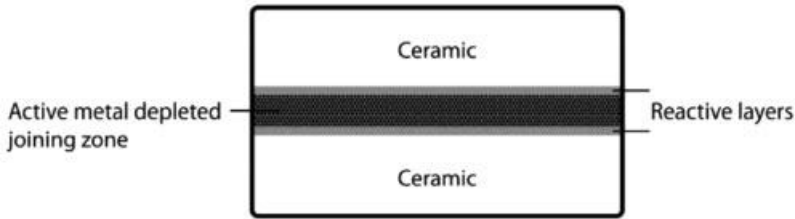
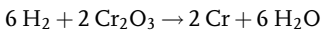


Figure 6.102 Schematic representation of the fusion zone structure for an active filler metal compound.

occur as a result of mechanical or chemical processes, or during the brazing process. Frequently, reducing-acting fluxes are used, though these must be very carefully removed following the brazing process in order to prevent corrosion damage. For furnace brazing, the metal oxides are reduced either utilizing a suitable shroud gas (e.g., argon, hydrogen, or a mixture of nitrogen and hydrogen), or decomposed in vacuum in a pressure range of 10^{-3} to 1 Pa.

Reduction of metal oxides in an H_2 atmosphere :



Furthermore, it is also possible to utilize self-flowing filler metals. These contain components which assume the reduction role of the flux, and include such elements as boron, phosphorus, silicon, germanium, and alkaline metals. The reduction effect can be introduced in different ways: one possibility is the reduction of adhering metal oxides by the filler metal components to volatile components. Another effect makes use of the fact that, during brazing, due to self-oxidation they act as a flux. Besides the possibility of such oxides evaporating, they can also be dispersed in the filler material.

Reduction of metal oxides by phosphorus : $MeO + P \rightarrow PO + Me$

Reduction of metal oxides by phosphorous oxide : $MeO + PO \rightarrow MePO_2$

For the brazing of ceramic materials, a fundamental distinction can be made between the brazing of previously metalized ceramics and active brazing. The active brazing process enables the manufacture of ceramic–ceramic and ceramic–metal compounds in a single-step joining process, without prior metallization of the ceramic surface. The use of a active filler metal ensures the wetting of the ceramic [112, 113]. Active filler metals contain small amounts of interfacially active elements (e.g., Ti, Zr, Hf, Nb, or Ta) with a high affinity for carbon, oxygen, or nitrogen. These are able to lower the interfacial energy to the extent that wetting can take place; in this case, the following wetting mechanism takes place, yielding a characteristic fusion zone structure (Figure 6.102):

- During the brazing process, an enhanced diffusion of the active metal contained in the active filler metal to the surface of the ceramic takes place.

- The active metal enters into a chemical reaction with the ceramic, leading to the formation of a reaction layer; for example, Ti forms TiN on a Si_3N_4 surface with a greater fraction of metal bonding than Si_3N_4 .
- The reaction layer forming possesses a character similar to that of a metal, with a considerably lower interfacial energy than ceramic, and can therefore be wetted by the now active metal-free filler metal matrix.

Due to the special properties of active filler metals, a number of requirements must be placed on the brazing process:

- Because of the high affinity of the active metals contained in the filler metal (e.g., Ti, Zr, Hf, Nb, Ta) for the atmospheric gases O_2 , N_2 and H_2 , the brazing process must be carried out in an inert atmosphere. Vacuum is particularly well suited for the active brazing process. However, brazing in a shroud gas atmosphere (e.g., Ar or He) is also fundamentally possible, whereby a far greater danger of active metal oxidation exists than with the vacuum brazing process, which can have a detrimental influence on the wetting behavior of the active filler metals.
- With active brazing under vacuum, the pressure in the vacuum chamber must be at least 10^{-2} Pa.
- Because of the poor flow properties of active filler metals, these are employed as filler metal foils on ceramic surfaces. In this way, the filler metal can be positioned to the fusion point immediately prior to the brazing process.
- The brazing temperature must be at least $850\text{--}900^\circ\text{C}$ in order to satisfy the energy requirements for an active metal–ceramic reaction, and thus enable the wetting of the active filler metal. With the use of active filler metals having a liquidus temperature $>900^\circ\text{C}$, the brazing temperature must be at least 50 K above the liquidus temperature of the active filler metal. As the active brazing process is a diffusion-controlled process, a brazing time of at least 5–10 min is required.

The simplest way to describe, quantitatively, the quality of wetting is the specification of the contact angle β , which can be empirically determined. The contact angle β encloses the surface of the base material and the tangent at the three-phase point of the solid, liquid, and gaseous phase to the droplet contour of the molten filler metal (Figure 6.103). The greater the solubility between the filler metal and the base material components, the smaller the contact angle β and the better the wetting. A contact angle of 0 to 30° is classified as “completely to satisfactorily wetted”, of 30 to 90° as “partially wetted”, and of greater than 90° as “not wetted”. The contact angle must, therefore, always be less than 30° .

6.2.8.2 Classification of Brazing Processes and Filler Metals

The classification of the different soldering and brazing processes follows different criteria (Figure 6.104; Table 6.24). The best-known and most important criterion is the liquidus temperature of the filler metal. Further classification follows, according to the type of soldering or brazing position, the type of filler metal feed, the atmosphere, and the type of energy carrier [114].

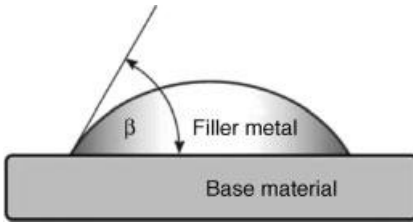


Figure 6.103 Contact angle β between the molten filler metal and the surface of the base material as a measure of wetting efficiency.

The designations of the filler metals for brazing (including high-temperature brazing) are summarized in DIN EN 1044. The filler metals belong largely to the groups of silver and copper-based filler metals, including brass and bronze filler metals. For higher operating temperatures, nickel-based fillers and noble filler metals with a base of gold, palladium, or platinum are employed (Figure 6.105). For furnace brazing under shroud gas or in vacuum, aluminum, copper or nickel-based filler metals are employed, whereby aluminum filler metals are used only for the brazing of aluminum and aluminum alloys, as undesirable metallurgical reactions would occur with steel and other nonferrous metals [115].

The coating materials developed for deposition brazing usually consist of metal–matrix composites (MMC). The metal matrix, for which predominantly Ni-based filler metals enriched with up to 70% hard materials is utilized, serves as a filler. Over the years, WC and Cr_3C_2 have become firmly established as hard material particles for many applications. Because of the high fraction of metallic bonding in WC and Cr_3C_2 , the brazing process takes place at the phase boundaries of the filler matrix and also of the hard material particles, which results in a firm bonding between the matrix and the particles [115]. The greatest strength is achieved with the use of Ni-based hard alloys of the system NiCrBSi, which – due to their self-flowing properties – are also well suited as brazing filler metals. The precipitation of borides and silicides and the mixed crystal formation with chromium during

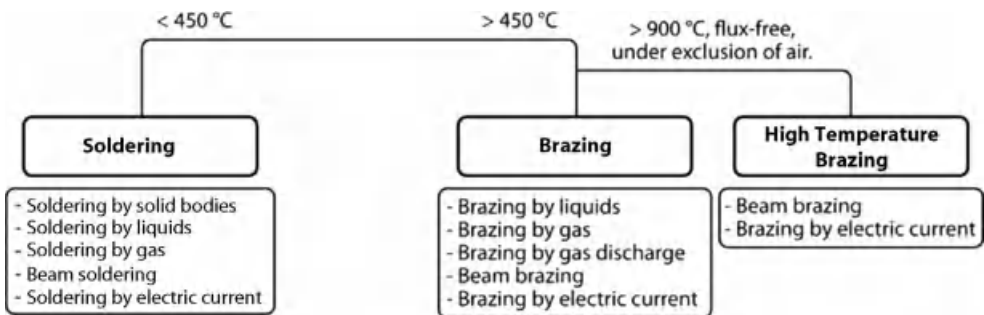


Figure 6.104 Classification of brazing and soldering processes according to liquidus temperature of the filler metal and energy carriers.

Table 6.24 Classification of soldering and brazing processes according to energy carriers.

Energy source	Process	Classification ^{a)}
Soldering by solid bodies	Hand soldering	S
	Block soldering	S
	Roller soldering	S
Soldering, brazing by liquids	Salt-bath brazing	B
	Filler bath brazing, soldering	S, B
	Wave soldering	S
	Drag soldering	S
	Ultrasonic soldering	S
	Reflow soldering	S
	Soldering, brazing by gas	Flame brazing, soldering
Warm gas soldering		S
Gas furnace soldering		S
Brazing by electric gas discharge	Arc brazing	B
	Plasma brazing	B
Brazing, soldering by beam	Light beam brazing, soldering	S, B
	Laser beam brazing, soldering	S, B, HTB
	Electron beam brazing	B, HTB
Soldering, brazing by electric current	Resistance brazing, soldering	S, B
	Induction brazing, soldering	S, B, HTB
	Furnace brazing, soldering	S, B, HTB

a) S: Soldering, B: Brazing, HTB: High-temperature brazing.

solidification of the Ni-based hard alloy simultaneously result in high strength values for the matrix. Furthermore, nickel offers good corrosion protection against a number of media.

For brazing and high-temperature brazing in mass production, furnace brazing is mostly used. Working with fluxing agents is possible in the furnace or under a shroud gas, with the brazing being carried out in vacuum. High-temperature brazing is, with few exceptions, carried out without fluxing agents in medium and high vacuum, or in

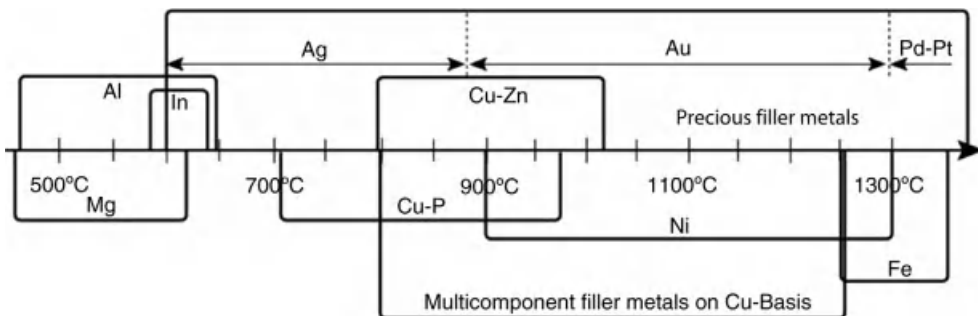


Figure 6.105 Filler metal groups for brazing and high-temperature brazing according to brazing temperature.



Figure 6.106 Furnace brazing systems. (a) High-vacuum brazing furnace; (b) Shroud gas brazing system. Illustrations courtesy of: (a) PVA TePla AG, Wettenberg; (b) Harnischmacher GmbH Fröndenberg.

a continuous furnace under a reduced shroud gas (Figure 6.106). The furnace is usually resistance-heated.

Vacuum furnaces are classified as either hot-wall or cold-wall furnaces. In the former case, the parts to be brazed are contained in a retort, which is heated from the outside. As the external heating takes place at atmospheric pressure, there is a clear danger of implosion, but this can be prevented by evacuating the space between the retort and the furnace wall. Such furnaces are referred to as “pressure-relieved vacuum hot-wall furnaces.” In the case of vacuum cold-wall furnaces, the housing is cooled by water, and the molybdenum plate heating chamber is situated in the inner space. The actual heating elements, which are made from graphite, molybdenum or tungsten, are located in the heating chamber. The heating elements serve to produce a homogeneous thermal radiation field for the heating of the parts to be brazed in the heating chamber.

For deposition brazing, induction brazing is also suitable. The most important feature of induction brazing is the direct heating of the work piece. The heat does not need to be transmitted by convection, radiation or thermal conduction, as with the other processes. Rather, the work piece is heated via induction coils; these generate an alternating electromagnetic field which induces strong eddy currents I in the tool which in turn, due to the tool’s electrical resistance R , generates the heat output P , resulting in the quantity of heat Q over the time t , in accordance with Joule’s law. This quantity of heat causes the heating of the tool:

$$\text{Quantity of heat } Q : \quad Q = P \cdot t \quad Q = R \cdot I^2 \cdot t$$

P : heat output

t : time

R : electrical resistance of the work piece

I : eddy current induced in the work piece

In order to generate the electromagnetic field, medium- and high-frequency generators, with frequencies of 5–10 kHz and >100 kHz, respectively, are utilized, while the induction coils are in the form of water-cooled copper tubes. One major

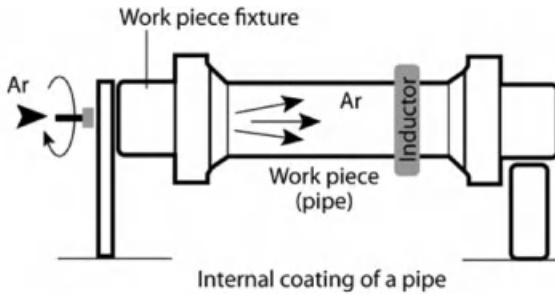


Figure 6.107 Induction brazing for the internal coating of cylindrical parts.

advantage of inductive heating is the ability to obtain high heating rates; this results in short process times and thus contributes to the cost-effectiveness of the process. Moreover, induction brazing can easily be automated, and also used for the internal coating of piping (Figure 6.107).

In principle, all welding processes employed for deposition welding (see Section 6.2.7) can also be used for deposition brazing. The difference consists only in terms of the applied temperature, which lies below the solidus temperature of the base material for deposition brazing. For targeted local heating, beam processes (laser beam brazing, electron beam brazing) are particularly well suited.

6.2.8.3 Deposition Brazing of Hard Material–Filler Metal Composite Systems

The deposition brazing of wear-resistant hard material–brazing filler metal compound systems has developed by way of the brazing of coarse hard material granulations. Initially, coarse-grained tungsten carbides were deposited with copper-based filler metals onto metallic substrates, both for the grinding machining of metallic and mineral-form materials, and in the area of emergency braking systems. These developments led to two different processes which differed principally in the type of hard material and filler metal application: (i) the suspension process; and (ii) the fleece process. With these processes, a broad range of coating thicknesses, from 0.05 to 4 mm, can be produced.

The Suspension Process For the suspension process, fine-grained hard materials ($d \geq 15 \mu\text{m}$) and powder-form filler metal alloys are intensively mixed with an organic binder and suitable solvents, and processed to a suspension. Polyacrylates, polybutenes, polystyrenes or cellulose derivatives are preferentially used as binding agents, whilst carbohydrates, glycol ethers, glycol esters, alcohols and ketones with volatility numbers between 10 and 10 000 have proven to be suitable as solvents. The powdered particles remain homogeneously distributed in this suspension for the time of processing, which can extend to several hours.

Deposition of the suspension occurs similarly to finishing using simple application techniques, such as dipping, spraying, brushing or priming, and also on complex geometries. The deposition process can be repeated following drying of the sus-

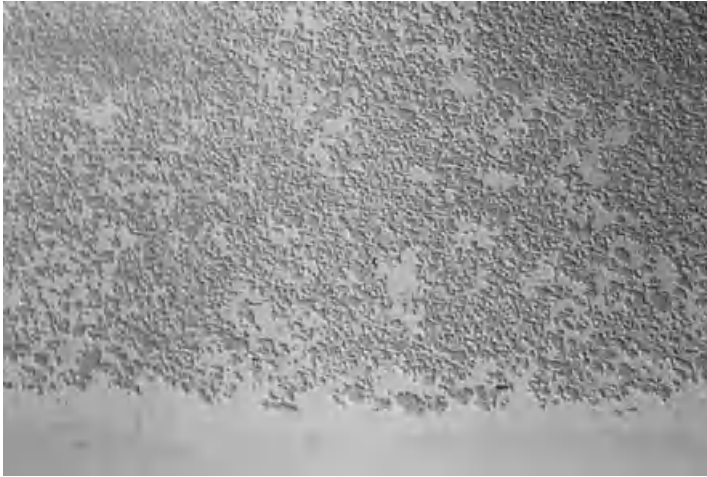


Figure 6.108 Photomicrograph of a wear protection coating produced with the suspension process, WC/Ni 106.

pension, so that coating thicknesses of between 0.05 and 0.5 mm can be obtained. According to the deposition method, it is possible to achieve coating thicknesses of between 0.05 and 0.1 mm with a single application, whereby the standard coating thicknesses are in the range of 0.05–0.2 mm. During the follow-on heat treatment in furnace processes (these are mostly continuous-flow hydrogen furnaces or hydrogen chamber furnaces), the hard materials enter into a compound with the molten filler metal alloy, while the organic binder evaporates and the base material is simultaneously wetted. The resultant coatings are dense, smooth and virtually free from pores, with porosities of <1% (Figure 6.108) and, for most applications, mechanical post-processing is not required [115]. Due to the high fraction of hard material of >60 vol%, high hardness values of about 65 HRC are achieved. Typically, WC and Cr_3C_2 are employed as hard materials, while the phosphorus-containing nickel-based filler metals NI 106 and NI 107 are used as filler metal alloys (Table 6.25).

Deposition brazing with the suspension process has proven to be of use for hydraulics applications, where pronounced abrasive attack is to be expected due to the extreme uptake of dirt and grime, for example, in the hydraulic cylinders of tunnel advance working machines and steering-head rods in zeolite production (Figure 6.109). Due to the low wear of the coatings, the suspension process finds

Table 6.25 Typical nickel-based filler metals for deposition brazing utilizing the suspension process.

DIN EN 1044	DIN 8513	EN ISO 3677	AWS	Composition
Ni 106	L-Ni6	B-Ni89P-875	B Ni-6	Ni11P
Ni 107	L-Ni7	B-Ni76CrP-890	B Ni-7	Ni14Cr10P

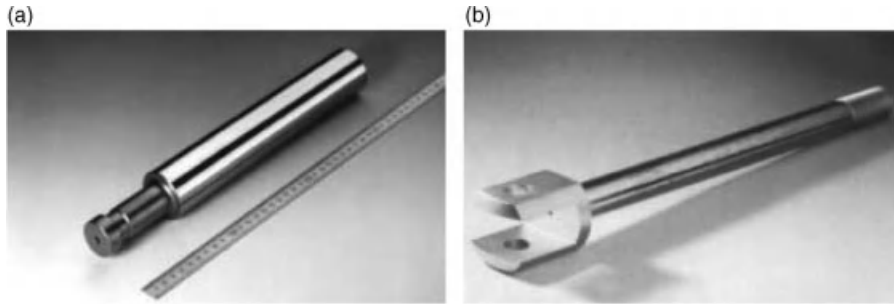


Figure 6.109 Deposition brazing applied with the suspension process for wear protection. (a) Hydraulic cylinder; (b) Steering head rod. Illustrations courtesy of Innobraz GmbH, Esslingen.

application for grinding machinery when the purity of the ground goods must be ensured, such as in the foodstuffs industry (flour, cocoa beans), in the manufacture of graphite for toners, or in attritor mixers for paste production. Other areas of application include the coating of housings, rotors or quadrant pipes, in which abrasive particles are transported pneumatically or in a liquid stream (e.g., blowers, pumps, sluices or whirl gates) [115]. The possibility of internally coating even thin pipes and quadrant pipes offers new technical solutions for wear protection [115].

The Fleece Process For deposition brazing utilizing the fleece process, two types of fleece are required, with which the components of the compound formed later (filler metal matrix and hard material) are initially separated. To produce the fleece, the respective materials are intensively mixed with an organic binder and processed by conventional shaping methods, such as extrusion and rolling, to the required coating thickness. The maximum fraction of organic binder in these fleeces is 2 wt%, in order to satisfy the requirement of a good brazing capability for the required surface brazing. The standard fleece thicknesses are 1, 2, 3, or 4 mm, whereby the thickness of the hard material fleece determines the final coating thickness. The wetting of the individual powdered particles by the plastic binder (Figure 6.110a) leads to a rubbery-elastic consistence of the fleece. This requires that the fleece be first processed by simple punching and cutting processes to arbitrarily configured shaped pieces (Figure 6.110b). The fleece can also be attached to curved surfaces, thus extending the potential applications of this coating technology in respect of complex component geometries. The coatings formed have precise contours and sharply defined edge structures; that is, the geometry of the shaped piece remains intact following the process.

The nickel-based powders used belong to the group of NiCrBSi filler metals (e.g., Ni 102; see Table 6.26), and are characterized by grain sizes of about 50 μm . As hard materials, WC and Cr_3C_2 with mean grain diameters of 4–20 μm are utilized. The organic binder used is a polyvinyl acetate with a density of 0.98 g cm^{-3} .

For the coating process, the hard material fleece is applied as the first layer to the substrate and the filler material fleece applied thereafter. For the coating of curved surfaces, it may be necessary to fix the fleece by using specially developed organic

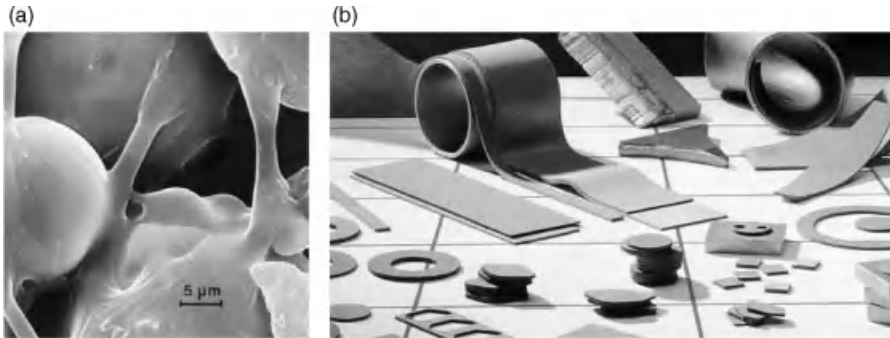


Figure 6.110 Fleece systems for deposition brazing. (a) REM image of a filler material fleece; (b) Hard material and shaped filler pieces. Illustrations courtesy of Innobraise GmbH, Esslingen.

Table 6.26 Typical nickel-based filler metal for deposition brazing with the fleece process.

DIN EN 1044	DIN 8513	EN ISO 3677	AWS designation	Composition
NI 102	L-Ni2	B-Ni82CrSiBFe-970/1000	B Ni-2	Ni7Cr4,5Si3B3Fe

adhesives. During heating, both the organic binder and the adhesive material evaporate nearly residue-free at about 450 °C. Evaporation of the binder fraction results in a defined porosity in the shaped hard material pieces, giving rise to a pronounced capillary effect in the brazing filler alloy applied on top of this. The molten filler metal infiltrates the porous shaped hard material pieces via metallurgical interactions with the substrate (Figure 6.111). The advantages of the fleece process compared to other coating technologies lie primarily in the high hard

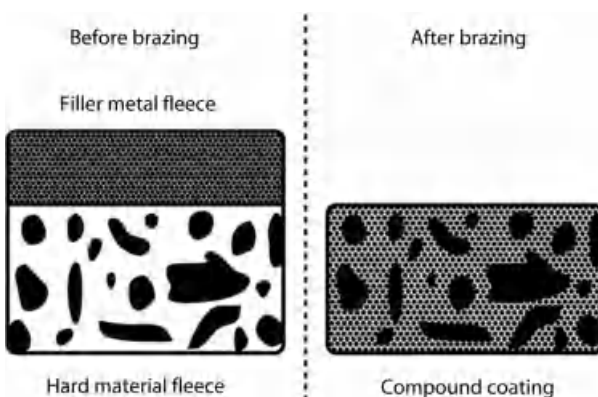


Figure 6.111 Principle of deposition brazing with the fleece process.

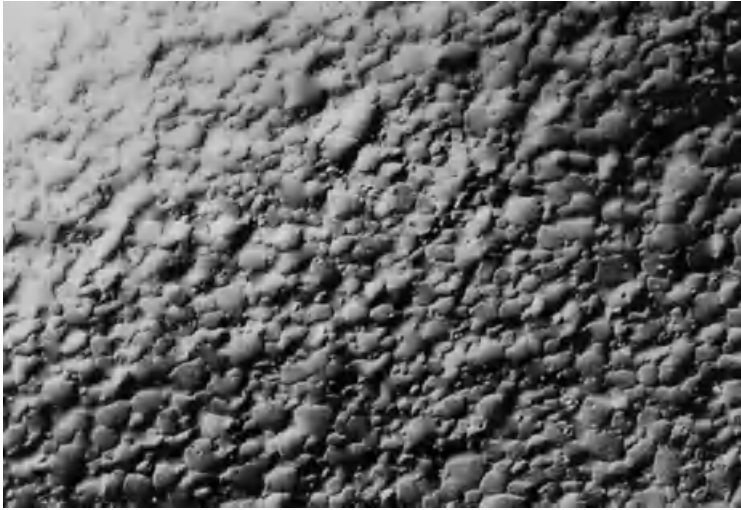


Figure 6.112 Photomicrograph of a $\text{Cr}_3\text{C}_2/\text{Ni}$ 102 compound coating produced with the fleece process.

material content of up to 70 vol% with a porosity of $<1\%$. No other coating process is capable of achieving a comparably high content of hard material.

Deposition brazing with the fleece process is carried out predominantly in continuous-flow hydrogen furnaces or hydrogen chamber furnaces. Inductive heating is also possible and, above all, interesting in relation to shortening the process times. According to the coil geometry used, the heating rates can be as high as 900 K min^{-1} , and greater. The inductive brazing process takes place in the atmosphere, not only to prevent oxidation of the tools and coating materials during the process, but also to enable wetting of the substrate and hard material particles by the filler metal. The hard material–hard alloy compound coatings produced using these materials are characterized by their high hardness and a homogeneous coating structure (Figure 6.112). The firm bonding of the coating to the base material yields bonding and shear strengths of $250\text{--}400 \text{ N mm}^{-2}$, depending upon the combination of materials. Because of the thermal expansion coefficients of the compound layers (Table 6.27), only structural steels or ferritic steels may be used as base materials, in order to prevent excessive internal stresses in the compound as a result of too great a difference in the expansion coefficients.

Table 6.27 Thermal expansion coefficients of typical deposition brazing coatings and base materials at 20°C .

	$\text{Cr}_3\text{C}_2/\text{Ni}102$	$\text{WC}/\text{Ni}102$	Ferritic steel	Austenitic steel
α [$10^{-6}/\text{K}$]	11.4	8.1	12–15	17–19

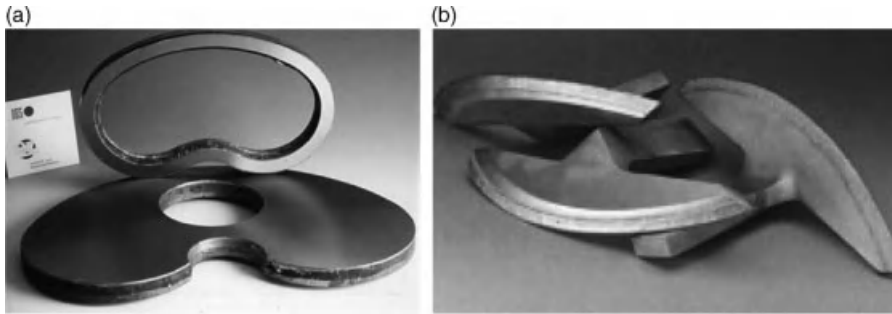


Figure 6.113 3 mm-thick $\text{Cr}_3\text{C}_2/\text{Ni}$ 102 deposition brazing coating produced by the fleece process. (a) Housing cladding with sliding ring of a concrete pump; (b) Wear protection of mixer paddles. Illustrations courtesy of Innobraise GmbH, Esslingen.

This process finds application in the area of wear protection against abrasive and erosive wear. The coatings can also be applied for additionally superimposed corrosion protection. Initial applications were in the chemical industry for the coating of mixer paddles, in the construction industry for housing cladding, and in general for baffle plates, guide rails, contact overlays, blades and wear protection inserts for various construction elements. Figure 6.113a shows parts of a concrete pump (housing cladding with associated sliding ring) with a $\text{Cr}_3\text{C}_2/\text{Ni}$ 102 layer applied by deposition brazing. The operating pressure of this pump is 600 bar, increasing the pump lift by 250–350 m. Figure 6.113b shows mixer paddles with the same coating; in this case, compared with a conventional stellite (CoCrWC) deposit weld, the service life could be increased from 750 h to 3000 h.

6.2.8.4 Application of Armoring by Brazing

During the past 100 years, and particularly in the case of metal cutting tools, a wide variety of cutting materials have been developed with the goal of achieving the greatest possible wear resistance, in addition to high hot hardness and good strength properties (Figure 6.114). These include ceramic materials, such as Al_2O_3 and Si_3N_4 , or diamond and composite materials, such as cemented carbide, polycrystalline diamond (PCD) and cubic boron nitride (CBN). The application of these materials by brazing to component or tool surfaces subjected to very high loading is described by the term *armoring*. Here, brazing offers the possibility of cost-effectively bonding metal substrates of high strength to ceramic armoring of high hardness. Furthermore, cemented carbide tools can also be armored with ceramic cutting surfaces for high performance cutting operations [116].

Brazing of Metallized Ceramics As ceramic materials with a high fraction of ionic and/or covalent bonds cannot be wetted with conventional brazing, a two-stage brazing process is required. In this case, the ceramic surface is first metallized, and then brazed in vacuum or under a shroud gas without flux. Metallization takes place either:

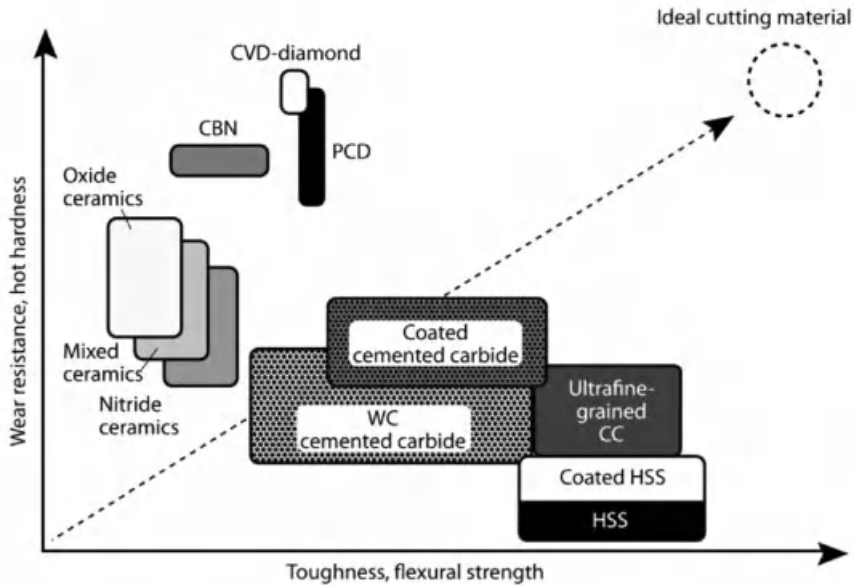


Figure 6.114 Comparison of cutting materials in respect of their mechanical properties [117].

- In the Wo/Mn or Mo/Mn process, followed by Ni- and Cu-coating for the brazing of oxide ceramics (Al_2O_3 , ZrO_2) [118].
- By the “burn-in technique,” in which a mixture of a powdered metal and a glass frit is applied to the ceramic by means of an organic binder and then burned in [119].
- By brushing reactive metal salts onto oxide ceramics (Al_2O_3 , ZrO_2), which are then dried. Heat treatment reduces the metal salts, which then react with the ceramic to form stable compounds.
- By thin film processes (PVD, CVD, thermal spraying). Refractory metals, predominantly titanium, are utilized as coating metals.

The brazing process which follows can be carried out as usual with brazing filler metals typically, silver- and silver-copper-based filler metals are employed (Table 6.28).

Table 6.28 Commercially available filler metals for joining metalized engineering ceramics [112].

Filler metal	Cu	In (Weight %)	Pd	Ag	T_{solidus}	T_{liquidus} (°C)	T_{brazing}
Ag-Cu-In	25	14.5	—	61.5	630	705	755
Ag-Cu-In	27	10	—	63	685	730	780
Ag-Cu	28	—	—	72	780	780	830
Ag-Cu-Pd	31.5	—	10	58.5	824	852	900
Ag-Cu-Pd	21	—	25	54	901	950	1,000
Ag-Pd	—	—	5	95	970	1,010	1,050

Table 6.29 Commercially available active filler metals for joining engineering ceramics.

Filler metal	Weight %	T_{solidus}	T_{liquidus} (°C)	T_{brazing}
AgCuInTi ₃	72.5–19.4–5–3	730	760	900
AgCuTi ₃	70.5–26.5–3	780	805	900
AgInTi1	98–1–1	950	960	1030
AgTi4	96–4	970	970	1030
CuSiAlTi _{2,25}	92.75–3–2–2.5	958	1024	1050
AuPdTi	91–7–2	1148	1203	1250
PdNiTi	59–38–3	1224	1236	1250
SnAgTi ₄	86–10–4	221	300	900
PbInTi ₄	92–4–4	320	325	900

Active Brazing of Ceramic Materials Active filler metals enable the joining of ceramic materials in a single-step process. Wetting occurs (as described in Section 6.2.8.1) via the surface-active elements (Ti, Zr, Hf, Ta, Nb) in the filler metal, whereby titanium has proved to be best suited and is used almost exclusively. The active metal content must be kept as low as possible in order to prevent the interfacial formation of brittle bonds. Most commercially available active filler metals are silver- or silver-copper-based. The compound joint then possesses sufficient thermal stability up to a maximum temperature of 500 °C. For higher temperature ranges, noble filler metals are available (Table 6.29). All active filler metals must be processed in high vacuum or in a pure inert gas atmosphere, in order to suppress the premature oxidation of the active metal [112] (Figure 6.115). For the brazing of ceramic-metal compounds, particular attention must be given to the design of the brazing joint and the temperature control during the brazing process, as thermally induced stresses caused by the different thermal expansion coefficients would result in premature failure of the part.

Brazing of Cemented Carbides Cemented carbides, as one of the most important cutting materials, is brazed to steel substrates for a number of applications. Cemented carbides are manufactured in a sintering process, and are principally comprised of WC (50–95 wt%), TiC and TaC (<45 wt%), and also (in part) of NbC, VC and Cr₃C₂. Notably, Co is employed as the binder metal. Although the carbides in the cemented carbide are not soluble in most metals, the wetting behavior of common silver and copper filler metals that results from their high fractions of metal-carbide bonding is satisfactory. As wetting-promoting and strength-enhancing components, the filler metals contain primarily nickel and manganese. Yet, by using ductile filler metals, it is possible to reduce the thermally induced stresses in a steel cemented carbide compound to an acceptable level, which is why the use of high-temperature filler metals is out of the question. Excessively high brazing temperatures may furthermore cause coarse granulation in the steel material. In order to limit the high costs of silver, zinc is often used instead, although this somewhat limits the ductility. Silicon is then added in small concentrations to these filler metals, not only to suppress the evaporation of zinc at higher temperatures (>900 °C) but also to improve the flow



Figure 6.115 Active-brazed ceramic-steel compound, brazed at 1000 °C for 10 min in vacuum. Illustration courtesy of IOT, RWTH Aachen.)

properties of the filler metals. Common cemented carbide filler metals are processed at brazing temperatures of 700–1100 °C; the hottest cemented carbide filler metal fusion is with so-called “Corson bronze” (Cu₂,5Ni), with a brazing temperature of 1100 °C.

The requirements for the greatest possible strength of the brazing joint at the lowest possible brazing temperatures, in order to prevent thermally induced stresses, are contradictory. Here, the use of layered filler metal, which has a copper core in the center of the filler metal foil, offers a solution. These filler metals can relax via the plastic deformation of the intermediate copper layer caused by cooling stresses. However, in order to control the brazing process it must be ensured that the copper layer will not dissolve as a result of excessive heating in the molten filler metal, and thus rendered ineffective.

Besides the goal of producing compounds of high strength, the choice of filler metal must also consider possible metallurgical interactions between the steel, filler metal, and cemented carbide. A basic problem in cemented carbide brazing with copper-based fillers onto steel with a low C content (<0.15%) is a possible η -phase formation in the cemented carbide. Due to the development of a carbon content gradient and the onset of carbon diffusion via the filler metal, this results in the decarburization of the cemented carbide. η -phases, having the composition Co₃W₃C or Co₆W₆C, may then form in the cemented carbide, leading to embrittlement of the cemented carbide. Although carbon does not dissolve in copper, diffusion can take place via the iron and cobalt bridges cleaved in the filler metal (Figure 6.116). Nevertheless, the η -phase formation can be controlled, first by the brazing parameters (holding time, brazing temperature), and second by the plating applied prior to the brazing process.

Examples of Applications for Armoring Applied by Brazing For applications in which the joint position between the component and the armoring is subjected to large mechanical forces, possibly in combination with operating temperatures of several hundred degrees Celsius, the armoring with cemented carbide and technical ceramics applied by brazing is frequently successful (Figure 6.117). For cutting tools, there are

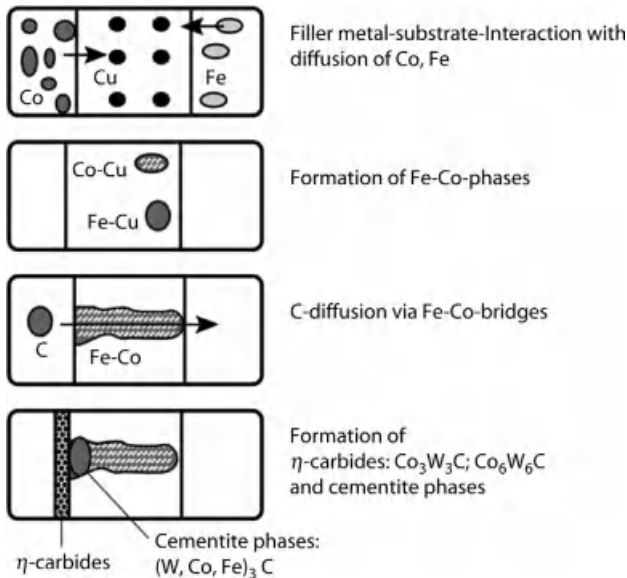


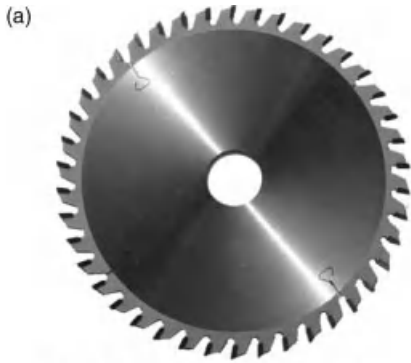
Figure 6.116 Schematic representation of η -phase formation during brazing of cemented carbide and low-carbon steel with copper-based filler metal.

numerous applications with cutting materials applied by brazing. Dredger teeth, for example, of gray cast iron used in the mining and also the construction industry, are frequently outfitted with cemented carbide segment armoring applied by brazing. In the area of motor construction, applications are found in the form of technical ceramics as armoring for metallic parts, such as rocker arms and tappets for valve operation in diesel motors. In both cases, the application of a Si_3N_4 plate by brazing vastly improves the wear behavior of the part.

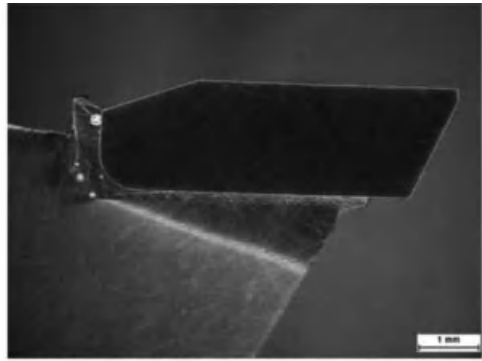
6.2.9

Thermo-Chemical Diffusion Treatment

With thermo-chemical diffusion treatments, the surface layer of a work piece is chemically altered by diffusion processes. In order to initiate the diffusion, these processes require high temperatures; typically, the components are exposed to temperatures between 350 and 1150 °C in a gaseous, liquid, or solid ambient medium. The ambient medium contains the required elements for diffusion into the boundary zone of the work piece, while the thermo-chemical heat treatment takes place in the furnace process. These cost-effective processes find application in mass production. Figure 6.118 provides an overview of thermo-chemical diffusion processes. Distinction can be made here between processes with and without follow-on heat treatment. A follow-on heat treatment is, in particular, necessary when the temperatures of the thermo-chemical diffusion process are so high that the required structure of the base material must be subsequently restored.



Saw blade equipped with hard metal
(Source: Westphalia)



Cemented carbide cutting edge laser brazed on a saw blade
(Source: Laserzentrum Hannover e.V.)



Si₃N₄ equipped tool for precision forging
(Source: IW, Leibniz Universität Hannover)



Si₃N₄ equipped rocker arm of a Diesel engine
(Source: IOT RWTH Aachen)



PCD equipped milling cutter
(Source: vhg camfacture AG, Ammerbruch)



CBN equipped hard metal cutting inserts
(Source: PVA TePla AG, Wetztenberg; Bro08)

Figure 6.117 Examples of applications for armoring applied by brazing to cutting materials. See individual panels for details.

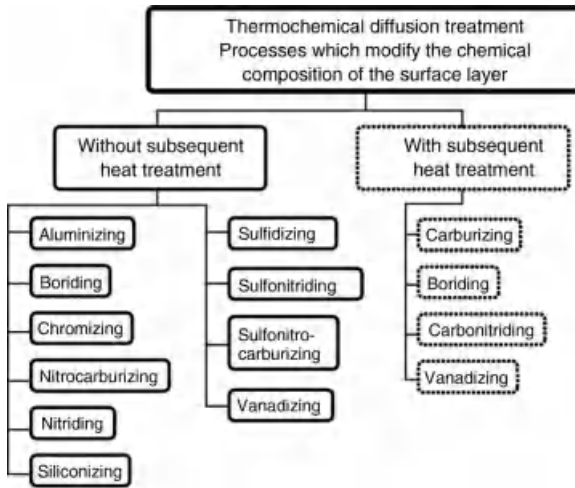


Figure 6.118 An overview of thermo-chemical diffusion processes.

The choice of the respective process is made in accordance with the type of loading and the base materials of the component (Table 6.30). For abrasive loading, the surface layer should possess a high degree of hardness, as well as sufficient toughness. In order to prevent adhesion between the two component surfaces, it is helpful to apply a dissimilar surface layer having a high degree of hardness to the friction partner. A diffusion layer stable against chemical reactions should be applied to protect against corrosive loading. In order to prevent thermal fatigue of the component, the surface layer should possess a high thermal stability and a homogeneous structure.

Whereas, aluminizing, chromizing and siliconizing are used predominantly in combustion engines to improve high-temperature corrosion stability, carburizing (case-hardening), nitriding, nitro-carburizing, boriding and chromizing find numerous applications with tribologic components.

6.2.9.1 Principles of Diffusion

Diffusion describes the time- and temperature-dependent transport of mass and material resulting from the migration of atoms, ions or molecules in gases, liquids and solids. The underlying cause of diffusion is the presence of differences in concentration, leading to a potential difference between the adjacent phases. Due to diffusion, the atoms strive to attain equilibrium. For surface treatment, this entails solid diffusion (Figure 6.119), as described by vacancy, interstitial, and exchange-diffusion (ringexchange). The vacancy mechanism (also known as the Wagner–Schottky mechanism) is enabled by the presence of lattice vacancies. Here, the diffusing atom leaves its normal lattice site and occupies a vacancy which either existed already at the start of diffusion, or has arisen due to atomic displacement

Table 6.30 Application of thermo-chemical diffusion processes according to base materials.

Thermo-chemical diffusion process	Process temperature (°C)	Penetration depth (coating thickness) (µm)	Base material			
			Low-alloyed steels	Cr steels	CrNi steels Ni/Co alloys	Ti alloy
Carburizing,	C	850–970	•	•	•	
Case-hardening		200–3000				
Nitriding	N	350–600	•	•		•
Nitro-carburizing,	N + C	50–800				
Carbo-nitriding		200–1000	•	•		
Boriding	B	800–1050	•	•	•	•
Siliconizing	Si	950–1000	•	•		•
Alitizing,	Al	750–1150	•	•	•	
Aluminizing		25–100				
Chromatizing,	Cr	980–1150	•	•	•	
Chromizing		25–100				

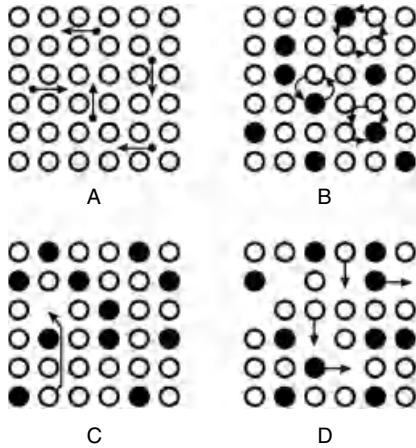


Figure 6.119 Volume diffusion in a solid. (A) Foreign diffusion, interstitial diffusion interstitially dissolved elements, in the substitution mixed crystal. (B) Ring exchange (rare). (C) Interstitial diffusion (with neutron bombardment). (D) Diffusion via vacancies (predominantly in metals).

during diffusion. With interstitial diffusion, foreign atoms migrate to neighboring interstitial sites. This mechanism occurs predominantly when the foreign atom dissolved in the interstitial atomic space has a much smaller atomic radius than the atoms of the matrix lattice. An example of this mechanism is the diffusion of carbon or nitrogen into iron. The exchange mechanism describes the direct exchange of two similar atoms (self-diffusion), or of two dissimilar atoms (foreign diffusion).

The various transposition processes are temperature- and concentration-dependent, and thus also depend on the stability of the respective medium or material. A material system constantly attempts to attain a state of equilibrium, in which the different materials have the same energy. This equilibrium state can be achieved by the introduction of energy to the material, often in the form of heat. The thermal or activation energy causes oscillations of the atoms in the material which, above a critical intensity, lead to transpositions among the atoms. Within a material system, these oscillations can lead to a rearrangement of the atoms, as a result of which the material system can attain a state of equilibrium. The rate of the transposition processes and the rate of diffusion are described by Fick's first law, where the diffusion depth x approximately follows the parabolic time rate law (Figure 6.120):

$$\text{Fick's first law : } j = -\frac{1}{A} \cdot \frac{\partial m}{\partial t} = -D \frac{\partial c}{\partial x}$$

- j : mass flux ($\text{mol cm}^{-2} \text{ s}^{-1}$),
- m : amount of diffusion material,
- D : Diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$),
- A : Diffusion cross-section (cm^2),
- $\partial c / \partial x$: Concentration gradient (atoms cm^{-4})

- m = Diffusion rate (atom/s)
 D = Diffusion coefficient (cm²/s)
 A = Diffusion cross-section (cm²)
 $\partial c/\partial x$ = Concentration gradient (atoms/cm⁴)

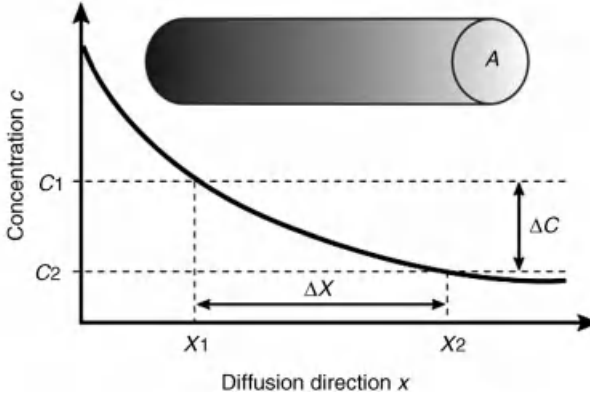


Figure 6.120 Graphical illustration of Fick's first law.

The term $\partial c/\partial x$ represents the concentration gradient at the point x ; the partial derivative is necessary, because the concentration is a function of both x and t . The negative sign is introduced in Fick's first law in order to give a positive mass flux in the x direction, even when the concentration gradient is necessarily negative in accordance with the problem posed. The diffusion coefficient D is a measure of the rate at which concentration equilibrium is achieved, and is a function of both temperature and applied energy. The required activation energy Q depends upon the material.

$$\text{Diffusion coefficient } D: \quad D = D_0 \cdot \exp\left(-\frac{Q}{RT}\right)$$

- D_0 : material-specific constant (cm² s⁻¹),
 Q : activation energy (J mol⁻¹),
 R : gas constant,
 T : absolute temperature (K).

Fick's first law describes the concentration equilibrium only for the case that stationary diffusion conditions exist in the material – that is, the concentration at a given point does not change in time. In materials engineering, however, the concentrations at the exchange surface are in fact a function of time (Figure 6.121).

For the calculation of non-steady diffusion processes, it is necessary to use Fick's second law, with the help of which it is possible to calculate also the position-dependent diffusion coefficient D :

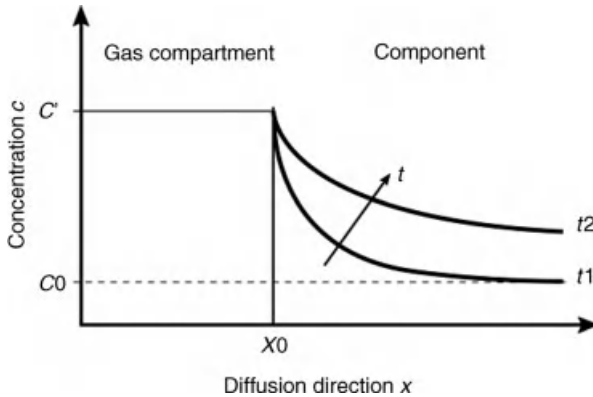


Figure 6.121 Change in concentration during the diffusion process over the time t (c_0 = concentration in the component at the onset of diffusion, the curves show the concentration with increasing time).

$$\text{Fick's second law : } \frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2}$$

The analytical solution of this differential equation is, however, a very complicated matter. Although, previously, many solutions have been offered, according to the boundary conditions, these will not be further pursued at this point.

6.2.9.2 Carburizing

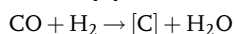
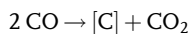
Carburizing, which is also referred to as case-hardening, is one of the oldest techniques used to improve the hardness and strength of steel components. Case-hardening is a process complex that consists of the process steps of carburizing and hardening. With case-hardening, steels with a low carbon content of <0.3 wt% (so-called “case-hardening steels”) are carburized in a carbon-emitting medium between about 850 and 970 °C, during which carbon diffuses into the surface layer of the steel. The chemical composition of the carbon-emitting medium, which usually is present in gaseous form, is held constant in order to ensure also a constant C concentration over time at the steel–ambient medium boundary surface. The diffusion rate of the carbon is determined primarily by the temperature and the concentration gradients between the carbon concentrations at the surface and in the core [120]. The duration of the carburizing process, and its success, are greatly influenced by the condition of the surface, such as the roughness, and the presence of residues of foreign substances and/or oxide layers. Either of the latter two factors will inhibit the diffusion of carbon into the component [121].

The carburizing process assumes the solubility of carbon in the iron lattice, which is greater with a face-centered cubic (fcc) lattice (2.1 wt%) than for a body-centered cubic (bcc) lattice, for which the maximum solubility of carbon is only 0.02 wt%. In order for a case-hardening steel to be hardened, it is first heated to temperatures at which the fcc γ -iron (austenite) is stable. Following diffusion of the carbon into the steel, the component is quenched in order to suppress the diffusion of carbon away

from the surface zone. During quenching, the fcc lattice is transformed to a bcc lattice (α -iron, ferrite), with the excess carbon remaining compulsorily dissolved in the bcc lattice. This results in a lattice distortion and, consequently, enhances the strength and hardness (martensite hardness) in the surface zone. The enrichment of the surface zone is limited to a carbon content of 0.6–0.9 wt%, as higher carbon contents would stabilize the austenitic fcc structure and lead to embrittlement due to cementite precipitation at the grain boundaries. In addition, strongly oversaturated micro-crack-susceptible martensite and residual austenite would be formed. Typically, with carburizing, case-hardening depths of 0.2–3 mm can be achieved, depending upon the process employed.

Today, three different processes are mostly employed for the carburizing process, namely salt-bath carburizing, powder-pack carburizing, and gas carburizing:

- With *salt-bath carburizing*, the steel is heated in a cyanide-free salt melt or in a cyanide bath. In the cyanide bath, carburizing occurs via the formation of cyanates, which decompose to carbon dioxide (CO_2) and C as a result of ensuing chemical reactions. By contrast, cyanide-free salt baths consist of mixtures of sodium carbonate and alkaline chlorides with SiC admixtures, in which chemical reactions set free the carbon monoxide (CO) required for carburizing. Due to the high diffusion rates, with these processes a short immersion time of 3 h is chosen, after which the surface layer is carburized to a depth of up to 0.8 mm. With excessively long immersion times, the salt mixtures will attack the work piece.
- With *powder-pack carburizing*, both inorganic (carbonates) and organic (wood and brown coal) materials are used. Here, activators (alkaline or earth alkaline carbonates) are usually added to the materials. The work piece is placed in the powder. As a result of the vaporization of carbon contained in the powder to CO, this is taken up directly by the surface of the work piece. The process is well suited for large carburizing depths and large work pieces in single-part production. The disadvantages of this method are the very considerable manual effort and the limited possibilities for influencing the carburizing conditions. The diffusion rate with this process is around 0.15 mm h^{-1} .
- With *gas carburizing*, specially prepared natural gas or long-distance gas is employed, to which a definite amount of CO or methane is added as a carrier gas compound supplying carbon:



Here, [C] is the carbon dissolved in the austenite, which is in equilibrium with the ambient gaseous atmosphere. The process is well suited for serial production, as the CO concentration in the gaseous atmosphere can be well controlled. With this method, diffusion rates of up to 0.4 mm h^{-1} can be obtained [122].

In order to obtain the required hardness on the component surface, the components are subsequently hardened. For this step, five different processes can be used

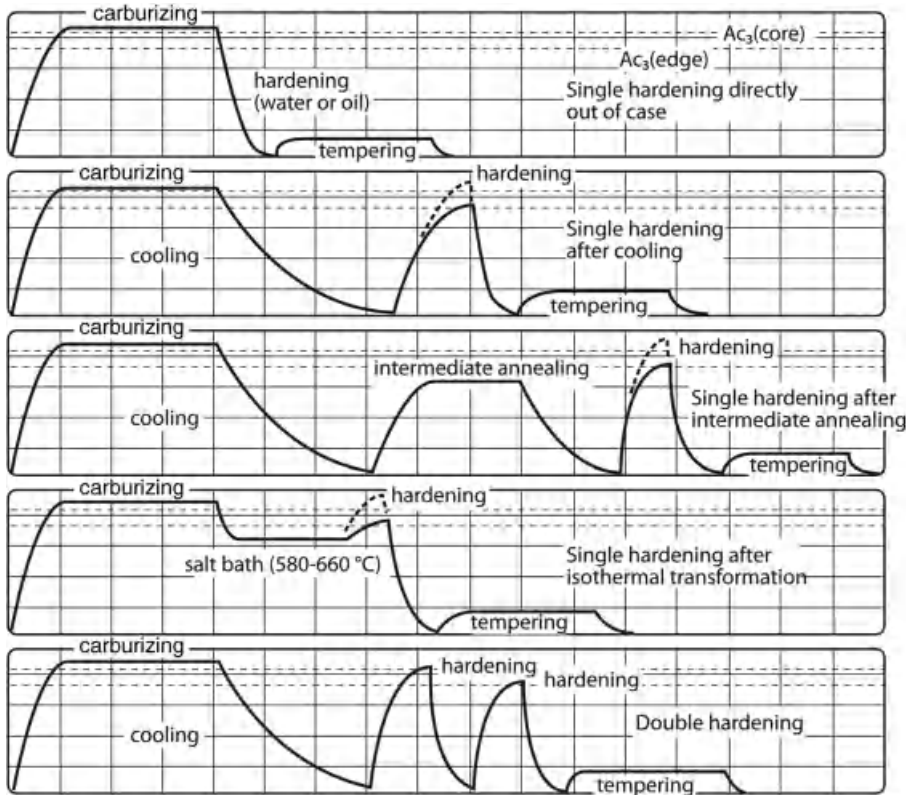


Figure 6.122 Time-temperature curves for case-hardening.

(Figure 6.122). The most commonly employed process is *direct hardening*, in which, following carburization, the component is quenched from the carburizing temperature with the use of widely different media. Another process is *single hardening*, which is utilized for carburizing within solid media. Following carburization, the component is again austenitized and then quenched. In this case, the toughness of the component can be increased by a structural refinement. Following an isothermal transformation, the components can be hardened in the perlitic phase. Here, the component is cooled from the initial temperature to a temperature in the range of the perlitic phase (600°C), and then kept at this temperature until the austenite is completely transformed. Following complete transformation, the component is again heated to the required hardening temperature, and then quenched. The last such process is *double hardening*, in which the component is hardened twice. With the first hardening, the component is quenched from the hardening temperature of the core material, and with subsequent hardening from that of the surface layer.

Due to the volume increase which results from the high carbon content in the surface layer, internal stresses arise therein, which have a positive influence on the fatigue strength of the work piece. The achievable hardness ($\sim 700\text{--}800\text{ HV}$) is less

Table 6.31 Typical case-hardened steels and examples of their applications.

Name	Material no.	Tensile strength (MPa)	Typical application(s)
C10	1.0301	460	Low core strength, moderate loading
Ck10	1.1121	460	e.g., levers, tappets, bushings, pressed and punched parts, typewriter parts, sewing machine parts
C15	1.0401	500	Low core strength
Ck15	1.1141	500	e.g., levers, joints, bushings, bolts, tappets, spindles, gearwheels, measuring tools
17Cr3	1.7016	600	e.g., machine parts, automotive parts, precision-cut parts for the automotive industry, gudgeon pins
20Cr4	1.7028	690	e.g., machine parts, automotive industry, transmission parts
20CrS4	1.7028	690	
16MnCr5	1.7131	800	e.g., gearwheels, ring gears and transmission gears, control parts, universal joints, shafts, bolts, tappets
20MnCr5	1.7147	1000	

than with other diffusion processes, for example, with the nitriding (1200 HV) or boriding (2000 HV) of steel. On the other hand, the hardness gradient with carburizing can be very well controlled; that is, the hardness gradient between the core and the surface layer can be well defined, and set according to the application. And not least, carburizing belongs to the most cost-effective diffusion methods. A selection of typical case-hardened steels and their applications is provided in Table 6.31. Classical areas of application for carburizing include gearwheels and camshafts.

6.2.9.3 Nitriding

In accordance with DIN EN 10052 Part 1, nitriding refers to the nitrogen-enrichment of a surface layer by thermo-chemical diffusion treatment. The first nitriding process to be investigated on a scientific basis was *gas nitriding* when, in 1923, Fry carried out an annealing below 580 °C in an ammonia gas stream which resulted in a “. . . previously unknown distortion-free surface hardening of steel and iron” [123]. Due to the treatment temperature, which lies between 350 and 600 °C, no structural transformation occurs during hardening, as does with austenitization [124]. Today, the main goals of nitriding are to improve the hardness, fatigue strength and endurance limit of Ti alloys and steels. The corrosion resistance of low-alloyed steels can also be improved by using this process.

In gas nitriding (the most widely used nitriding process), nitrogen is produced via the decomposition of ammonia (NH₃). Due to its small atomic radius, nitrogen is easily able to penetrate into the iron lattice and become incorporated into interstitial positions. The improvement in hardening results from both, the formation of nitrides (precipitation hardening), and dissolution of the nitrogen in the iron mixed

crystal (mixed crystal hardening). Fundamentally, all steels and cast iron are amenable to nitriding. The hardening effect can be considerably improved by adding small amounts of nitride-forming alloy elements, such as Cr, Mo, Al or V, as alloying components; the most effective of these is aluminum. For the nitriding process, special steels (so-called “nitriding steels”) have been developed, the alloy compositions of which are matched to the nitriding process (Table 6.33). Nitriding steels are characterized by a chromium content of 1.0–3.5 wt%, and contain smaller concentrations of Al, V, and Mo (and occasionally also Ni). The C content may exceed the critical limit of 0.3 wt%, since with nitriding there is no danger of martensite formation in the base structure. In contrast to carburizing, the component after nitriding no longer needs to be quenched, which means that crack formation in the more brittle boundary zone is avoided. The nitrided layer can be divided into two basic regions: the compound layer and the diffusion zone (Figure 6.123), both of which grow into the base material.

According to its chemical composition, the resulting compound layer can be divided into the γ' -layer (Fe_4N) and the ϵ -layer (Fe_{2-3}N). Depending on the duration of nitriding, the compound layer will in general have a thickness of 25 μm , while the underlying diffusion layer can attain a depth of up to 800 μm . In the diffusion zone, N atoms and also fine nitrides are interstitially incorporated in the form of nitride precipitations. The mechanical properties of the diffusion zone are primarily determined by the type, form, and distribution of the nitride precipitations from the alloying elements (special nitrides) [126] (Figure 6.124).

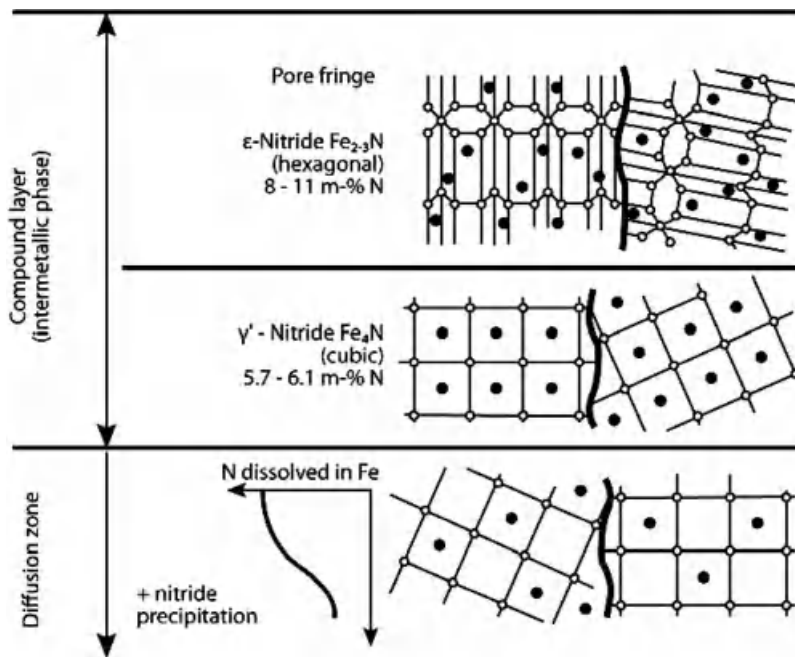


Figure 6.123 Schematic representation of the structure following nitriding [125].

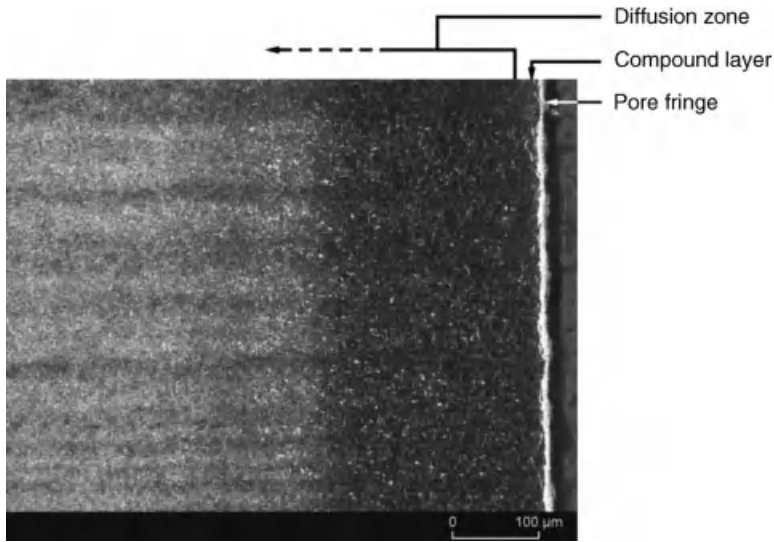


Figure 6.124 Polished cross-section of a plasma-nitrided 31CrMoV9. Illustrations courtesy of IOT, RWTH Aachen.

The compound and diffusion layers are characterized by different properties, as a result of which they permit a wide range of applications. The properties of the two different layers and their behavior(s) during use are shown schematically in Figure 6.125. The most important property is the high degree of hardness of the compound layer, as a result of which this layer possesses high resistance to abrasive wear. Normal hardness values which can be obtained here are 700–900 HV0.01 with non-alloyed steel, and 1000–1300 HV0.01 with alloyed steel [125].

Over the course of time, many nitriding processes have been developed, all of which have differed in terms of the state of aggregation of the nitrogen present. These have included the processes of salt-bath nitriding, gas nitriding, plasma nitriding, and powder-pack nitriding. Details of these nitriding processes, together with their process-specific parameters, are listed in Table 6.32.

In the case of powder-pack nitriding, calcium cyanamide (CaCN_2) may be used, which sets ammonia gas free as a result of the temperature acting on it. As with gas nitriding, the ammonia is broken down into nitrogen and hydrogen [127], after which the nitrogen diffuses into the base material. With salt-bath nitriding, either sodium cyanate (NaOCN) or potassium cyanate (KOCN) are used; these decompose on the surface of the steel to form cyanide, carbonate, and adsorbed nitrogen (Figure 6.126). In order to prevent any carry-over of the highly toxic bath components, the tools or component parts must be intensively washed after treatment. In recent years, based on concerns for adverse effects on the environment, industrial salt-bath nitriding has been increasingly replaced by gas and plasma nitriding [124].

The nitriding process offers certain advantages. First, the treatment causes no appreciable changes in volume, so that the work pieces can be produced net shaped before nitriding, and also no longer require any post-processing. The hardness of the

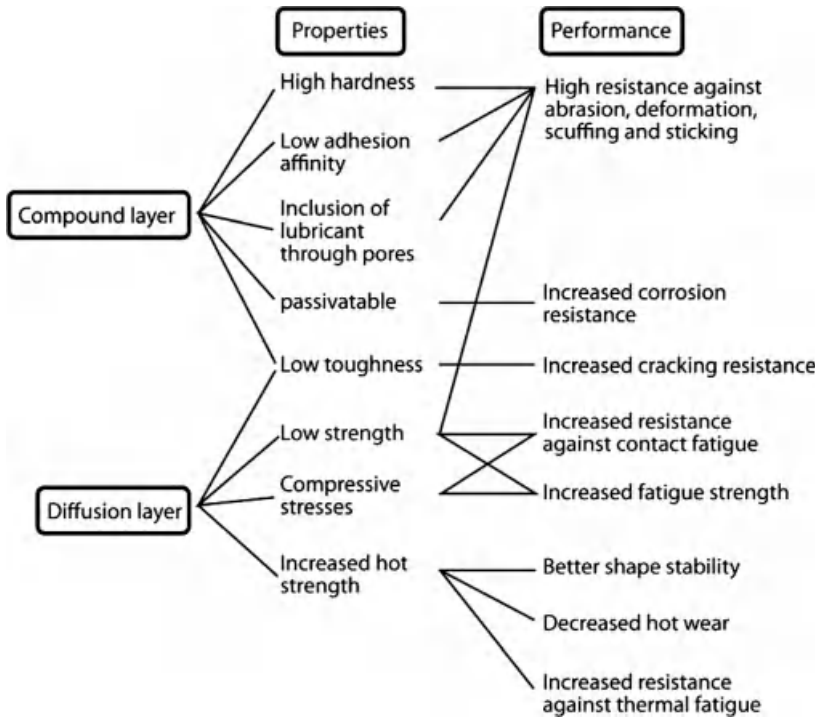


Figure 6.125 Properties of nitrided surface layers, and their behavior in use [125].

nitride layer is considerably greater than the martensite hardness that could be achieved, which means that the surface will be extremely wear-resistant. Whilst the fatigue strength of dynamically loaded components can be greatly improved by nitriding, the corrosion resistance can be either improved or worsened, depending upon the nitrided work piece. For non-alloyed and low-alloyed steels, nitriding improves the corrosion resistance; however, the nitriding of stainless steels can result in a reduced corrosion resistance, as the chromium fraction serving for passivation is transformed to chromium nitride as a result of the nitriding process [128].

Table 6.32 Nitriding processes, with their process-specific parameters.

Nitriding process	Nitrogen carrier	Process data	
		Temperature (°C)	Time (h)
Salt-bath nitriding	Sodium-, potassium cyanate	550–570	0.5–10
Gas nitriding	Ammonia	500–520	20–100
Plasma nitriding	Nitrogen, ammonia	350–600	10–50
Powder-pack nitriding	Calcium cyanamide	550–570	3–25

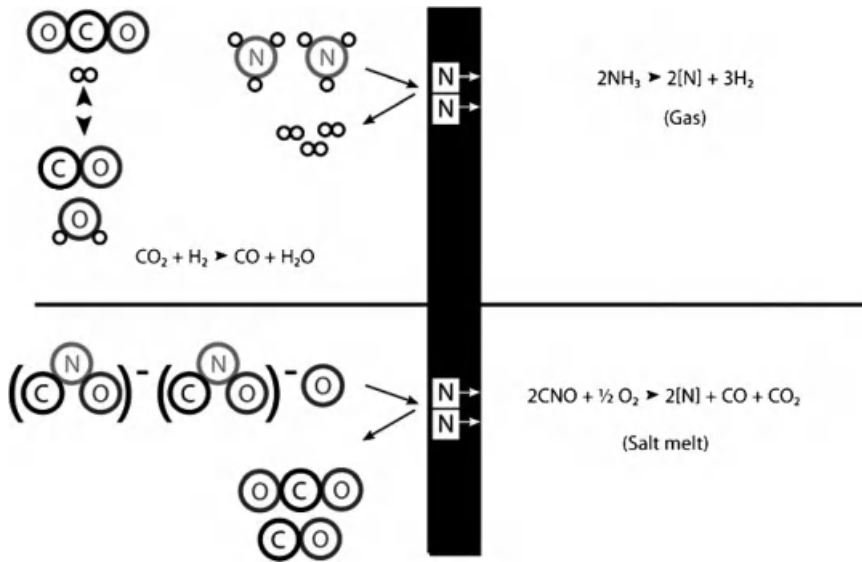


Figure 6.126 Reaction processes on the material surface with gas and salt-bath nitriding.

Table 6.33 Typical nitrided steels, and examples of their applications.

Name	Material no.	Tensile strength (MPa)	Hardness (HV)	Application
34CrAlMo5-10	1.8507	1000	950	Super-heated steam load-bearing valve parts up to 80 mm thickness, 350–500 °C operating temperature
41CrAlMo7-10	1.8509	980	950	Super-heated steam load-bearing valve parts up to 100 mm thickness, 350–500 °C operating temperature
34CrAlNi7-10	1.8550	1470	950	Heavy machine parts, piston rods, plungers and spindles with especially large dimensions and diameters
31CrMoV9	1.8519	1.230	800	Super-heated steam load-bearing valve parts, valve spindles, crankshafts up to 100 mm thickness
31CrMo12	1.8515	1130	800	Heavy, machine parts subject to wear, up to 250 mm thickness

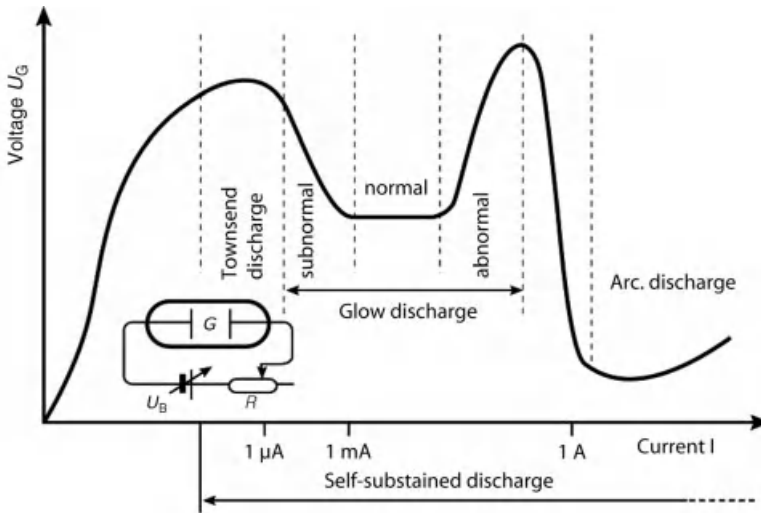


Figure 6.127 Current–voltage curve for a glow discharge. Illustration courtesy of U. Huchel.

For the plasma required with *plasma nitriding*, a voltage of 300–800 V is applied between the component (cathode) and the container wall (anode), in vacuum. Depending on the conducting capacity of the gases utilized, a certain current density will result from the applied voltage. The relationship between the voltage and the current of a glow discharge, which dissociates and ionizes the nitrogen, is illustrated in Figure 6.127. The material is bombarded with nitrogen ions at low pressure (10–1000 Pa) and a high electric field strength. The working range used for plasma nitriding is that of anomalous discharge.

Until the early 1980s, water-cooled plants in which the discharge was fed from a DC voltage (cold-wall technique) constituted the “state of the art” of this technology. However, the serious disadvantages of this process technology were the large temperature differences within a batch and, consequently, the wide scatter in the result of treatment, together with a relatively low charging density, high energy consumption, and a close coupling of the thermal and chemical processes. Subsequently, significant progress was achieved with the use of a pulsed discharge. Pulsing reduces the energy influx to the plant and improves the uniformity of temperature in the batch such that, today, all industrial plants are equipped with this pulsed technology. Typical values for the pulse duration are in the range of 50–100 μs , while the pulse repetition time is in the range of 100–300 μs [125].

Figure 6.128 shows, schematically, a plasma nitriding process. Following closing off of the plant facility, a vacuum is generated and the components are heated from the wall heating (hot-wall technique). The pump-down time to the final pressure (e.g., 10 Pa) is about 10–15 min, after which the component surfaces are activated in a hydrogen plasma in the form of a “particle bombardment” (sputtering). As any passive layers are removed, even steels with a high chromium content can be

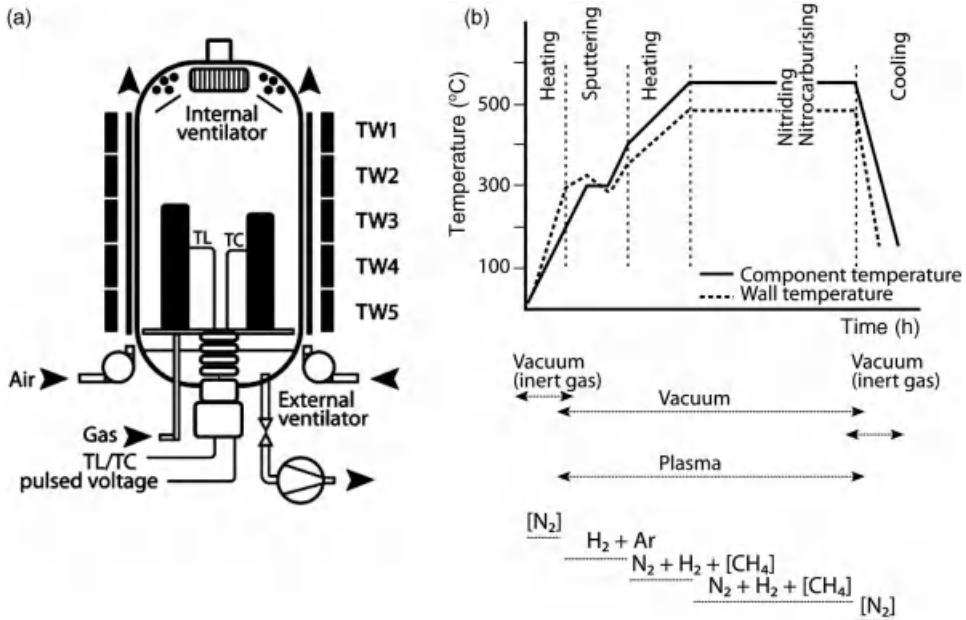


Figure 6.128 Schematic representation of the plasma nitriding process. (a) Hot wall reactor for plasma nitriding. TL/TC = thermocouples. TW1 to TW5 = external heating; (b) Plasma nitriding cycle. Illustration courtesy of U. Huchel.

nitrided. By using the plasma energy and wall heating, the components are heated to the nitriding temperature, and then nitrided. When the specified holding period of the nitriding process has been reached, the wall heating is switched off, and the batch then cooled using external cooling fans. The additional use of rapid cooling units (gas–water heat exchangers) is also possible since, in certain cases, cooling in the plasma is expedient.

With present-day plant technology, plasma nitriding is characterized by its high reproducibility, narrow tolerances with regards to treatment, and environmental acceptability (Figure 6.129; Table 6.34). In contrast to bath and powder-pack nitriding, the exact process control enables a low surface roughness to be obtained. Moreover, by using plasma nitriding the layer structure can be better matched to the loading than with the other nitriding processes. For example, an optimized process control would enable a thin compound layer with a high nitriding hardness depth to be obtained, and permit the combination of a low adhesion tendency and increased temperature stability. The main disadvantage of the plasma process is the need for a well-defined charging of the parts to be treated. In addition, as the plasma cannot penetrate into gaps smaller than 0.6–0.8 mm, the nitriding of bulk material is not possible using this method. Hence, bath nitriding is generally used for nitriding bulk materials.

Due to the brittle properties of the compound layer, further coating of the nitrided components (e.g., with PVD or PE-CVD processes) is virtually impossible, as the

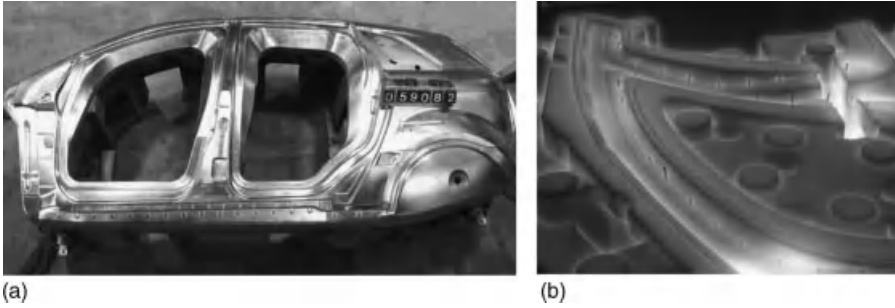


Figure 6.129 (a) Plasma-nitrided side panel tool of GGG70L; (b) Side panel tool during the nitriding process. Illustrations courtesy of Oerlikon Balzers VST.

bonding of the deposited layer would not be sufficient. However, in recent years process control during plasma nitriding has developed sufficiently that, with a suitable choice of parameters, the compound layer can be suppressed during nitriding such that it is now possible to coat the components following nitriding. This coating is applied immediately following the nitriding process, as the plasma plants can be used for both plasma nitriding and PVD or PE-CVD coating. These processes are referred to as “duplex” processes, the main advantage of such a process combination being the ability to define the hardness gradient. Typically, a hard boundary zone of 700–1300 HV will provide a better supporting effect for the harder material layer (ca. 2000–3600 HV) (Figure 6.130).

6.2.9.4 Nitro-Carburizing

Nitro-carburizing, or carbonitriding, is the more recent designation for short-term nitriding; that is, in addition to nitrogen atoms, carbon atoms also diffuse into the

Table 6.34 Typical characteristics of plasma-nitrided steels [124].

Description: -steel	AISI SAE	DIN	Name	Surface hardness (HV2)	Nitriding hardness depth (μm)	Compound layer thickness (μm)
Structural	1020	1.0037	St 37-2 G	150–350	300–800	4–10
Carbon	1045	1.0503	C 45	350–500	300–800	4–15
Case hardening	5115	1.7131	16MnCr5	550–700	300–700	6–10
Tempering	4140	1.7225	42CrMo4	550–650	200–600	4–8
Nitriding	A355	1.8550	34CrAlNi7-10	900–1100	200–500	2–10
Hot-work	H13	1.2344	X40CrMoV5-1	900–1200	100–300	2–10
Cold-work	D2	1.2379	X153CrMoV12	900–1250	100–200	—
High-speed	M2	1.3343	HS 6-5-2	1000–1250	5–100	—
Stainless	316	1.4571	X6CrNiMoTi 17-12-2	950–1300	50–100	—

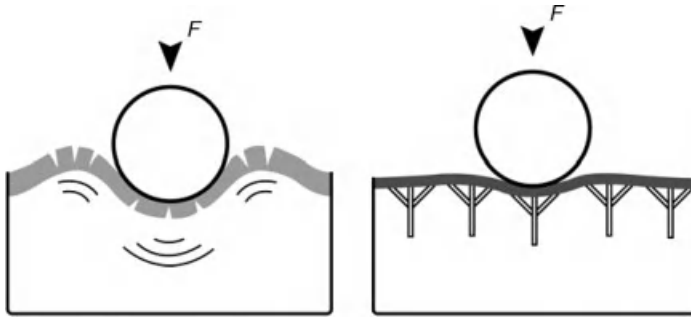


Figure 6.130 Improving the supporting effect with duplex processes, combining plasma nitriding with PVD or PECVD coatings.

material, thus considerably shortening the process time. While gas nitriding requires between 20 and 100 h for completion, nitro-carburizing at higher temperatures can be performed in less than 10 h, and frequently in 2–3 h [128]. This process is used principally to modify the surface layers of low-alloyed steels. Nitro-carburizing can be divided into two different processes: (i) the gas process, in which ammonia reacts with carbohydrates; and (ii) the bath process. As with nitriding, here again cyanides or cyanates are employed, to which ambient oxygen, CO and nitrogen are mixed during nitro-carburizing. The bath process is performed at temperatures of 750–900 °C, and the gas process at temperatures of 600 °C.

During nitro-carburizing or carbo-nitriding of the treated work piece, an approximately 15 µm-thick layer of ϵ -carbonitride is formed, beneath which an approximately 1 mm-deep diffusion zone is found. Following nitriding, the treated components are quenched with oil or water, in order that a martensitic structure is formed in the diffusion zone. Even when the size of the component is increased during carbo-nitriding, the components should not be post-processed, in order that the outermost compound layer – which may be responsible for a high resistance to adhesive wear and therefore will lessen the tendency to scuffing and fusing to a metallic counterbody – remains intact. The formation of carbonitrides protects the surface against abrasive wear [128].

In order to match the surface layers of the work pieces to the requirements, the loading of the components must first be exactly defined; only then can the required processes be correctly chosen. Several types of loading, in combination with the base materials foreseen and the possible diffusion processes for surface layer treatment, are listed in Table 6.35. The expected hardness for several substrate materials are given in Table 6.36.

In order to improve the corrosion resistance, frictional and gliding properties, or even for decorative reasons, nitro-carburized surfaces can be subsequently oxidized. The prerequisite here is the presence of a sufficiently thick compound layer, which preferably consists of the diffusion-dense ϵ -carbonitride phase. Together with the compound layer, a magnetite layer (Fe_2O_3) on only 1–2 µm thickness will offer an excellent protection against corrosion [124].

Table 6.35 Diffusion processes chosen according to type of loading.

Type of loading	Material	Process
Adhesion wear “scuffing”	Steels, cast iron, sintered steels	Nitro-carburizing, (nitriding)
Abrasion wear	Steels, cast iron, sintered steels	Nitro-carburizing
(score grooving)	Nitrided steels	Nitriding
Rolling wear	Nitrided steels	Nitriding
	Alloyed tempering steels	Nitriding, (nitro-carburizing)
Tribo-oxidation (“frictional corrosion”), corrosion	Steels, cast iron, sintered steels	Nitro-carburizing
Fatigue strength	Nitrided steels	Nitriding
	Steels, cast iron, sintered steels	Nitro-carburizing

6.2.9.5 Boriding

With boriding, hard surface layers are produced as a result of boron diffusing into the metallic surface. Viewed historically, the boriding process is quite new, yet today – due to its simple application – it is frequently employed industrially with both steels and alloys of Co, Ni and Ti. The process time is, as a rule, between 1 and 12 h.

The boriding process, which generally takes place in the temperature range of 800–1050 °C, can be carried out with various boron-donating media. In industry, gaseous, liquid and solid media are used. With the use of gaseous media a boriding agent (e.g., BF₃, BCl₃, BBr₃ or B₂H₆) is led through an inductively heated component or a component heated in the tube furnace, so that layer formation takes place on the surface of the component. The boron, together with the metal (Me) of the work pieces, forms stable borides of the types MeB and Me₂B, which possess very high degrees of hardness, depending upon the base material and different boriding depths:

- Steel : ~ 1600–2000 HV $s = 10\text{--}350\ \mu\text{m}$ (up to 500 μm possible)
- Ni-base alloy : ~ 2800 HV $s \leq 300\ \mu\text{m}$
- Ti-base alloy : ~ 4000 HV $s = 10\text{--}20\ \mu\text{m}$

Increasing hardness is coupled with an extreme increase in abrasive wear resistance. On non-alloyed and low-alloyed steels, a single-phase boride layer of

Table 6.36 Surface hardnesses following 2 h period of nitro-carburizing [121].

Steel type	Hardness (HV10)
Non-alloyed steels	300–400
Alloyed tempering steels	500–650
Roller bearing steel	about 600
Alloyed case-hardening steels	600–700
Nitrided steels	800–950
Hot-work steels	ca. 900
High-speed steels hardened	1200–1400

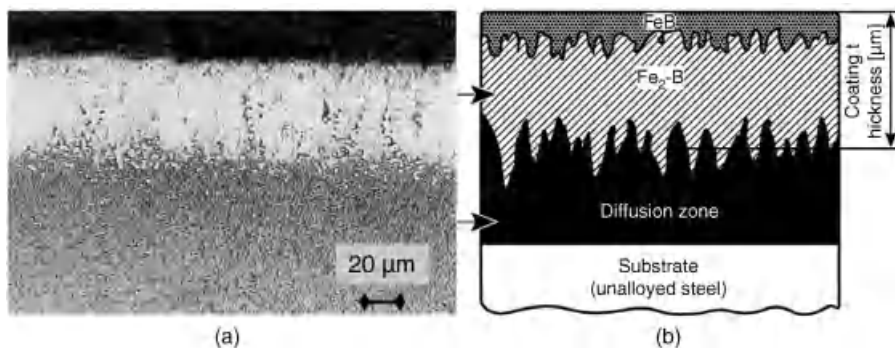


Figure 6.131 (a) Polished cross-section of a borided 100Cr6 roller bearing steel; (b) Schematic representation of the boride layer.

Fe_2B is formed, whereas on high-alloyed steels a two-phase boride layer forms, which is linked in toothed form to the base material, as illustrated in Figure 6.131.

When using a liquid medium, layer formation takes place as a result of the immersion of a component in the fused salts, for example, $\text{B}_4\text{C} + (\text{NaCl}/\text{BaCl}_2/\text{NaBF}_7)$. In another process variant, a component immersed in an aqueous solution ($\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{O}$) is inductively heated [129]. With the use of solid media, pastes (e.g., $\text{B}_4\text{C} + \text{Na}_3\text{AlF}_6 + \text{ethyl silicate}$ or ferroboron + $\text{Na}_3\text{AlF}_6 + \text{water glass}$) are generally applied to the component surface, and then heated inductively. A further possibility involves placing the components for the boriding treatment, together with the corresponding powder (amorphous boron, ferroboron or B_4C , in each case with an activator), in a closed container which is then heated in a batch furnace. With paste boriding under a protective gas, single-phase Fe_2B boride layers can be produced, that have a higher ductility than the two-phase FeB and Fe_2B layers produced during powder-pack boriding. This second FeB phase causes embrittlement, which can lead to delamination of the layer; the paste, therefore, yields improved properties in the boride layer. Alternative boriding agents, together with the corresponding boriding processes, are listed in Table 6.37.

Although, in general, the boride layers are applied to net shaped surfaces, the surface qualities may be worsened as boriding is a coating process. With the boriding process, which lasts up to 12 h, layer thicknesses of up to 500 μm can be achieved. As can be seen in Figure 6.132, the growth rate of these layers depends upon the base material of the work piece and the boriding temperature. Due to the high degree of hardness and the brittle properties, post-processing is difficult and must be executed as hard machining (grinding or hard turning). The components to be coated are intensively heated during the process, which may result in deformation [130]. An influence of boriding on the structure of the substrate material can be corrected by follow-on heat treatment. Boride layers on steels are characterized by their very high resistance to abrasion and adhesion, in so far as oxidic reaction layers are formed. Due to the high surface pressures which occur, however, the use of boride layers in connection with rolling loading is unfavorable [129]. Moreover, borided components possess a lower toughness and are therefore sensitive to shock and impact loading.

Table 6.37 Overview of boriding agents and the corresponding boriding processes.

State of aggregation of the boriding agent	Composition	Process
Gaseous	BF ₃ , BCl ₃ , BBr ₃ pure or + H ₂ B ₂ H ₆ + H ₂ (CH ₃) ₃ B/(C ₂ H ₅)B	The boriding agent, in gaseous form at the treatment temperature, circulates around the work piece, which is heated inductively or in a tube furnace
Liquid	Na ₂ B ₄ O ₇ (+ NaCl/ + B ₂ O ₃) HBO ₂ + NaF	Electrolysis: work piece cathodic, graphite or platinum electrode anodic
	Boron or solid boron compounds in fluoride melts	Electrolysis: work piece cathodic, boriding agent anodic, fluoride as bath
	B ₄ C (+ NaCl/ + BaCl ₂ / + NaBF ₄) Na ₂ B ₄ O ₇ + B ₄ C	Immersion in the fused salt
	Aqueous solutions of Na ₂ B ₄ O ₇	Inductive heating in aqueous solution
Solid	B ₄ C + Na ₃ AlF ₆ + ethyl silicate Ferroboron + Na ₃ AlF ₆ + water glass	Inductive heating following application of a paste
	Amorphous boron (+ activator) Ferroboron (+ activator)	Heating in batch furnace; packing in powder or (partially) in paste
	B ₄ C + activator	

Boriding finds widespread application in the general area of machine construction, for example, in tractor manufacturing, crude oil drilling (bushings, pistons, bearing parts), and the treatment of hot-work steel materials (punch, re-shaping, and die-casting tools) [131]. For manufacturing reasons, the area of application for borided barrel extruders and cylinders is limited to small diameters and lengths. The service lives of borided machine parts can, depending on the application, be extended by a factor of between 2 and 13 [122]. Furthermore, extrusion dies (so-called “glass levels”) for bottle production are borided because of the good anti-adhesive properties and the high abrasion resistance of the layer at high temperatures (Figure 6.133).

6.2.9.6 Chromizing

Chromium coatings are applied to pretreated, mostly shot-blasted, steel component surfaces and extremely temperature-stable materials, in order to improve their corrosion and wear resistance. With these materials, the major concern is with austenitic steels and steels with a low carbon content. The chromium layers are

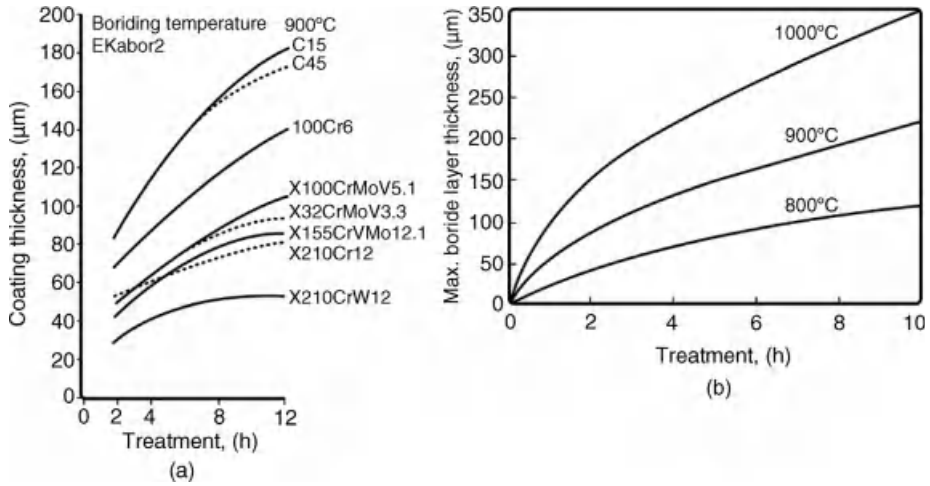


Figure 6.132 Dependence of the boriding layer thickness on (a) the boriding temperature and (b) the base material of the work piece. Illustration courtesy of BorTec GmbH.

formed by the precipitation and diffusion of chromium into the surface of the substrate. The boundary zone can be enriched with up to 35 wt% chromium. For chromizing, both gaseous-phase and powder-pack coatings are possible. With powder-pack coating, the powder consists of a donor (chromium metal or a



Figure 6.133 Borided extrusion dies (glass levels) for glass bottle production. Illustration courtesy of BorTec GmbH.

chromium alloy), an activator (ammonium chloride, NH_4Cl), and a diluting agent (aluminum oxide). During heating of the coating powder to the coating temperature ($980\text{--}1150^\circ\text{C}$), chromium chloride (CrCl_2) is formed, which then decomposes with the formation of free chromium halogenides. These halogenides are deposited on the surface and diffuse into the component, where they react with the metal of the base material. The chlorine gas (Cl_2) set free during this process is then again available for the further transport of Cr to the surface in the form of CrCl_2 :

- 1) $\text{Cr} + 2 \text{NH}_4\text{Cl} \rightarrow \text{CrCl}_2 + 2 \text{NH}_3 + \text{H}_2$
- 2) $\text{CrCl}_2 + \text{Me} \rightarrow \text{CrMe} + \text{Cl}_2$
- 3) $\text{Cl}_2 + \text{Cr} \rightarrow \text{CrCl}_2$

With the chromizing of low-alloyed steels, relatively thick layers of more than $100\ \mu\text{m}$ are formed; such formation is not hindered by the chromium carbide formed. These chromized layers, which comprise build-up and diffusion zones, serve up to 800°C as protection against oxidation. In contrast, for steels with a higher carbon content ($\text{C} > 0.45\%$), iron chromium carbide $(\text{Cr,Fe})_7\text{C}_3$ and, in part, also $(\text{Cr,Fe})_{23}\text{C}_6$ forms, with a thickness of up to $50\ \mu\text{m}$ and a hardness of $1400\text{--}2000\ \text{HV}\ 0.2$. This high degree of hardness provides a high resistance to abrasive wear. The inter-metallic chromium–iron compounds can achieve a high degree of protection against oxidation at high temperatures. Chromized layers on highly heat-resistant nickel materials offer protection against corrosion and oxidation up to 850°C . In both cases, the chromium reacts with ambient oxygen, forming a stable protective Cr_2O_3 layer on the surface. At higher temperatures, the application of alitized layers or chromium alitized layers is recommended. Chromized layer thicknesses on highly heat-resistant nickel superalloys are in the range of 25 to $100\ \mu\text{m}$.



Figure 6.134 Chromized ball valve with a diameter of about $80\ \text{cm}$. Illustration courtesy of Chromin, NL.

Chromizing, as a coating process [126, 129], produces layers that protect against abrasive wear, an example being that of tool manufacture. For carbon steels, this offers an alternative to nitrided coatings since, as the chromizing temperatures may be as high as 1060 °C, warping-endangered components tend to undergo deformation. For this reason, it is always necessary when employing this method of surface improvement to recognize the temperature stability of the base material. Chromized coatings are applied to net shaped surfaces, and are not post-processed. Coatings with a high concentration of chromium may be brittle and, for a larger layer thickness, tend to undergo cracking. However, such brittleness can, to a large extent, be reduced when a follow-on annealing process is employed [126].

Because a layer which is resistant to wear and corrosion can be produced with this process, chromized machine elements are used, for example, in textile processing in the area of thread guidance or as eyelets, where lubricants cannot be used. Pump parts, such as ball valves (Figure 6.134), or also bulk goods, such as bolts and screws, are also chromized.

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7

Lubricants

7.1

Lubricants and their Market

In times when saving energy and resources and cutting emissions have become central environmental matters, lubricants continue increasingly to attract public awareness. Scientific research has shown that an important volume of money could be saved in terms of energy in Western industrialized countries if current tribological knowledge—that is, the science of friction, wear, and lubrication—were to be applied only to lubricated processes (see Chapter 1). Apart from important applications in internal combustion engines, vehicles and industrial gearboxes, compressors, or hydraulic systems, there exist a vast number of other applications, many of which require specifically tailored lubricants. In fact, between 5000 and 10 000 different lubricant formulations are necessary to satisfy more than 90% of all lubricant applications. If one thinks of lubricants today, the first type to come to mind are mineral oil-based variants, and mineral oil components continue to form, quantitatively, the most important foundation of lubricants. Petrochemical components, and increasingly derivatives of natural, harvestable raw materials from the oleochemical industry, are finding increasing acceptance because of their environmental compatibility and some technical advantages. On average, lubricating oils, which account quantitatively for about 90% of lubricant consumption, consist of about 93% base oils and 7% chemical additives and other components (between 0.5% and 40%). Today's lubricants may be classified into two major groups: automotive lubricants and industrial lubricants. *Industrial lubricants* can be subdivided into industrial oils and industrial specialties which, in this case, are principally greases and metalworking fluids. *Process oils* are often included in lubricant statistics; these are oils which are included as raw materials in many processes but mainly serve as plasticizers for the rubber industry. The only link between process oils and lubricants is that they are mineral oil products resulting from the refining of base oils, although they often distort lubricant consumption figures. Although details of process oil are not provided in this book, in order to provide a degree of comparison they have been included in the following lubricant statistics. In 2007, a total of 37.2 million tons of

Global Lubricant Demand 2007: 37.2 mn t

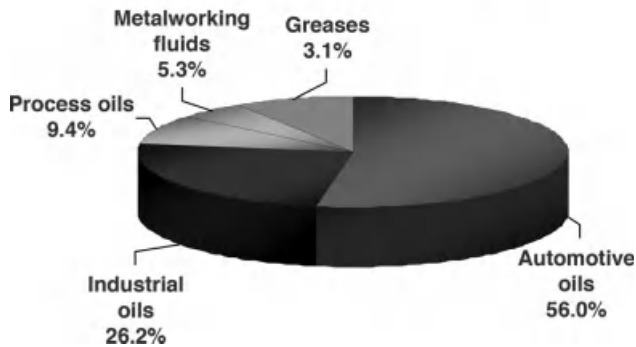


Figure 7.1 Segment break down of the global lubricant market in 2007. Illustration courtesy of A. Gosalia, Fuchs Petrolub AG [1].

lubricants was consumed worldwide (56% automotive oils, 35% industrial lubricants, including related specialties, and 9% process oils). Among the total industrial lubricants, 37% were hydraulic oils, 7% industrial gear oils, 31% other industrial oils, 16% metalworking fluids (including temporary corrosion preventives, the multipurpose function of which often includes lubrication), and 9% greases. The segmental and regional breakdowns of the global lubricant market are shown on Figure 7.1 and Table 7.1.

Figure 7.2 shows the 2007 *per capita* consumption for various regions. Notably, the North Americas *per capita* consumption is double that of Western Europe.

In almost all areas, products now not only have a longer life but also offer a greater performance; that is, specific lubricant consumption has declined, but specific revenues have increased noticeably. This is also confirmed by the volumetrically very important group of engine oils: the doubling of requirements with extended oil-change intervals during recent years has quadrupled the cost of such oils. The efforts to increase the life of lubricants are not based on the wish to reduce lubricant

Table 7.1 Regional development of the global lubricant market.

Region	2007(in kT)
North America	7835
Latin America	3395
Western Europe	4645
Central/Eastern Europe	5060
Near Middle East	1855
Africa	1935
Asia-Pacific	12 445
WORLD	37 170

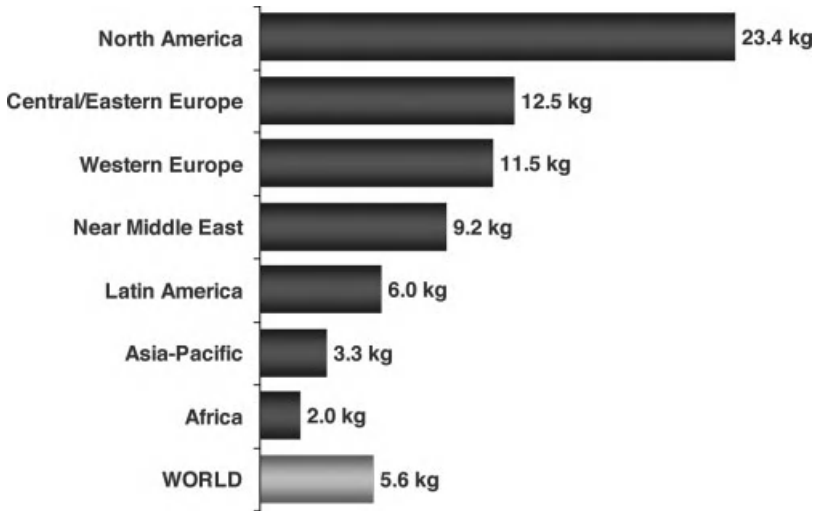


Figure 7.2 The *per capita* consumption of lubricants in 2007 [1].

costs; much more important is the reduction of service and maintenance costs which result from periodic oil changing or regreasing. As about 50% of the lubricants sold worldwide end up in—and thus pollute—the environment, every effort is made to minimize spillages and evaporation. An example of this is diesel engine particulate emissions, about one-third of which are caused by engine oil evaporation. These high lubricant losses into the environment were behind the development of the environmentally friendly lubricants that are extensively described in this book. A further incentive to reduce specific consumption is the ever-increasing cost of disposal or recycling of used lubricants. Yet, this again creates new demands on lubricants because reduced leakage losses means less topping-up and less refreshing of the used oil. Consequently, the new oils must display a good aging stability. Bearing in mind the growth potential in Asia (where the *per capita* consumption in some areas is extremely low) and the continuing reduction in volumes (or even stagnation) in Western industrialized countries, a modest global growth is forecast overall which has been estimated as 1.0% per year for the next 10 years. The growth in value will be more pronounced because the rapid globalization of technologies will promote high-value products, even in the new lubricant markets such as China, India, or Indonesia, and because the machinery and plant used in these countries will be similar or identical to those used in the developed industrialized countries.

Worldwide, there are some hundreds of lubricant manufacturers, ranging from large to small. On the one hand, there are vertically integrated petroleum companies, the main business objective of which is the discovery, extraction, and refining of crude oil, with lubricants accounting for only a very small part of their oil business. There are at present about 180 such national and multinational oil companies

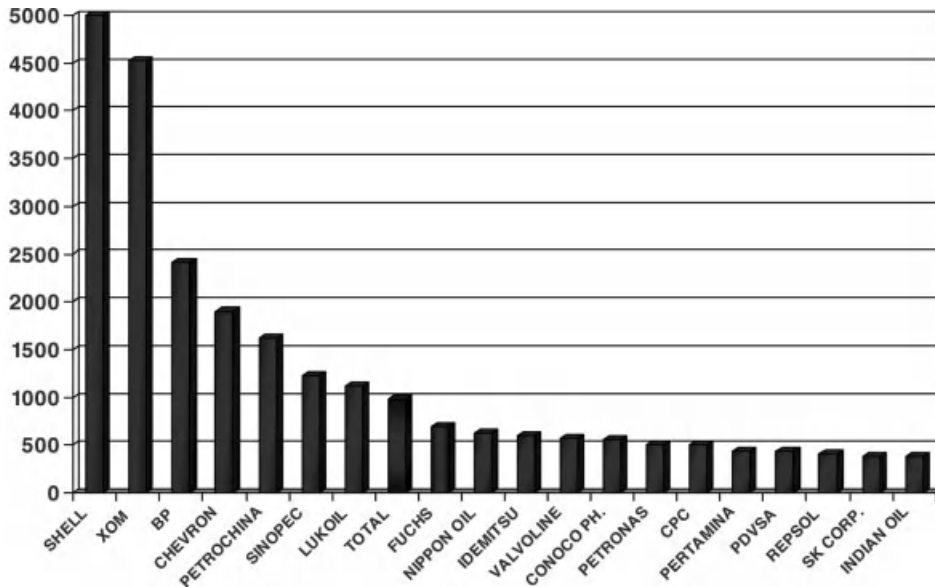


Figure 7.3 World ranking of the largest manufacturers of lubricants in 2007 (ktonnes per year) [1].

engaged in the manufacture of lubricants. In contrast, many hundreds of independent lubricant companies mainly concentrate on the manufacture and marketing of lubricants, and view lubricants as their core business. While the large, integrated companies focus on high-volume lubricants, such as engine, gear and hydraulic oils, many independent lube companies concentrate on specialties and niche business where, apart from some tailor-made lubricants, a comprehensive and expert customer service forms part of the package. Details of the world's largest manufacturers of finished lubricants are listed in Figure 7.3.

7.2

Mineral Base Oils

In terms of volume, the base oils represent the most important components of lubricants; as a weighted average of all lubricants, they account for more than 95% of lubricant formulations. In fact, in some lubricant families (e.g., certain hydraulic and compressor oils), the chemical additives account for only 1%, while the remaining 99% are base oils. In contrast, other lubricants (e.g., some metalworking fluids, greases, or gear lubricants) may contain up to 30% additives.

The origin of the overwhelming quantity of mineral lubricant base oils has led to lubricants being viewed as a part of the petroleum industry, and this is underlined by their inclusion in petroleum statistics. Over the past few years, lubricants have increasingly become a separate discipline with clear differences from petroleum mass products. This was a result of the high added value that is generated in this

product segment, along with the fact that many high-performance lubricants no longer contain petroleum base oils.

7.2.1

Base Oils: A Historical Review and Outlook

Although, during the 1950s, the most important requirement of base oils was the correct viscosity and an absence of acidic components, base oils during the 1960s were downgraded to solvents or carriers for additives in the euphoria surrounding chemical additives. During the 1970s, it was first realized that some synthetic fluids with uniform basic chemical structures would offer performances superior to that of mineral base oils, although at that time the considerably higher price of these products hindered their market acceptance. In the 1980s, however, lower-price, quasi-synthetic hydrocracked oils were introduced in Western Europe which closely matched the properties of synthetic hydrocarbons (Shell, BP, Fuchs). During the 1990s, base oil developments were influenced by the ever-increasing demands on lubricant performance, and by environmental and health and safety criteria. This led to chemically more pure oils, such as hydrocracked products, polyalphaolefins and esters, gaining acceptance. More recently, natural fatty oils—and particularly their oleochemical derivatives—have experienced a renaissance, not only on the basis of their technical characteristics but also because of their rapid biodegradability.

The trend towards ever-greater performance and even better environmental compatibility has continued during the first decade of the new millennium. The significantly higher price of the new lubricants, which will be increasingly characterized by their base oils and less so by their chemical additives, will most likely be accepted by users who will benefit from a long product life and lower overall system costs. In 2007, worldwide, approximately 8% (w/w) of base oils were synthetic products (including Group III hydrocracked oils; Section 7.2.6), and this segment is forecast to grow to 10% in 2015 [2]. In Germany, furthermore, in 2007 approximately 6% of lubricant base oils were rapidly biodegradable (natural and synthetic) esters. In addition, the gasification of carbon-containing raw materials (e.g., natural gas, biomass, and carbon) will enable the production of synthetic lubricant base oils of high quality.

7.2.2

Chemical Characterization of Mineral Base Oils

The characterization of mineral oil fractions, whether crude oil or lubricant base oil fractions, by using normal chemical practices to determine their exact structure is not possible without incurring major expense. Crude oil generally consists of many thousands of single components, and these are reflected in the processing of each fraction. Consequently, there has always been an objective to describe mineral oil fractions by the comparatively simple expedient of defining their technical properties, or to identify and quantitatively determine groups of components with similar

chemical character. Advanced physico-chemical methods are, however, increasingly being used in routine testing.

7.2.2.1 Carbon Distribution

The most important means of analysis for the characterization of mineral oil hydrocarbons was, and remains, the determination of carbon in terms of its three categories of chemical bond, namely aromatic carbon (CA), naphthenic carbon (CN), and paraffinic carbon (CP).

The n-d-M (refractive index/density/molecular weight) analysis uses physico-chemical data which are easy to obtain, such as refractive index, density, and molecular weight. The molecular weight can be determined by measuring the viscosity at different temperatures (e.g., ASTM D 2502-92). The carbon distribution is given as % CA, % CN, and % CP (100% in total). N-D-M analysis is also used to determine the average total number of rings per molecule (RT), and the breakdown into aromatic and naphthenic rings (RN) per molecule ($RN = RT - RA$).

Brandes [3] created a method of determining carbon distribution according to specific bands in the infrared (IR) spectrum; the method has been proven effective for lube base oils, and can be performed at acceptable expense. An exact determination of the aromatic carbon content can be performed using high-resolution nuclear magnetic resonance (NMR) (ASTM D 5292-91).

7.2.2.2 Hydrocarbon Composition

A further refinement in the characterization of lubricant base oils is the determination of molecular families. Chromatography is first used to separate components, after which the fractions are subjected to advanced analytical procedures. To differentiate among mineral oils including lube base oils in the boiling range from 200 to 550 °C, high ionizing voltage mass spectrometry (ASTM D 2786-91) is used for saturated fractions, and ASTM D 3239-91 for aromatic fractions. The saturated fractions are separated into alkanes (0-ring), 1-ring, 2-ring, 3-ring, 4-ring and 5-ring naphthenes, while the aromatic fractions are subdivided into seven classes: monaromatics; diaromatics; triaromatics; tetra-aromatics; penta-aromatics; thiopheno aromatics; and unidentified aromatics.

7.2.2.3 Polycyclic Aromatics in Base Oils

Polycyclic aromatics [e.g., polycyclic aromatic hydrocarbons (PAH), or, in general, polycyclic aromatics (PCA)] are carcinogenic, environmentally harmful substances which are found in crude oils. In general, they are not created when a lubricant is used; rather, PAH are formed by the combustion of gasoline, and may gather in engine oils and also in quenching oils after long periods of heavy-duty use.

In traditional solvent-refining processes, the PAH largely remain in the extract; typically, nonsolvent-extracted distillates will contain PAH in line with their boiling points.

The carcinogenic characteristics of non-severely treated distillates in the petroleum industry was established by the International Agency for Research on Cancer (IARC) in 1983 [4]. This led to considerable limitations in the manufacture and

application of naphthenic base oils, and the cessation of using aromatic extracts as lube base oils. Previously, Grimmer and Jakobs [5–7], in particular, had confirmed the presence of PAH in lubricant base oils analytically, and highlighted their carcinogenic characteristics.

The standardization of analytical methods of determining PAH and the setting of threshold values was the subject of lively discussions between 1985 and 1995. Whereas, one group was primarily interested in establishing exact analyses while others sought to use benzo(a)pyrene as a reference, another group was pressing ahead with the IP 346 method, which was later adopted into national legislation in several countries. PAH can be determined using high-performance liquid chromatography (HPLC) with anthracenes or other aromatics as markers, or by using gas chromatography–mass spectrometry (GC-MS) after appropriate sample preparation.

The IP 346 method does not provide a direct analysis of PAH; rather, an extract is obtained in dimethylsulfoxide (DMSO), in which PAH accumulate. As a rule, the extract (which is often wrongly referred to as a “PAH concentrate”) largely contains naphthenes or mono-aromatics; according to IP 346, DMSO extracts contain only 0.1% PAH. Following numerous skin-painting tests on mice, the carcinogenicity of petroleum products was shown to correspond to the PAH content (percentage) of the DMSO extract.

Today, criticism of the IP 346 threshold value continues, with the weakness of the criterion becoming clearer when used gasoline engine oils are evaluated. Typically, PCA enrichment resulting from gasoline combustion is not considered by the IP method, since a 1000 ppm increase in PCA will cause only a very minor increase in the PCA content of a DMSO extract of a “used” base oil, from 1.0% (for fresh oil) to 1.1%.

Figure 7.4 illustrates the increasing carcinogenicity of petroleum products corresponding to the PCA content of the DMSO extract, and various analytical methods for determining the PAH/PCA content [8–12].

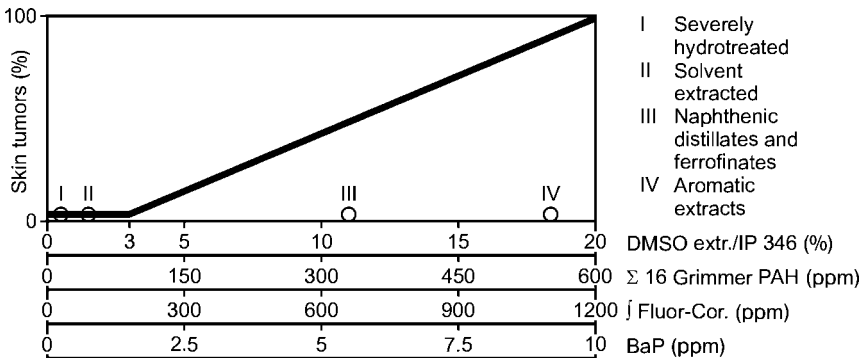


Figure 7.4 Dependence of the carcinogenicity of petroleum products on the PAH content [6], based on skin painting tests and a rough statistical classification of different PAH analyses.

7.2.3

Refining

Since the beginning of the petroleum industry, mineral oils have been used for lubricant base oils, with the process of converting crude oil into a finished base oil being referred to as *refining*. As far as base oil manufacturing is concerned, the actual refining process begins only after the distillation stages; hence, the term refining is often used to describe all of the manufacturing stages that follow vacuum distillation.

Lubricant refineries are divided into integrated and non-integrated plants (Figure 7.5). The integrated refineries are linked to primary crude oil refineries and fed with vacuum distillate by pipeline, whereas the non-integrated refineries either purchase vacuum distillate on the open market or buy atmospheric residues and perform their own vacuum distillation. Occasionally, they may perform vacuum distillations on crude oil.

7.2.3.1 **Distillation**

By way of fractional distillation, products are removed from crude oil which approximately meet the viscosity grades ultimately required; quite often, only four or five cuts are sufficient to fulfill lubricant requirements. As described below, the viscosity of the primary vacuum distillate is independent of the finished base oils in

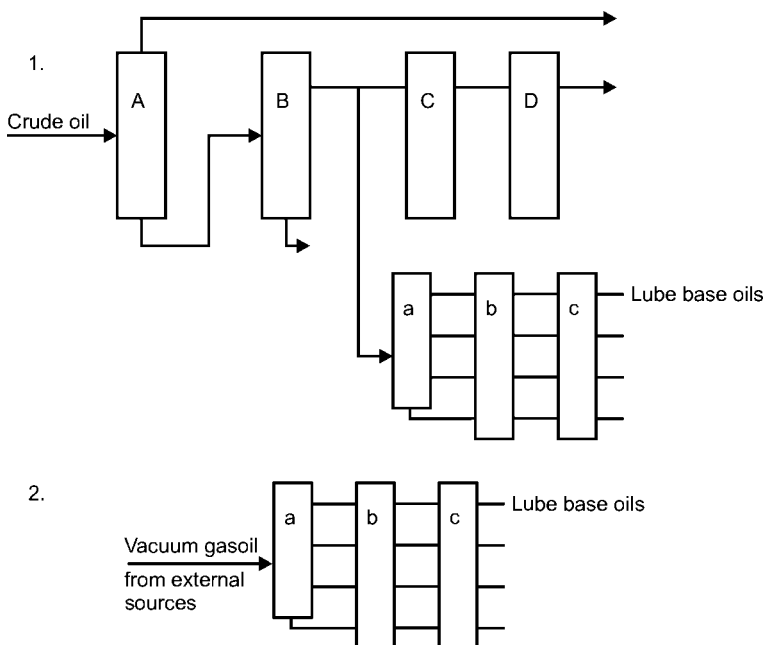


Figure 7.5 Integrated (scheme 1) and non-integrated (scheme 2) lube refinery. A, atmospheric distillation; B, vacuum distillation; C and D, processing of vacuum distillates for non-lube production; a, fractionating vacuum distillation; b and c, lube refining processes.

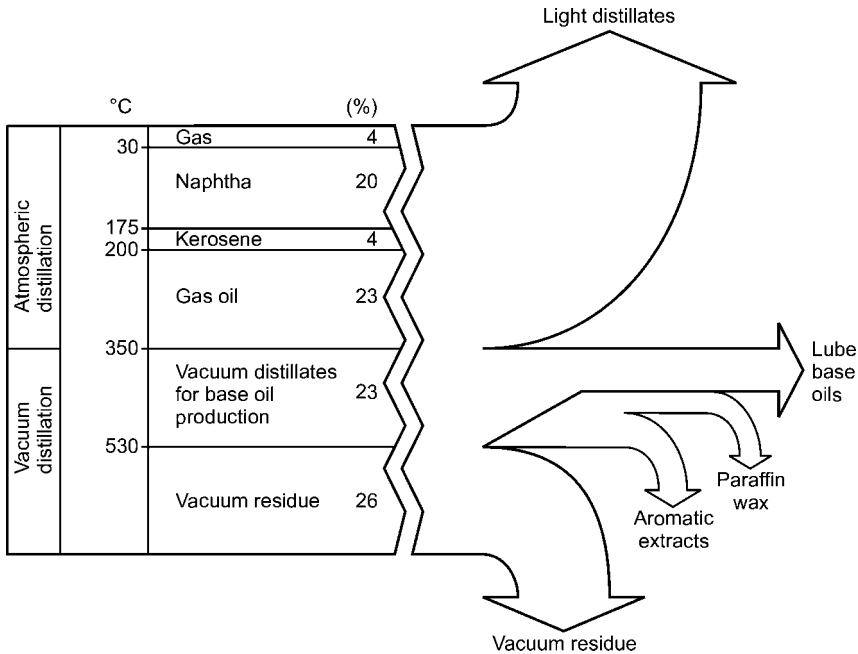


Figure 7.6 Yield of the various cuts in conventional lube oil refining of a typical lube crude.

hydrocracking processes, because the hydrocracking process creates new molecular dimensions.

Following a corresponding separation of the lighter components from the crude oil by atmospheric distillation, the lubricant components will remain in the atmospheric residue. The yields of the various cuts in conventional lube oil refining, with the corresponding boiling ranges of a typical lube crude, are shown in Figure 7.6. The atmospheric residue is then subjected to vacuum distillation to remove the components required for lubricants. In a vacuum, the boiling points of the heavier cuts are lowered, so that distillation without thermal destruction (cracking) is possible.

7.2.3.2 De-Asphalting

Although the vacuum residue still contains highly viscous hydrocarbons which can supply valuable components for lube base oils, distillation cannot separate these from the asphalt which is also present, and extraction processes must be used to separate the highly viscous base oils, commonly known as *brightstocks*. These are produced in lube oil refineries when use of the asphaltene byproduct (hard asphalt) is worthwhile. The quality of the hard asphalt used to manufacture high-quality bitumen depends on the crude oil. AN extractive separation uses light hydrocarbons (propane to heptane), of which propane is the leading product for de-asphalting. Brightstocks can be manufactured with viscosities of more than $45 \text{ mm}^2 \text{ s}^{-1}$ at 100°C .

Figure 7.7 shows a flow chart for the manufacture of suitable feeds for lube oil refining by distillation and propane de-asphalting.

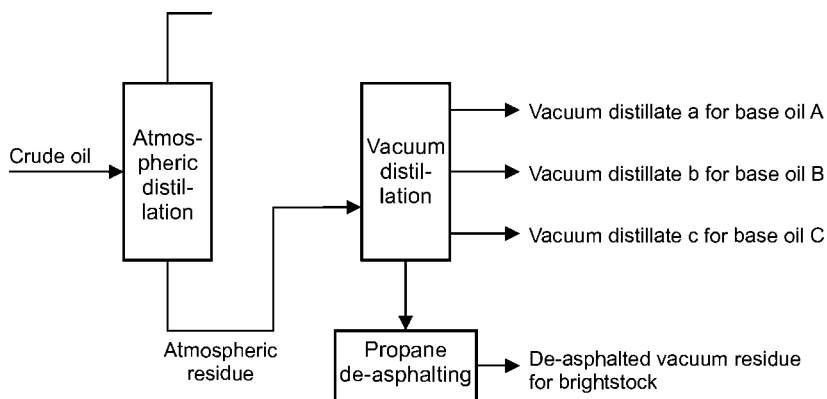


Figure 7.7 Flow chart for the manufacture of suitable feeds for lube oil refining by distillation and propane de-asphalting.

7.2.3.3 Traditional Refining Processes

Vacuum distillation cuts principally determine the viscosity and flashpoint of later base oils. The precision of the fraction at the upper and lower boiling limits of a cut are of great importance, as the distillates may still contain components that can have detrimental effects on aging, viscosity–temperature behavior and flowing characteristics, as well as components that are hazardous to health. In order to eliminate these disadvantages several refining methods were developed, of which solvent refining has become the most accepted over the past few decades. Today, however, new plants increasingly use hydrotreatment.

Acid Refining Acid refining has become less popular, mainly because the acid sludge waste produced is difficult to dispose of; hence, the method has been replaced by solvent extraction. Nonetheless, acid refining is still used to some extent for the re-refining of used lubricating oils (see Section 7.16), and for the production of very light-colored technical or pharmaceutical white oils and petroleum sulfonates as byproducts.

When the distillates are treated with concentrated sulfuric acid or fuming sulfuric acid (oleum), any substances which accelerate oil aging are removed. Oleum treatment (wet refining) has a greater chemical effect on the structure of aromatics, as it not only readily removes reactive oil components such as olefins but also reduces the aromatic content, which in turn increases the viscosity index of the product. Reactions with saturated paraffinic structures lead to refining losses. Acid-refined oils require complex neutralization and absorption follow-up treatment to remove all traces of acid and undesirable byproducts.

Solvent Extraction Whereas, acid refining uses a chemical reaction to reduce the aromatic content and to eliminate reactive, oil-aging accelerators, solvent extraction is based on physico-chemical separation (Figure 7.8). Solvent extraction creates base oils which are known as solvent *raffinates* or solvent-neutrals (SNs). Extraction

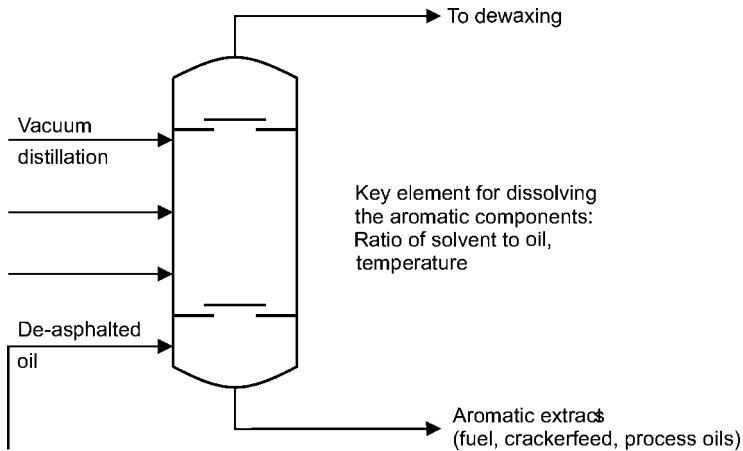


Figure 7.8 Stages of solvent extraction.

processes using solvents create both a base oil and, after evaporation of the solvent, an aromatic-rich extract.

The selectivity of the extraction media for aromatics is an important selection parameter. In particular, selectivity towards polycyclic aromatics with three or more aromatic rings has attracted attention, because of the carcinogenicity of these compounds. Numerous extraction media have been developed, of which furfural, NMP (*N*-methyl-2-pyrrolidone), and phenol have become economically significant. Sulfur dioxide should also be mentioned because of its historical importance, when B. Edeleanu introduced extraction to petroleum technology in 1912. In 1999, sulfur dioxide was used in only very few refineries (one in Germany until 1999) for the refining of naphthenic distillates.

In recent years, several furfural extraction plants have been converted into NMP plants, and even phenol plants have taken a back seat. NMP is a nontoxic solvent that can be used in a low solvent-to-oil ratio, with high selectivity, so as to generate significant energy savings. NMP in new plants results in a need for physically smaller units and, thus, a lower capital expenditure.

As a rule, extraction plants represent the first refining step for vacuum distillates, because subsequent solvent dewaxing is the more complex refining process in terms of capital expenditure and operating costs. This route means that the extract part does not undergo unnecessary dewaxing.

Depending on the crude material, the extract part of paraffinic oils can be 30–50%. As the standard requirement of solvent neutral oils is a viscosity index (VI) of at least 95, the extraction severity is matched to this demand.

A higher proportion of aromatic and naphthenic hydrocarbons in the distillates requires a greater extraction severity, and thus a larger quantity of extract. The percentage share of the extract is a major economic factor in conventional lube refining. In general, extracts can only be used as products which are of lower value than the finished base oils; the large quantities are used as cracker feed, with

only a comparatively small proportion being used as process oil. Their use as plasticizers has been severely limited in recent years because of their carcinogenicity, and the same applies to their use as lubricant base oils. Aromatic extracts have a very high viscosity-pressure coefficient (see Section 7.4), and in the past have often been used in metal-forming operations, such as cold extrusion.

A one-point increase in VI as a result of greater extraction severity creates, on average, 1% more extract.

Solvent Dewaxing In traditional refining processes, solvent extraction is followed by solvent dewaxing. Long-chain, high-melting-point paraffins negatively affect the cold flow properties of lube oil distillates, and this leads to a high pour point. This effect is caused by the crystallization of waxy substances at low temperatures, leading to turbidity and an increase in viscosity. Consequently, their removal has been an important consideration since the early days of crude oil refining.

Dewaxing by the crystallization of paraffins at low temperatures and separation by filtration represent the principal processes in traditional refining. Compared to catalytic dewaxing with hydrogen, urea-dewaxing to separate *n*-paraffins is of relatively minor importance in lube oil refining. The crystallization methods involve mixing the solvent with the oil; this leads to an improved filtration as a result of dilution, and promotes the growth of large crystal formations.

The important solvents are ketones and chlorinated hydrocarbons. Dewaxing with ketones [dimethyl ketone, methyl ethyl ketone (MEK)] is normally used for pour points down to -12°C , but for lower pour points the Di-Me (dichloroethane–dichloromethane mixture) method is used. This also enables the manufacture of hard and soft waxes; moreover, as with extracts created by solvent extraction, the byproduct situation is again problematic. The paraffins produced are only worthwhile if their quality and processing are good, allowing them to be sold as candle wax, for coatings, and for other purposes. They are also often used as cracker feed in fuel catalytic crackers (FCCs), whereby the cracker yield is assessed by using special formulas.

Finishing A finishing stage often follows the two refining stages of extraction and dewaxing. In the past, methods that employed absorbents were often used, but today the processes almost all use hydrogen (hydrofinishing). The aim of finishing is to improve the color of the product and remove surface-active substances which might negatively affect the air-release or demulsifying properties of a lubricating oil.

Depending on the temperature, pressure, catalyst, and space velocity of the hydrofinishing, a more or less severe hydrogenating process can be initiated. In general, the hydrofinishing process is referred to as “mild hydro treating,” and focuses on improving the color, odor, and ultraviolet stability. Ferrofining (BP) has achieved major economic importance as a finishing process in which the process parameters do not generally lead to de-sulfurization. More severe processes, with pressures in excess of 100 bar, can bring about significant de-sulfurization and some de-aromatization.

Additional finishing with absorbents (bleaching clays, bauxite) is sometimes used for the manufacture of refrigerator, transformer, or turbine oils. The subsequent

filtration process in filter presses or other filtering equipment represents an additional complexity, however, while the disposal of the filter residue is an increasing problem.

Lube Crudes Crude oils which yield high-grade base oils are preferred for the production of lube base oils. Of particular importance to the vacuum gas oils (VGO), which are derived from the crude oil and serve as the direct feeds for lube refining, are the VI and the wax and sulfur contents. For a VGO, a high VI will lead to low extraction losses in solvent extraction processes, and low hydrogen consumption during hydrogenating processes. High wax contents increase production costs, due not only to the high operating costs of the dewaxing plant but also to a reduction in base oil yield. In a base oil production unit using a wax isomerization process, a high wax content can also contribute to a higher VI. The finished base oils will have a high sulfur content, especially after conventional solvent refining. Although the hydrogenating processes will almost fully eliminate sulfur, the process of desulfurization consumes large amounts of hydrogen.

7.2.4

Base Oil Manufacturing by Hydrogenation and Hydrocracking

Traditionally, solvent refining involves the separation of unwanted components from vacuum distillates, while hydrogenation and hydrocracking in the manufacture of lubricant base oils has a significant influence on the chemical structures of mineral oil molecules. On the one hand, any unstable molecules will be chemically stabilized by removal of the heteroatoms (sulfur, oxygen, nitrogen), while on the other hand, a severe hydrogenation can lead to aromatics being converted into saturated naphthenic or paraffinic structures. In addition to the hydrogenation process, hydrocracking breaks down or “cracks” larger molecules into smaller ones, while larger molecular structures may be re-formed from small fragments. The principal process criteria here are the temperature, pressure, the nature of the catalyst, and the space velocity. If any special conditions are met, the isomerization of paraffinic structures becomes the focal point of the process. Besides the saturation of aromatics, an opening of the naphthene rings may occur.

It is clear that lubricant base oils can be much more easily tailored using these processes than is possible with a simple solvent-refining separation. Consequently, the future of lube base oil production would appear to lie with hydrogenation and hydrocracking. An additional advantage of advanced hydrocracking is a lesser dependence on the quality of the crude oil. Although the economic boundaries of solvent refining are set by the yield (extract and paraffin quantities), alterations in the hydrocracking process parameters can compensate for variations in crude oil quality.

The roots of manufacturing lubricant base oils by hydrogenation lie in previous attempts to liquefy coal by high-pressure hydrogenation. On the basis of the results obtained by Bergius (1913) in Hanover, Germany, the first technical plant began operations in 1921 in Mannheim-Rheinau, Germany.

7.2.4.1 Lube Hydrocracking

The principal elements of the lube hydrocracking process are the cracking of low-VI components, and the saturation of aromatics.

Hydrocracking as a major method of future mineral base oil manufacture can be performed in two types of refinery. The first type is a lube oil refinery, which operates a hydrocracker with the principal objective of producing lubricating oils; the second types of refinery operates a fuel hydrocracker to convert vacuum gas oil into high-grade fuels. Fuel hydrocracker residues may serve as excellent feeds for the manufacture of lubricant base oils, while the hydrocrackers used to make olefin feeds for steam crackers can supply a premium quality feed for lube base oils. The most important effect on the quality of the base oil produced is that of extraction severity; for example, a high-severity base oil (e.g., 80% light products) will generate a high-VI but low-evaporation oil. Whilst hydrocracking refineries for base oils with normal VIs and normal Noack evaporation [high-viscosity index (HVI) oils, Group 1 oils; see Section 7.2.5] with moderate severity are being built in the USA and the Far East (based mainly on Chevron Technology), Western European hydrocracking plants have been designed to accommodate low-evaporation base oils (Shell, Petit Couronne, France, 1972; Union FUCHS, Wesseling, Germany, 1986; BP, Lavera, France). The latter type produce Group III oils, on the one hand from waxes, and on the other hand from vacuum gas oils with hydrocracker residues.

Hydrocracked base oils differ from solvent-extracted oils by their extremely low aromatic content and their chemical purity; that is, they contain only traces of heteroatoms such as sulfur, nitrogen, or oxygen. Furthermore, Group III oils (see Section 7.2.6) which have been manufactured at high severity or from waxes, have Noack evaporation characteristics which are about 50% down on equiviscous, solvent-extracted vacuum distillates. If catalytic dewaxing is performed, even lower pour points can be achieved than with SN oils.

Since 1995, more than half of all new base oil manufacturing plants have been built, or are being planned, using hydrocracking technology.

Apart from high-value base oils, sufficiently large hydrocracking plants offer favorable operating costs and greater crude oil flexibility, despite the high initial investment costs. A lube oil hydrocracking plant which operates at approximately 50% vacuum distillate severity generates just as many high-quality light products as do lube base oils, although at present just as many low-value extracts and paraffin waxes are generated by solvent extraction.

In order to increase the VI from 100 to 125, the hydrocracking severity must be increased to such a degree that up to one-half of the base oil yield is lost [13]. The increasing number of fuel hydrocrackers, which have been developed in response to increasing demands for low-sulfur oils (diesel fuels with <50 ppm sulfur), represents a growing source of hydrocracked feeds. Fuel hydrocracker residues can be processed into high-quality, hydrocracked base oils by distillation and subsequent dewaxing (wax isomerization), at acceptable cost.

During the hydrocracking process, and especially if vacuum gas oils are severely treated to create very high-viscosity index (VHVI) oils, polycyclic aromatics can be formed along with saturated structures (aromatics to naphthenes or paraffins and

isoparaffins) under certain process conditions. However, these must be removed by subsequent high-pressure hydrogenation, or by extraction if hybrid methods are to be used. This subsequent hydrogenation can be manipulated so that it also produces a significant increase in VI.

7.2.4.2 Catalytic Dewaxing

The most complex stage of traditional base oil refining is that of solvent dewaxing. In addition to the high capital expenditure and, above all, high operating costs, the solvent-related limits to the achievable pour point represent a major disadvantage.

During recent years, a variety of methods have been developed that are capable of removing unbranched, long-chain or short-chain paraffins, less-branched paraffins, and some other petroleum components. The removal of these materials may be effected by catalytic and hydrogenation reactions, or by their conversion into components which will improve the low-temperature characteristics of the base oil.

The first such technologies were based on the catalytic cracking of these above-mentioned substances. In 1979, Mobil introduced the “Mobil Lube Dewaxing Process” (MLDW), since which time the development of additional catalysts has led to a strong hydroisomerization activity process termed Mobil Selective Dewaxing (MSDW).

While the MLDW process mainly involves the cracking of long-chain paraffins and the production of larger quantities of light byproducts and poor base oil yields, the MSDW processes create high-yield, non-waxy isoparaffins from the waxy parts of the feed.

During the early 1990s, Chevron successfully introduced its isodewaxing process which, by 1999, had become recognized as the most important technology for catalytic dewaxing [13]. The process combines relatively high yields with low pour points and high VIs, while employing a hydrogenation component as an intermediate-pore silicoaluminumphosphate molecular sieve (e.g., Pt on SAPO-11). In terms of process economy, the high base oil yields and the creation of mainly high-value C5 + liquids as byproducts were especially significant, while the formation of low-value byproducts (e.g., propane) was avoided.

In the development of new dewaxing catalysts, it is important to achieve the correct balance between hydrogenation activity and acid activity. Increasing the hydrogenating properties usually leads to a reduction in isomerization, and thus to a worsening of the pour point. A higher acid activity will increase the cracking and thus cause a reduced yield. Notably, sulfur and nitrogen in the feed play important roles; nitrogen is detrimental to acid activity, while sulfur has a “poisoning” effect on the catalysts for metal hydrogenation components.

Although isodewaxing enables the manufacture of lubricant base oils with pour points below -45°C , with catalytic dewaxing processes it must never be forgotten that dewaxing to very low pour points (depending on process conditions and catalysts) leads to VI losses. One major success of this new dewaxing process is the molecular sieve catalyst zeolite, which is available with exactly defined mesh sizes.

Although highly branched paraffins or polycyclic naphthenes or aromatics are not affected by the zeolites, the long-chain, less-branched or unbranched molecules are each acted on by the catalysts [14–16].

7.2.4.3 Wax Isomerization

The manufacture of VHVI oils from waxes has been conducted since the early 1970s, when the feeds used were in fact wax cuts from solvent extraction processes. The conversion of long-chain normal paraffins or less-branched paraffinic components into isomerized products with good low-temperature characteristics and high VIs was successful, with suitable catalysts functioning in isomerizing hydrocracking processes. Yet, because the input feed is already aromatic- and naphthene-free, the catalysts can be fully optimized to conversion of the paraffinic material. At relatively high yield losses, the process can create high-quality but comparatively expensive hydrocracked oils (Shell XHVI, Exxon Exxyn, Mobil MWI-2 catalyst).

7.2.4.4 Hybrid Lube Oil Processing

The combination of traditional solvent refining with severe hydrotreating and hydrocracking processes is known as “hybrid processing.” On the one hand, these processes should represent an extension of existing refineries operations, while on the other hand they should exploit the favorable properties of hydrogen processes. In order to create higher VIs (>105) and to reduce sulfur contents, hydrotreating can follow solvent extraction (e.g., in the manufacture of turbine oils).

The combination of a mild furfural extraction with hydrocracking can produce hydrocracked oils by low-hydrocracking conversion in small hydrocracking reactors. The low hydrogen consumption adds to the economy of such processes, given that the extraction plant exists and the hydrocracker can be integrated into the infrastructure of a lube oil refinery. The introduction of a hydrocracking stage into a conventional solvent refinery offers the attractive possibilities of de-bottlenecking if the corresponding dewaxing capacity is available. Catalytic dewaxing can, on the other hand, follow solvent refining; however, this presupposes that the catalytic dewaxing catalysts can withstand, and are not poisoned by, the sulfur and nitrogen components in the solvent raffinate. In the Mobil processes, this is more likely with MLDW catalysts than with MSDW catalysts.

In connection with the isomerization of slack waxes from petroleum distillates, several other high-paraffin components should be considered as future base oil feeds. These could include high-wax (>70%) natural distillates and Fischer–Tropsch waxes or synthetic fluids from natural gas. Significant future importance is given to this latter group of products.

7.2.4.5 The All-Hydrogen Route

The production of base oils by hydrocracking and catalytic, solvent-free dewaxing is referred to as the “all-hydrogen route”; a flowchart for such a refinery, used to manufacture VHVI oils, is shown in Figure 7.9. Depending on the severity of the hydrocracker, Group II HVI or Group III VHVI oils can be produced (HC-I and HC-2 oils; see Table 7.2).

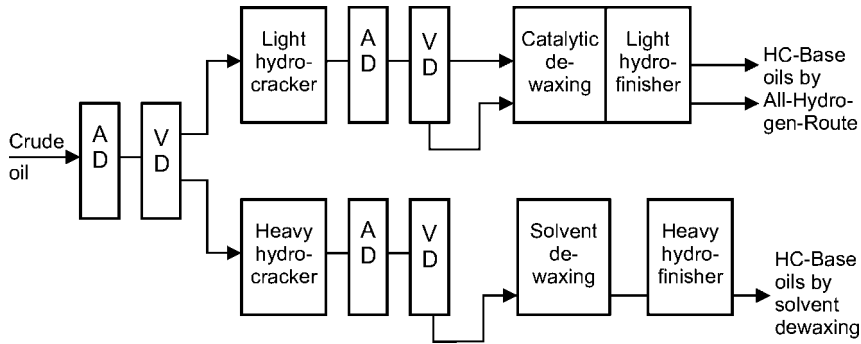


Figure 7.9 The “all-hydrogen route” in Chevron’s Richmond (California, USA) refinery. AD, atmospheric distillation; VD, vacuum distillation.

The use of a fuel hydrocracker for the production of base oils using the all-hydrogen route was first realized by the SK Corporation (Ulsan, Korea) in 1995. By recycling the hydrocracker bottom and the special integration of the fuel hydrocracker in the lube oil process, SK also developed a specific method (the UCO process) [17].

7.2.4.6 Gas-to-Liquids Conversion Technology

As a result of efforts to increase the value of natural gas in logistically favorable locations, the chemical liquefaction of natural gas (also the chemical reaction route) was developed (on the basis of the Fischer–Tropsch process). This process creates high-quality liquid products and paraffin wax. High-quality ultra-high viscosity index (UHVI) oils can then be obtained from natural gas by part oxidation, polymerization, and isomerization (Figure 7.10) [18, 19].

The base oil market could undergo dramatic changes if Fischer–Tropsch waxes, which form part of the gas-to-liquid (GTL) technology, were to become more generally available. The 80-year-old Fischer–Tropsch technology has attracted considerable attention in the past few years, the main attention being a better utilization

Table 7.2 The API/ATIEL classification of base oils.

Group	Sulfur (% w/w)		Saturates (% w/w)	Viscosity index ($\text{mm}^2 \text{s}^{-1}$)
I	>0.03	and/or	<90	80–120
II	≤0.03	and	≥90	80–120
III	≤0.03	and	≥90	>120
IV	All polyalphaolefins (PAO)			
V	All base oils not included in Groups I–IV or VI			
VI	All polyinternalolefins (PiO)			

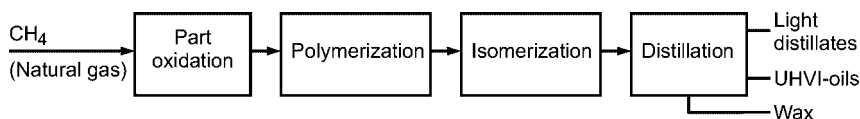


Figure 7.10 UHVI lube base oil production with gas to liquid conversion technology.

of natural gas. Syngas (CO and hydrogen) is created from methane, oxygen (air) and water vapor and this, in turn, is made into fluid and solid hydrocarbons in the Fischer–Tropsch reactor. The solid hydrocarbon waxes (>99% paraffins) are hydrocracked, hydro-isomerized and iso-dewaxed into super-clean base oils. Shell has used such waxes from its Bintulu plant in Malaysia for its extra-high viscosity index (XHVI) oils.

It is, nevertheless, most likely that the major oil companies will be the first to operate large-scale GTL plants, with ExxonMobil, Shell, and SasolChevron each having announced GTL projects (including base-oil-production units) in Qatar [20] that are due to start production between 2010 and 2012.

GTL base oils will have premium characteristics, including VHVI, essentially no sulfur and nitrogen, very low evaporative losses, and almost no aromatic content [21]. They will most probably be classified as Group III + base oils, because their characteristics will vary between those of UHVI base oils (Group IIII) and poly-alphaolefins (Group IV). Besides natural gas, all carbon-containing materials can, in principle, be used for the production of liquid products and paraffin wax by Fischer–Tropsch technology. Because of the limited availability of crude oil, however, the gasification and liquefaction of carbon, biomass, and even of oil sands [22] are of increasing interest.

7.2.4.7 Breakdown of the Base oil Market

The development of the base oil market, relating to base oil qualities and country groups, is shown in Figure 7.11.

7.2.5

Boiling and Evaporation Behavior of Base Oils

In traditional solvent refining, the boiling point distribution of base oils is largely determined during vacuum distillation. In this case, three, four or five (including bright stock) cuts are taken, the boiling point distribution of which is reflected in the finished base oil.

Lighter products can only be created during hydrofinishing as the final refining stage. Those components which negatively affect the evaporation behavior of the base oil can remain if these light components are not fully stripped.

In hydrocracking processes, the decisive distillation stages take place after cracking or after catalytic dewaxing. The function of the stripper or fractional distillation columns plays an important role whenever light cracked products are created.

The target of base oil distillation is the viscosity desired at 40 and 100 °C. The same distillation cut (same boiling point distribution) with different chemical structures

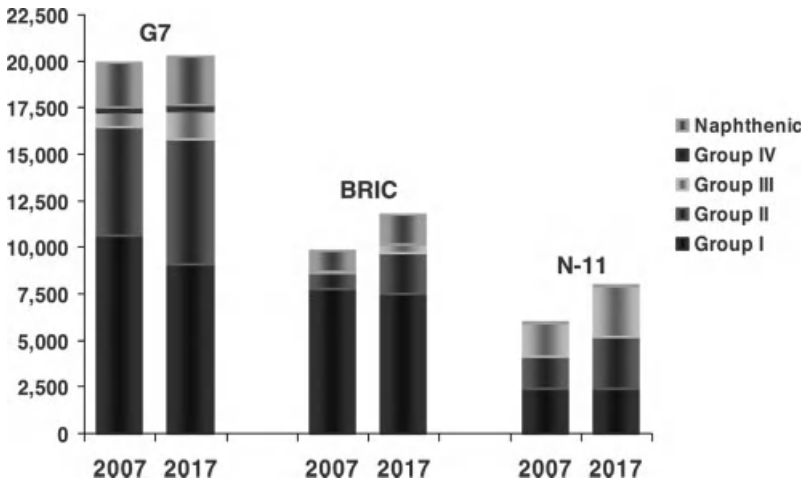


Figure 7.11 Development and breakdown of the base oil market. BRIC = Brasilia, Russia, India and China; N-11 = the emerging markets [1].

leads to different viscosities. Typically, a highly naphthenic cut will produce a higher viscosity than a paraffinic cut; in other words, equiviscous cuts of different chemical structures have different boiling-point distributions.

In practice, ISO viscosity grades or other required viscosities are created by blending different cuts, although if the boiling points of both cuts are too far apart, then the flashpoint will drop significantly and evaporation will be increased. The flashpoint and evaporation are generally determined by the base oil components with the lowest boiling points. The distillation curves of three paraffinic solvent refined cuts are shown in Figure 7.12, where one line is a blend of cut A with cut C, which creates an equiviscous oil with cut B. The share with a boiling range up to 380 °C is increased, from 10% (equiviscous cut) to 20% (equiviscous blend).

Apart from the use of a variety of laboratory distillation apparatus to determine the boiling point distribution of a base oil, gas chromatographic methods for determining boiling points have gained popularity over the past few years. The use of GC to determine the boiling range has undergone a continuous development, notably as a result of improvements in both columns and software, and has today found its way into various standards. Both, nonpolar packed and capillary gas chromatographic columns can be used, with the injection port temperature being between 360 and 390 °C, depending on the column length. The initial column temperature may be as low as -50 °C, and the final column temperature between 360 and 390 °C; the typical programming rate is below 10° min⁻¹. The maximum temperatures stated here are the decomposition thresholds of the fractions being tested, or of the column material.

Vapor pressure is dependent on temperature, and follows the Antoine equation for base oil components. Mathematical models have been created for complex hydrocarbon mixtures. As a simple laboratory method, Noack evaporation (1 h at 250 °C) has become the established method for characterizing evaporation behavior in lubricant specifications, with the evaporation losses being expressed as %(w/w).

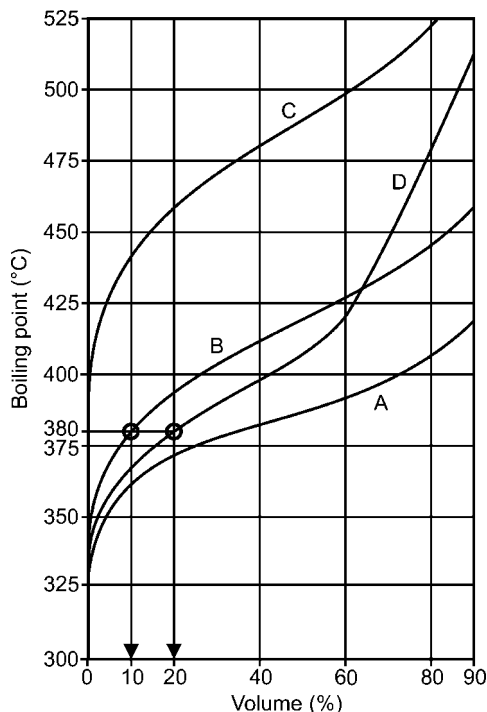


Figure 7.12 Distillation curves of three paraffinic solvent refined cuts. A, light cut (low boiling); B, medium light cut; C, heavy cut (high-boiling); D, blend of A and C, equiviscous with B.

Although gas chromatographic methods have also been used, they tend to produce variable results.

This led to the creation of a simulated Noack evaporation method which employed GC. In the USA, a gas chromatographic process had been developed earlier to determine engine oil volatility (ASTM D5480), in which evaporation took place at 371 °C (700 °F) and the evaporating components were measured to approximately n-C22. Although the process was easily reproducible, the values obtained were not comparable to those obtained with the Noack method.

Typical evaporation losses for well-cut paraffinic solvates are shown in Figure 7.13; values for VHVI oils (HC-2 oils, API Group III oils) and typical ester base oils are shown for comparison.

7.2.6

Other Physical–Chemical Properties of Base Oils

7.2.6.1 Thermal Volume-Expansion Coefficient

As the coefficient of thermal expansion for mineral oils is approximately 7 per 10 000 K, the volume would increase by 0.7% if its temperature were to be increased by 10 °C.

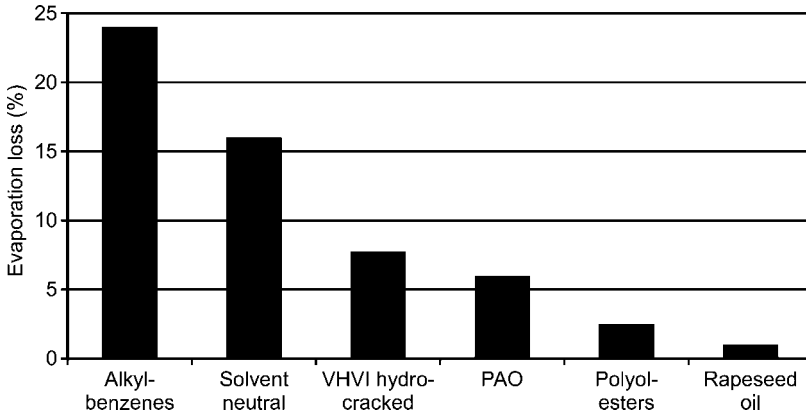


Figure 7.13 Typical evaporation losses (Noack evaporation) of various lube base oils (250 °C, 1 h).

7.2.6.2 Compressibility

The compressibility of mineral oil depends on temperature and pressure. At pressures up to 400 bar and temperatures up to 70 °C (which are top-end values in many industrial systems), compressibility is irrelevant to such cases. At pressures ranging from 1000 to 10 000 bar, however, changes in the compressibility of the medium can be observed. Compressibility is expressed in terms of the compressibility coefficient β , or the compressibility modulus M ($M = 1/\beta$ bar).

7.2.6.3 Gas Solubility

Air and other gases are able to dissolve in fluids; typically, a fluid can absorb a gas until a saturation point is reached, though this need not negatively affect the characteristics of the fluid. The solubility of a gas in a fluid depends on the base fluid, the type of gas, the pressure, and the temperature. Up to approximately 300 bar, the gas solubility is proportional to the pressure, and Henry's law applies. In Henry's law, the important factor is the *Bunsen coefficient* (1.013 mbar, 20 °C); this is highly dependent on the base fluid, and indicates how much (% v/v) gas is dissolved in a unit volume of the fluid under normal conditions. The dissolved gas can escape from the fluid at low static pressure (high flow velocity and shearing stress), until a new saturation point is reached. The speed at which the gas escapes is usually higher than the speed at which it is absorbed. When gas escapes as bubbles, it changes the compressibility of the fluid, and this can especially affect the performance of hydraulic oils. Up to approximately 5% (v/v) undissolved air can be found in mobile hydraulic systems with a high fluid circulation, although this results in bad rigidity and dynamics of a system, and also in foaming. As the pressurization of fluids in hydraulic systems is usually very rapid, any air bubbles can suddenly be heated up to a high temperature (adiabatic compression); indeed, in extreme cases the ignition temperature of the fluid might be reached and micro-diesel effects can occur. The gas bubbles can also collapse in pumps as a result of pressurization, and this can cause erosion damage (sometimes termed *cavitation* or *pseudo-cavitation*).

7.2.7

Base Oil Categories and Evaluation of Various Petroleum Base Oils

The American Petroleum Institute (API) and the Association Technique de l'Industrie Européenne des Lubrifiants (ATIEL) have classified base oils according to their chemical composition. Initially, there were four groups, but after the introduction of VHVI oils in Europe this was increased to five. The most important reason for these groups was the need to regulate base oil interchangeability for engine oils.

The classification of petroleum base oils (Groups I to III) considers three parameters: saturates content; sulfur content; and VI (see Table 7.2). Accordingly, Group I oils are solvent-extracted HVI oils (SN oils), Group II oils are hydrogenated or hydrocracked oils (as the sulfur content of < 300 ppm shows), and Group III products are VHVI oils manufactured by severe hydrocracking and or wax isomerization (VI > 120, sulfur < 300 ppm).

Table 7.3 shows typical data of various hydrocracked base oils (HC-oils), in comparison with solvent-refined oils and polyalphaolefins. Although there are several technical intermediate possibilities, severely hydrocracked Group III oils have become well established on the market.

The first characteristics of hydrocracked oils which attracts attention is their low sulfur content, or even the absence of sulfur, and the high VI and low evaporation characteristics of HC-2 and HC-3 oils. The expected, poorer additive response of antioxidants (see Section 7.5), pour point depressors, or other additive groups were not confirmed when hydrocracked oils were introduced. When inhibitor compositions were optimized, all hydrocracked oils were more stable to oxidation than solvent refined oils (if the correct additives were used), this being primarily a result of their high chemical purity. The missing "natural" sulfur inhibitors are more than compensated for by the addition of suitable antioxidants.

Currently, HC-2 and HC-3 oils are being increasingly compared with synthetic polyalphaolefins (PAOs); the close similarity of the performances of some hydrocracked oils and PAOs, and their significantly lower cost, make them increasingly

Table 7.3 Typical data for 4 mm² s⁻¹ base oils and HC oils, in comparison with conventional solvent-refined oils and polyalphaolefins.

	Solvent-refined	HC-1	HC-2	HC-3	Polyalphaolefins
Viscosity (mm ² s ⁻¹ at 100 °C)	4	4	4	4	4
Viscosity index	100	105	125	130	125
Volatility, Noack evaporation loss (% w/w).	23	18	14	13	12
Pour point (°C)	-15	-15	-18	-20	-65
API group	I	II	III		IV

attractive for lubricant formulations. The term “synthetic,” which has been used in Europe and recently also in the USA, has led to heated legal arguments. As considerable synthesis takes place during severe hydrocracking and catalytic dewaxing, the term seems justified, although this then eliminates the terminological differentiation into HC-2 and HC-3 oils. In Germany, the term HC-synthesis has gained acceptance for HC-2 oils. The synthesis terminology applies even more to oils which originate from liquefied natural gas and which can be classified as HC-3.

7.3 Synthetic Base Oils

According to Zisman [23], the rise of synthetic lubricating oils on an industrial scale began in 1931, when Sullivan and coworkers [24] published the results of their attempts to make tailor-made saturated lubricating oils with low pour points by the catalytic polymerization of olefins. In 1926, Gunderson and Hart [25] edited an outstanding book on synthetic lubricants, which described nine classes of lubricating oils and also contained Zisman’s contribution to their history. In 1993, Shubkin [26] edited a remarkable new book on the subject that omitted some of the older classes and added some new ones instead. Subsequently, Dresel updated the situation of synthetic base oils in 2007 [27], and the following is based essentially on Dresel’s scheme.

Although many of the synthetic base oils available today had been developed decades ago, their use on a large technical scale has increased only slowly because of their considerably higher cost. In general, the consumption of synthesized lubricating oils has responded only reluctantly to benefits which have long been recognized, and to the needs of machinery that must operate under increasingly extreme conditions, in terrestrial applications mainly at higher temperatures and pressures, in space applications mainly at lower temperatures and very low pressures. Yet, the consumption of polyalphaolefins, the most common synthetic lubricating oils, has increased *enormously* during the past two decades.

In contrast with mineral oil-based oils, that contain many different hydrocarbons, and nitrogen-, oxygen-, and sulfur-containing chemical derivatives of these hydrocarbons, that must be purified and refined and distilled (see Section 7.2), synthetic base oils usually are prepared by reaction of a few defined chemical compounds (though in many cases also based on petroleum) and tailored to their application by the correct choice of reaction conditions. Whilst this comparably simple chemistry has certain advantages, it also has some disadvantages, mainly with regard to additive response and elastomer compatibility.

Synthetic hydrocarbons were developed simultaneously in Germany and the USA. In Germany, low-temperature performance and a need to overcome the general shortage of petroleum base stocks were the driving forces behind the studies of Zorn [28]. Today, it is well known that all synthetic hydrocarbons—as well as other economically important synthetic lubricating oils – can be synthesized starting with

ethylene. Indeed, ethylene itself is one of the most important petrochemicals that, today, is mainly produced in steam crackers.

7.3.1

Polyalphaolefins

The term polyalphaolefin (PAO) is derived from the source of this class of base oil, usually α -decene or a mixture of α -olefins containing, in general, a minimum of six and a maximum of 12 carbon atoms. The oligomers are saturated (i.e., hydrogenated), and therefore belong to the aliphatic or branched paraffinic hydrocarbons.

The free radical- or thermal-oligomerization of α -olefins is possible, but is no longer important because of high activation energy, low yield, and quality, even when peroxides are used as catalysts. Oligomerization with Ziegler–Natta catalysts of the aluminum triethyltitanium tetrachloride type tends to yield a wide range of oligomers that can be controlled more easily when a catalyst of the alkylaluminum halide-alkoxide-zirconium halide type is used. A boron trifluoride-based Friedel–Crafts oligomerization, with alcohols as co-catalysts has, nevertheless, proved superior. The boron trifluoride method has become predominant for the production of grades with lower viscosities ($2\text{--}10\text{ mm}^2\text{ s}^{-1}$). However, other catalysts must be used to produce grades with higher viscosities (40 and $100\text{ mm}^2\text{ s}^{-1}$), and grades with viscosities of $10\text{--}25\text{ mm}^2\text{ s}^{-1}$ that are intended to replace disadvantageous blends.

Polyalphaolefins satisfy some of the requirements of ideal hydrocarbon lubricants that can be predicted from chemical structure considerations: ideal hydrocarbon lubricants should have straight chains, be completely saturated, and crystallize at low temperatures. The viscosities of straight-chain alkanes do indeed increase with chain length, and the same is true for their pour points and VI values. At a constant molecular mass, branching leads to an increased viscosity and a decrease in pour point and VI. The length and position of the side chains influence all three properties; for example, when branching occurs in the middle of the main chain the pour points are lower, whereas long side chains lead to improvements in viscosity–temperature (VI) characteristics.

In addition, PAOs have several advantages, including narrow boiling ranges, very low pour points, and VI values > 135 for all grades with a kinematic viscosity $> 4\text{ mm}^2\text{ s}^{-1}$ at 100°C . Moreover, their volatility is lower than that of all possible and equiviscous mineral oil grades, and they contain only small quantities of unsaturated and polycyclic aromatic compounds (PACs) and only traces of nitrogen, sulfur, or other impurities.

Although, traditionally, PAOs have been used in aerospace and lifetime applications, today they are used in a wider variety of applications and have gained additional importance because of their increasing need in automotive lubricants.

The three steps of PAO production are shown in Figure 7.14.

The polyinternalolefins (PIOs) are rather similar to PAOs, as both types of hydrocarbon can be prepared by the oligomerization of linear olefins. The main difference is that PIOs are produced from cracked paraffinic base stocks.

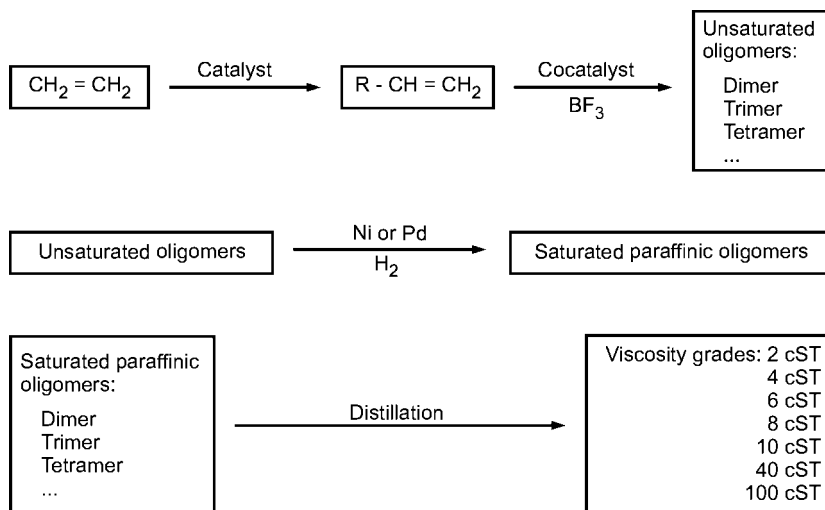


Figure 7.14 The three steps of polyalphaolefin production.

7.3.2

Polybutenes

Although polyisobutylene rubbers were first manufactured as early as the 1930s, it was not until about the late 1940s that their liquid analogs became available. Polybutenes (PBs) as synthetic base oils, have been described in detail by Fotheringham [29]; they consist mainly of isobutene and are, therefore, often also known as polyisobutenes (PIBs).

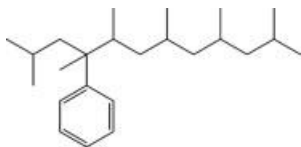
Polybutenes with molecular masses from about 300 to 6000 Da are important as VI improvers. They are used as components in two-stroke oils, gear and hydraulic oils, as metal-working lubricants, greases, compressor lubricants, and as wire-rope protectives [30]. One option for future polybutene application is the increased use as synergistic components in binary or ternary base oil systems.

7.3.3

Alkylated Aromatics

Alkylnaphthalenes as lubricants have been available in Germany since about 1930. Alkylated aromatics have been described by Dressler in detail [31], while low-cost dialkylbenzenes are produced as byproducts in the manufacture of linear and branched monoalkyl benzenes that themselves are feedstocks for the manufacture of detergents. The Friedel–Crafts alkylation of benzene with olefins tends to yield polyalkylated products, because of the reactivity of the primary product. With excess benzene, a suitable olefin (e.g., propene) and the correct choice of a catalyst, the reaction can be controlled and specialized alkyl benzenes synthesized. The structure

of a typical alkylbenzene comprises six propene units (1); the properties of synthetic alkylbenzenes vary widely and are difficult to generalize.



(1)

Some of the properties of the alkylated benzenes can be explained by considering their chemical structure: typically, ring formation would lead to a larger increase in viscosity and a fall in VI-value than would an alkyl substitution, whereas the side chains on a naphthenic ring would have the opposite effect. A shift of the cyclohexylsubstituents from the end towards the middle of an alkyl chain has only a small effect on viscosity, but a strong negative effect on the viscosity–temperature ($V-T$) relationship, as well as causing a lowering of the pour point. Lower-cost dialkylbenzenes are used in a wide variety of industrial areas, one example being in transformer oils, where a high resistance to gas evolution is important. Although tailored grades (especially the linear products) have poorer properties than PAOs, they remain an option on the basis of their excellent solvency, their suitability for low temperatures, and their compatibility with elastomers. The most widespread use of these products is, however, as refrigerator oils.

7.3.4

Synthetic Esters

7.3.4.1 Esters of Carboxylic Acids

Synthetic ester lubricants for the jet age were developed in Germany during World War II [32].

Hydrocarbon oils were unable to satisfy the demands on aircraft engine oils, whereas alkyl esters of aliphatic carboxylic acids had favorable properties. Carboxylic groups, because of their strong dipole moments, reduce the volatility and increase the flash point of lubricating oils, while simultaneously having positive effects on thermal stability (the bonds of the COO group are thermally more stable than the C–C bond), solvency, lubricity, and biodegradability. Unfortunately, however, they have negative effects on the hydrolytic stability of a lubricant, and on the reactivity with metals or alloys that contain copper or lead. The general properties of synthetic esters of carboxylic acids have been described in detail in *Ullmann's Encyclopedia of Industrial Chemistry* [33], and by Randles [34].

7.3.4.2 Dicarboxylic Acid Esters

Dicarboxylic acid esters have been described in detail by Dukek and Popkin [35]. Two types of ester molecule, or their combinations, have been found to be most suited as lubricant components: (i) esters of branched primary alcohols with straight dicarboxylic acids; and (ii) esters of straight primary alcohols with branched dicarboxylic acids.

7.3.4.3 Polyol Esters

Since the 1940s, neopentyl glycol ((2,2-dimethyl)-1,3-propanediol) (2), trimethylol-ethane and -propane (1,1,1-tris(hydroxymethyl)ethane and -propane) (3), and pentaerythritol (2,2-bis(hydroxymethyl)-1,3-propanediol) (4) have been recognized as the alcoholic components of esters (they have been described in detail by Smith [36]). Besides excellent thermal and oxidation stability, the esters have good $V-T$ and lubricating properties, and excellent viscosity characteristics at low temperatures. This is because the thermal stability of a primary OH group is greater than that of a secondary group, and the hydroxy derivatives of neopentane contain only primary hydroxy groups. Likewise, the short side-chains in a hydrocarbon not only reduce its pour point, but tertiary C or H atoms simultaneously facilitate the attack of oxygen. In contrast, the polyols have no tertiary H atoms, nor H atoms in the β -position, that can facilitate thermal cleavage.



The mechanism of the polymerization of polyol esters during aging has been studied, and benzotriazole derivatives have been proposed as multifunctional additives [37]. Since the 1960s, polyol esters have gained importance as lubricants for high-temperature applications, for example in aircraft engines designed to travel at speeds beyond Mach 2, and have become even more important since the introduction of biodegradable esters.

7.3.4.4 Other Carboxylic Esters

The structural counterparts of the polyol esters are the esters of some aromatic polycarboxylic acids, mainly phthalic acid, trimellitic acid, and pyromellitic acid, with monofunctional alcohols. The latter, also, are suited as high-temperature lubricants.

Monoesters—the reaction products of fatty acids and monofunctional alcohols—are used in metal working. The sulfurized esters serve as excellent extreme pressure (EP) additives for all types of lubricant.

7.3.4.5 Dimeric Acid Esters

The acids are prepared from oleic or tallow fat acid, and used as engine oil and thickener components.

7.3.4.6 Complex Esters

Esters that contain straight or branched diols or polyalkylene glycols and straight or branched dicarboxylic acids, as well as (mono)carboxylic acids and monofunctional alcohols, have attracted interest. Usually, the diol is first esterified with the dicarboxylic acid, after which—depending on the desired product—the intermediate product is reacted with either a carboxylic acid or a monoalcohol.

That complex esters have higher molecular weights and higher viscosities than the common esters was one of the main reasons for their introduction.

Medium molecular-weight oligomeric esters starting from (mainly vegetable) fatty acid triglycerides are of interest for environmentally friendly and high-performance applications, as are esters starting from adipic acid or sebacic acid and neopentyl glycol. The interest in these materials is based on their good biodegradability, and also because their pour points are similar to those of their monomers, despite their viscosities being higher [38].

High-molecular-weight complex esters have also been named as polymer esters, and find use mainly in applications where resistance to mineral oils and solvents is required.

7.3.4.7 Phosphate Esters

Although tertiary esters of phosphoric acid with alcohols or phenols were first prepared about 150 years ago, they were not introduced as antiwear additives until 1930. They have also gained importance as plasticizers, fire-resistant hydraulic fluids (see Section 7.8), compressor oils, and synthetic lubricants. Phosphate esters, which have been described in detail by Marino [39], are usually categorized as triaryl, trialkyl, and alkylaryl phosphates, and are prepared by reacting phosphoryl chloride with phenols or alcohols. Their properties range from low-viscosity fluids to high-melting solids, although with an increasing molecular weight the trialkyl phosphates change from water-soluble to water-insoluble liquids. The triaryl phosphates have higher viscosities and are insoluble in water. The presence of an aryl side-chain leads to a reduction in the melting point. The properties of alkylaryl phosphates locate between those of alkyl and aryl phosphates.

The lubricating properties of the phosphoric acid esters are excellent, particularly on steel. Whilst they can be blended with almost all lubricants and additives, their dissolving power causes them to be incompatible with rubbers, varnishes, and plastics. Notably, nylon-, epoxy-, and phenol-formaldehyde resins are stable.

7.3.5

Polyalkylene Glycols

The first polyalkylene glycols suitable as lubricants were developed during World War II. Polyalkylene glycols have been described in detail by Matlock and Clinton [40].

Polyalkylene glycols are prepared by the reaction of epoxides (usually ethylene and propylene oxide) with compounds that contain active hydrogen (usually alcohols or water), in the presence of a basic catalyst, for example, sodium or potassium

hydroxide. Variation of the ratio of the epoxides and the end groups leads to different products. Polymers with statistically distributed alkylene groups are prepared by using of a mixture of alkylene oxides; separate addition leads to the formation of block copolymers. Because ethylene oxide is more reactive than propylene oxide, random copolymers tend to bear the propylene oxide units at the chain ends.

Terpolymers with, for example, tetrahydrofuran (THF) have also been prepared. Pure THF polymers, which can be obtained by the polymerization of THF in the presence of a Friedel–Craft catalyst, are colorless oily or waxy substances of very low toxicity. Polyalkylene glycols have at least one hydroxyl group at one end of the molecule, and can therefore be regarded as alcohols. The number of hydroxyl groups is increased by the use of water or multifunctional starters. The reaction of the alcohols with acids leads to esters, whereas reaction with, for example, strong acids and olefins leads to ethers. Because the C–O bond is stronger than the C–C bond, polyalkylene glycols have solvent properties that differ somewhat from those of hydrocarbons. The miscibility with water increases with the number of ethylene oxide units, while solubility results from the hydrogen-bonding of water with the free electron pairs of the oxygen. In solution, the water-soluble grades are practically nonflammable (see Section 7.8).

The molecular weight and viscosity of polyalkylene glycols can be significantly influenced during production, and adjusted within narrow limits. The possibility of engineering products in this way distinguishes them from many other lubricants.

Low-molecular-weight polyalkylene glycols containing more than 50% propylene oxide have pour points that may be as low as -65°C . In contrast, pure high-molecular-weight polyethylene glycols are wax-like solids with pour points near $+4^{\circ}\text{C}$.

Kinematic viscosities range from 8 to $100\,000\text{ mm}^2\text{ s}^{-1}$ at 40°C . With the change from diols to monoethers, ester ethers and diethers, at the same molecular weight, the viscosities are reduced, particularly at low temperatures. In comparison with mineral oils (which give straight lines), the V – T diagrams of polyglycols show that their viscosities are too high at both low and high temperatures. The VI-values of polyalkylene glycols usually lie around 200, whereas high-molecular-weight polyethylene glycols have VI values of up to 400.

The prolonged heating of polyalkylene glycols to above 150°C leads to depolymerization.

The polar nature of polyalkylene glycols provides the products with a strong affinity for metals; consequently, the lubricating film will remain intact even at high surface pressure, a property that is very useful in lubricants and metal-cutting fluids. Because the swelling of elastomers decreases with increasing viscosity, polyalkylene glycols can be used with both natural and synthetic rubbers in hydraulic oils and brake fluids. Moreover, their easy removal by washing with water makes them suitable for applications that may be difficult for other products. Products with a high ethylene oxide content are up to 80% biodegradable. Polyalkylene glycols lower the freezing point of water. High-viscosity, water-soluble products are shear-stable liquid thickeners.

7.3.6

Perfluorinated Polyethers

Perfluoroalkylpolyethers (PFPEs) as lubricants were most likely first described by Gumprecht in 1965 [41], and have subsequently been described in detail by Schwickerath and Del Pesco [42, 43].

Perfluoropolyalkyl ethers possess all of the properties required by modern spacecraft: as lubricants and hydraulic fluids they are resistant to thermal and oxidative attack above 260 °C; they possess good low-temperature flow characteristics; and they are fire-resistant. They can also be used as power transmission and inert fluids, and in transformers and generators as dielectrics with outstanding properties.

7.3.7

Polysiloxanes (Silicone Oils)

Polysiloxanes may exist as both liquids and/or solids. A well-known book describing their chemistry and technology was produced by Noll [44]. Those silicone oils that are suitable as lubricants are generally straight-chain polymers of the dimethylsiloxane and phenylmethylsiloxanes.

Among the unique properties of silicone lubricating oils is their immiscibility with many organic fluids, the low temperature-dependence of their physical properties, and their physiological inertness. It is possible to prepare them with both very low pour points and high viscosity, by increasing the asymmetry of the molecules, usually by partial replacement of the dimethylsilyl groups by phenylmethylsilyl groups. The densities of silicone oils are in the region of that of water, while those of dimethylsilicone oils are slightly below, and those of phenylmethyl silicone oils are slightly above.

The thermal decomposition of silicone oils begins at approximately 300 °C. In general, the decomposition products are not corrosive, but they lower the viscosity of the oils. Up to 200 °C, the oxidation stability of silicone oils is superior to that of hydrocarbons, esters, and polyalkylene glycols.

Si–O bonds can also be broken by hydrolytic attack but, in contrast to silicic ester oils, there is no formation of silica or silicic acid gels.

The surface tension and foaming tendency of silicone oils are much lower than those of mineral oils, but the thermal expansion of the same order of magnitude; silicone oils are, therefore, ideal defoamers for the hydrocarbons. The lubricating properties of phenylmethylsilicone oils are better than those of the dimethylsiloxanes; trifluoropropylmethylsilicone oils perform even better [48]. Despite this, the phenylmethylsilicone oils have been widely superseded by perfluorinated polyethers.

Silicone oils may be found in all types of industrial and military installations. Typically, dimethylsilicone oils are used as lubricants for bearings and gears with rolling friction. However, in sliding friction, as their performance depends on the metal pairs, they may be used as lubricants for bronze or brass on aluminum, copper, or zinc at low surface pressures, and also as lubricants for porous bronze bearings. Silicone oils are among the best available lubricants for plastic bearings, although in

precision instrument applications their spreading must be prevented by the use of an epilamization agent. Silicone oils are also suitable lubricants for rubber parts, and may be used as switch and transformer oils. Silicone oils with a higher phenyl substitution are mainly used for the lubrication of turbines, ball bearings, and all types of instrument, especially at high temperatures. Their radiation stability is also remarkable.

Silicone oils can be used as base oils for all types of lubricating greases, whether for sealing and damping applications, for reasons of chemical inertness, or for high-performance applications at both low and high temperatures.

7.4 Rheology of Lubricants

Consistency, flow properties, viscous flow or viscosity in the case of oils, are key parameters to create lubrication efficiency and the application of lubricants. These are terms which appear in nearly all lubricant specifications. Viscosity is also the most important lubricant value which is adopted into the design process for hydrodynamic and elastohydrodynamic (EHD) lubrication.

7.4.1 Viscosity

Friction generated by a fluid surrounding contacting partners—that is, without contact of the partners—is the internal friction of the fluid. In the right-hand branch of the Stribeck graph (see Figure 3.7), internal friction increases with bearing speed. The measure of internal friction in a fluid is termed viscosity. Viscosity and its dimensions are best explained with a model of parallel layers of fluid which could be viewed molecularly (Figure 7.15). If this packet of fluid layers is sheared, the individual fluid layers are displaced in the direction of the shearing force. The upper layers move more rapidly than the lower layers because molecular forces act to resist movement between the layers. These forces create resistance to shearing, and this resistance is

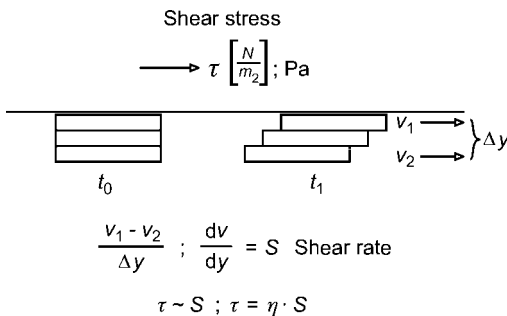


Figure 7.15 Explanation of viscosity. For details, see the text.

given the term *dynamic viscosity*. The difference in velocity between two given fluid layers, related to their linear displacement, is referred to as the shear rate S . This velocity gradient is proportional to the shear stress τ . The proportionality constant μ is called *dynamic viscosity*, and has the units Pa·s. An analysis of the dimensions uses the following equations:

$$S = \frac{dv}{dy} \left[\frac{\text{m}}{\text{s} \cdot \text{m}} \right] \text{ or } [\text{s}^{-1}] \quad (7.1)$$

$$\eta = \frac{\tau}{S} \left[\frac{\text{N}}{\text{m}^2 \cdot \text{s}^{-1}} \right] \text{ or } \left[\frac{\text{Pa}}{\text{s}} \right] \text{ or } [\text{mPa} \cdot \text{s}] \text{ or } (\text{Centipoise}) \quad (7.2)$$

The laboratory determination of viscosity in run-out or capillary tubes is influenced by the weight of the fluid. The relationship between dynamic viscosity and specific gravity is referred to as *kinematic viscosity*, ν , for which the following unit analysis applies:

$$\nu = \frac{\eta}{\rho} \left[\frac{\text{Pa} \cdot \text{s}}{\text{kg} \cdot \text{m}^{-3}} \right] \text{ or } \left[\frac{\text{N} \cdot \text{s} \cdot \text{m}^{-3}}{\text{m}^{-2} \cdot \text{kg}} \right] \text{ or } \left[\frac{\text{kg} \cdot \text{m} \cdot \text{s}^{-2} \cdot \text{s} \cdot \text{m}^{-3}}{\text{m}^{-2} \cdot \text{kg}} \right] \text{ or } \left[\frac{\text{m}^{-2}}{\text{s}} \right] \\ \left[\frac{\text{mm}^2}{\text{s}} \right] \text{ or } (\text{Centistoke}) \quad (7.3)$$

Fluids which display the above proportionality constant between shear stress and shear rate are referred to as “Newtonian” fluids; that is, the viscosity of Newtonian fluids is independent of shear rate (Figure 7.16). Deviations from this Newtonian behavior are sometimes referred to as *structural viscosity*, such viscosities are named as “apparent” viscosities.

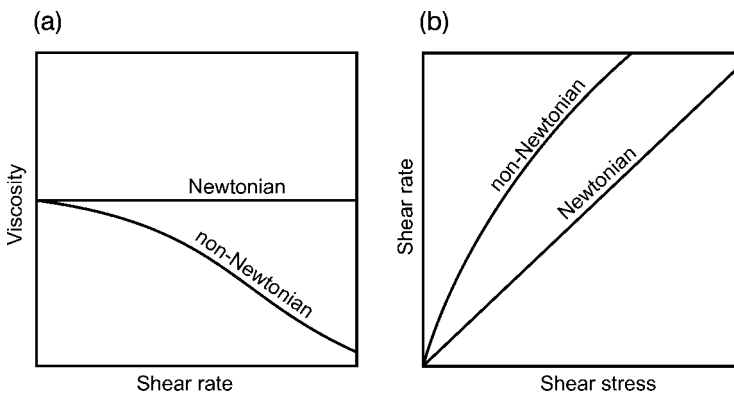


Figure 7.16 Flow characteristics of Newtonian and non-Newtonian lubricants. (A) Viscosity as a function of shear stress; (b) Shear rate as a function of shear stress.

As described above, kinematic and dynamic viscosity differ by way of density. Taking the example of a medium viscosity paraffinic mineral oil cut (ISO VG 32; see Section 7.4.7), the difference is between 12% and 25% at temperatures between 0 ° and 100 °C (the higher values apply to kinematic viscosity).

7.4.2

Influence of Temperature on Viscosity ($V - T$ Behavior)

The viscosity of all oils used for lubrication purposes drops significantly when their temperature increases. In linear systems, this $V-T$ behavior is hyperbolic and the practical differentiation necessary in practice is difficult to replicate; interpolation between two measured viscosities is also problematic. For these reasons, $V-T$ behavior has been allocated to a function which results in a straight-line graph if suitable coordinates are selected. The Ubbelohde-Walter equation has become generally accepted, and also forms the basis of ASTM, ISO and DIN calculation guidelines.

$$\lg \lg (\nu + C) = K - m \cdot \lg T \quad (7.4)$$

In this double-logarithmic formula, C and K are constants, T is temperature in Kelvin, and m is the $V-T$ line slope. Figure 7.17 show the linear and Ubbelohde-Walter double logarithmic $V-T$ curves of three oils with significantly differing $V-T$ lines (naphthenic oil, paraffinic Group III-oil/see Section 7.2) and a natural vegetable (rapeseed) oil. The constant C for mineral oils in the $V-T$ equation is between 0.6 and 0.9.

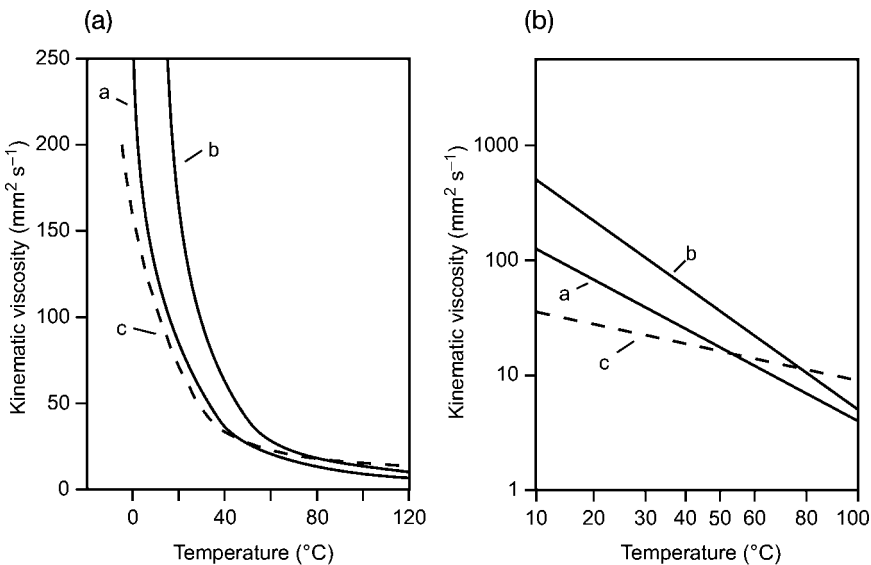


Figure 7.17 The $V-T$ behavior of various oils. (a) Linear; (b) Double-logarithmic. Curve a = paraffinic base oil; curve b = naphthenic base oil; curve c = rapeseed oil.

The constant C only plays a minor role in the viscosity calculation, as larger differences are apparent only at very low temperatures. The use of kinematic viscosity dominates in the lubricants industry, even though dynamic viscosity is a much more important parameter in lubrication technology. The Vogel–Cameron equation is used for the rapid, computer-based calculation of dynamic viscosity. The Vogel–Cameron V – T equation is:

$$\eta = A \cdot \exp\left(\frac{B}{T+C}\right) \quad (7.5)$$

where A , B , and C are constants, and T is the temperature in Kelvin. The m -value in the Ubbelohde–Walter equation which represents the double-logarithmic V – T graph slope is sometimes used to characterize the V – T behavior of oils, and for lubricant base oils is between 4.5 and 1.1 [46]. The smaller m -values apply to oils which are less affected by temperature.

$$m = \frac{\lg \lg (v_1 + 0.8) - \lg \lg (v_2 + 0.8)}{\lg T_2 - \lg T_1} \quad (7.6)$$

7.4.2.1 Viscosity Index

Although the m -value has found only limited acceptance in lubrication technology, this is not the case for the viscosity index, VI, which today defines the international description of viscosity–temperature behavior. This VI was first introduced in the USA in 1928, and was based on the greatest ($VI = 100$) and the smallest ($VI = 0$) temperature dependence of US base oils. The VI is illustrated graphically in Figure 7.18, where values over 100 are calculated as VIE. The VI is also defined in most international standards. The evaluation of V – T behavior at low temperatures,

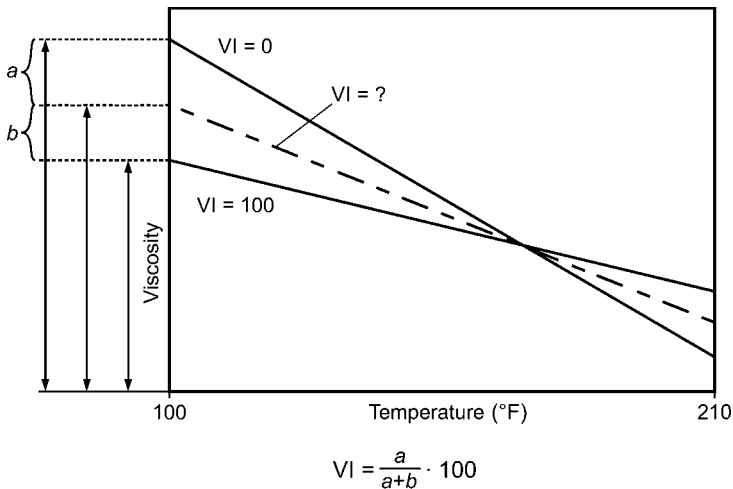


Figure 7.18 Graphical illustration of the viscosity index (VI).

Table 7.4 Various V - T characteristics for several oils [46].

Type of oil	Kinematic viscosity ($\text{mm}^2 \text{s}^{-1}$)		Viscosity index (VI)	m Constant
	40 °C	100 °C		
Naphthenic spindle oil	30	4.24	40	4.05
Paraffinic spindle oil	30	5.23	105	3.68
Medium solvent extract	120	8.0	-50	4.51
Medium polyglycol	120	20.9	200	2.53
Medium silicone oil	120	50.0	424	1.14
Multigrade motor oil (SAE 10W-30)	70	11.1	165	2.82
Ester oil	30	5.81	140	3.40

according to Ubbelohde–Walter lines or other straight-line V - T graphs, often leads to inaccuracies. The previously described dependency effects do not apply to base oils, which may suffer thickening caused by the crystallization of some components (e.g., paraffins) at low temperatures, or those in which the polymer molecules simulate viscosity effects at low temperatures. The V - T characteristics for a range of oils are listed in Table 7.4.

7.4.3

Viscosity–Pressure Dependency

The significance of viscosity–pressure dependency (V - p behavior) was, and still is, underestimated for numerous lubrication applications. V - p behavior has become a part of the calculation of EHD lubricant films. The exponential dependence of viscosity on pressure means that viscosity increases very rapidly with pressure. Metal-forming lubricants can be subject to such pressures that the viscosity of such oils can increase by a number powers of 10. The V - p behavior can be described by the following formula:

$$\eta_p = \eta_1 \cdot e^{\alpha(p-p_1)} \quad (7.7)$$

$$\alpha = \frac{1}{\eta_p} \cdot \left(\frac{d\eta_p}{dp} \right)_T \quad (7.8)$$

where η_p is the dynamic viscosity at a pressure p , η_1 is the dynamic viscosity at 1 bar, and α is the viscosity–pressure coefficient.

V - p dependence is defined by the chemical structure of the substances, with the steric geometry of the molecules being of particular significance. Figure 7.19 shows the development of viscosity against pressure for a number of oils with different chemical structures.

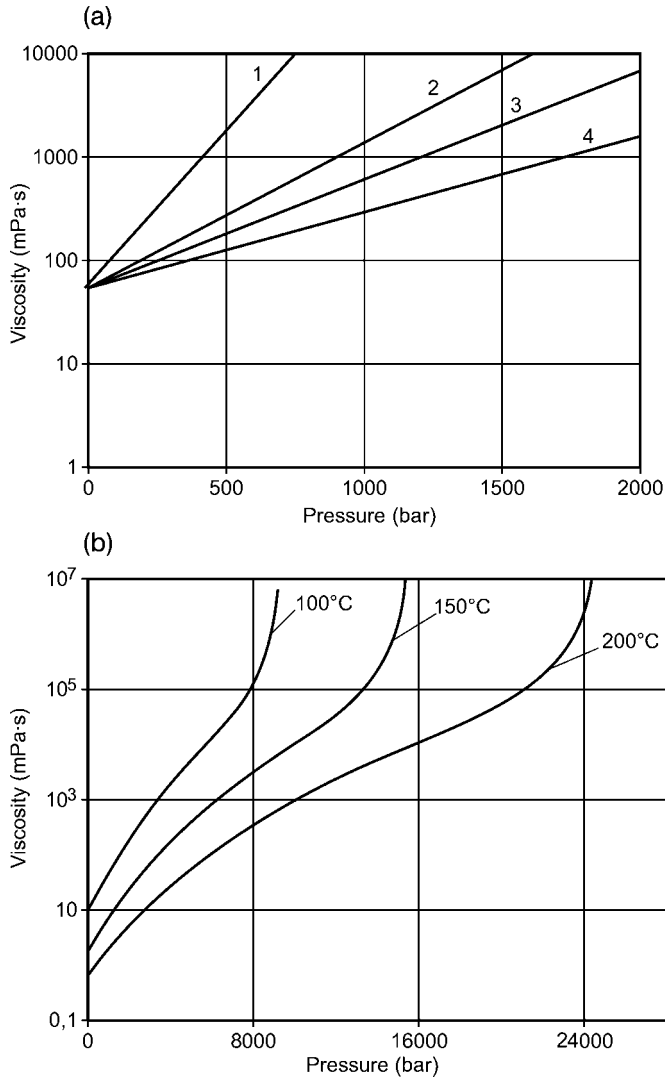


Figure 7.19 Development of viscosity against pressure. (a) Various oils: 1, aromatic oil; 2, naphthenic oil; 3, paraffinic oil; 4, biodegradable polyolester; (b) Increase of the viscosity–pressure coefficient with falling temperature (according to Ref. [47]).

Notably, α can increase significantly with falling temperature, which has an exponential effect on viscosity. Practical lubrication technology therefore necessitates the consideration of pressure and temperature to make a reasonable evaluation of viscosity. It has been shown [48] that VI improvers have an important effect on pressure–viscosity behavior, which affects the lubricant film thickness between lubricated highly stressed contacts under EHD conditions. Depending on the molecular weight and concentration of the VI improvers (see Section 7.5), lubricants

behave differently when such films are formed. At low temperatures, a thin lubricant film is formed, whereas at higher temperatures the VI-improved lubricants form a thicker film as a consequence of a higher viscosity pressure coefficient, α .

7.4.4

The Effect of Shear Rate on Viscosity

The definition of the viscosity of Newtonian fluids (Section 7.4.1), is a constant (proportionality factor) between the shear force τ and the shear rate S . This means that viscosity does not change (with the exception of temperature and pressure dependence) even when subjected to greater shear forces in a friction contact zone, under isothermal and isobaric conditions. Those lubricants which display a dependence on shear rate are known as non-Newtonian, or fluids with *structural viscosity*. Oils containing polymers with specific additives or thickeners and mineral oils at low temperatures (long-chain paraffin effects) display this type of structure-viscous behavior. At normal application temperatures most major lubricant base oils, such as hydrocarbon oils (mineral oil raffinates or synthetic hydrocarbons), synthetic esters and natural fatty oils, can withstand very high shearing forces, as are found in highly loaded machine elements (e.g., gearboxes), and are independent of shear rate. Engine oils containing polymer VI improvers (Section 7.5) or polymer ash-free dispersants display structural-viscosity effects at both low and high temperatures. Although, as a rule, the idea of viscosity depending on the shear rate is undesirable, this effect can be used in fuel-efficiency oils. For example, at high sliding speeds, when hydrodynamic lubrication is present, a lower viscosity will generate a lower friction and thus lead to a lower energy consumption. In an attempt to keep this process under control, the concept of high-temperature high-shear (HTHS) viscosity was introduced, where viscosity is measured at higher temperatures (corresponding to the oil temperature at friction points) and at high shear rates. Typically, this value will appear in an engine oil specification as a threshold value. While the reduction in viscosity caused by the shearing of structure-viscous fluids is reversible (i.e., after the shearing has stopped and the original viscosity has returned), polymer-based oils may suffer a permanent reduction in viscosity. In these cases, the shearing forces lead to a mechanical change or a reduction in the size of the polymer molecules, so that their desired effects are minimized. These effects have been observed, in particular, with multigrade engine oils and high-VI hydraulic oils. The shear stability of these polymers is, therefore, an important quality parameter.

7.4.5

Special Rheological Effects

Apart from the above-described structure-viscosity relationship, and the permanent reduction in viscosity caused by shearing, lubricants may be subjected to further rheological effects and, in particular, to colloidal systems consisting of solid or fluid dispersions (solid dispersions or emulsions). Even a small mechanical loading such as vigorous stirring may cause a system to change completely; for example, a “pasty”

system may break down into a low-viscosity system. If this process is time-based—that is, a continuous mechanical load causes the apparent viscosity to fall over time, while the original viscosity is restored after a certain rest period—these fluids are referred to as being *thixotropic*. This effect is used for sheet-forming lubricants (see Section 7.11), in which case a low-viscosity fluid is preferred for the application of the product (e.g., spraying), whereas a high-viscosity lubricant film which resists run-off is required on the panels. The “rheopexy effect,” in which continuous shearing causes the viscosity to increase, is not applicable to lubrication technology. Time-based viscosity changes can also be caused by the separation of colloidal particles, such as paraffins from mineral base oils, or additives during the storage of lubricants. This undesirable effect may occur during the cooling phase following production, or during long-term storage at low temperatures. This separation process may also be independent of temperature, and be caused by the solubility status of additives in the base oils.

7.4.5.1 Greases

The rheological description of greases is also complex because of their complex system structure (fluids, soap thickeners, solid thickeners, additives; see Section 7.12). The mathematical description of apparent viscosity has yet not gained general acceptance in practice, although the Sisko equation has acquired some significance for shear rates between 10^{-2} and 10^{-4} s^{-1} [46]:

$$\eta_s = \alpha + b\gamma^{n-1} \quad (7.9)$$

where α is the dynamic base oil viscosity, γ the shear rate, and the constants b and n describe pseudoplastic behavior. At lower shear loads, greases behave similarly to structure-viscous substances, but at high shear loads they act much like Newtonian base oils.

Because greases have rather complex rheological properties, they have been described as both solid and liquid or as viscoelastic plastic solids. During the “early days” of rotational viscosimetry, it was hoped that a correlation could be identified between the yield point and cone penetration and, indeed, attempts to accomplish this continue to this day, though with the call to replace cone penetration becoming louder. Beyond the yield point, where flow occurs under stress, greases have an apparent viscosity that depends on the shear rate, temperature and shear time and, to some extent, even on their mechanical pretreatment. This situation can be explained in simple terms, for example in the NLGI Lubricating Grease Guide. Today, controlled stress rheometers appear to be the best-suited devices for providing a better insight into grease rheology, although in the near future this may be aided by velocity imaging being performed in association with nuclear magnetic resonance (NMR) spectrometry.

7.4.6

Viscosity Grades

In order to simplify the classification of lubricants according to their application, a series of viscosity grades was introduced that today have become internationally

accepted. The ISO viscosity grades apply to industrial lubricants, while SAE classifications apply to automotive engine and gear oils.

7.4.6.1 ISO Viscosity Grades

A total of 18 viscosity grades are laid down in the ISO standard 3448. Over the range from 2 to $2500 \text{ mm}^2 \text{ s}^{-1}$, these are the international standard number series E6 rounded to whole numbers, when the '6' numerals correspond to one power of ten (the first and fourth power of 10 are reduced). These viscosity grades were also adopted into or added to national standards such as ASTM or DIN. Viscosity grades are not used for all industrial lubricants; in particular, oils for chip-forming and chip-less metalworking processes are not classified in this way. Apart from the viscosity grades, the ISO 3448 standard defines both tolerances and median viscosities.

7.4.6.2 Engine Oils

In order to define the viscosity of engine oils, two or three viscosity thresholds were selected to define their flow properties at low temperatures, and to define a minimum viscosity at high temperatures. A maximum viscosity at low temperature should ensure a rapid oil circulation to all lubrication points, while permitting a sufficiently higher cranking speed for starting. Likewise, a minimum viscosity at 100°C should ensure that an adequate lubrication of the bearings occurs at high temperatures. Although originally this classification system was devised by the Society of Automotive Engineers (SAE), together with the American Society for Testing and Materials (ASTM), it is today used worldwide and has been adopted into all national standards. Low-temperature viscosity is measured as dynamic viscosity at low shear rates, using a specially constructed rotational viscosimeter (cold-cranking simulator) (Section 7.5). Those oils which fit into only one viscosity grade are referred to as "monograde" oils, and have a V - T behavior which corresponds to that of conventional mineral oils without VI improvers. Those oils which cover two or more viscosity grades are termed "multigrade" oils, and are based on oils containing VI improvers or base oils with a high natural VI.

7.4.6.3 Automotive Gear Oils

Specific SAE viscosity grades have been created for automotive gearbox, axle, and differential oils. Compared to engine oils, the low-temperature behavior of these oils is more heavily weighted, in that a single maximum dynamic viscosity figure and the corresponding maximum temperatures are determined for a number of viscosity grades.

7.4.6.4 Industrial Gear Oils

The American Gear Manufacturers Association (AGMA) defines nine viscosity ranges for industrial gear oils.

7.4.6.5 Base Oils

Mineral base oils are traditionally classified according to Saybolt Universal Seconds (SUS). For example, a 150 N base oil shows a viscosity of 150 SUS at 100°F .

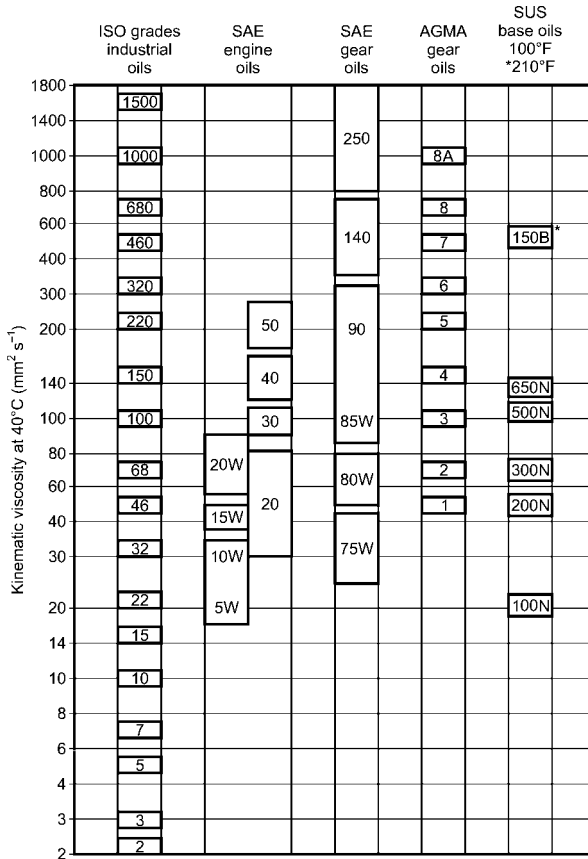


Figure 7.20 Comparison of viscosity grades for various applications.

The viscosity ranges of oils used for various applications are compared in Figure 7.20.

7.5 Additives

Recently, Jürgen Braun has provided a comprehensive review of lubricant additives [65], including detailed formulas and the mechanisms of the effects; the following section is an updated extract of this review. In general, base fluids (i.e., mineral oils and also synthetic products) cannot satisfy the requirements of high-performance lubricants without employing the benefits of modern additive technology. The term “additives” refers to synthetic chemical substances that have the ability to improve many different parameters of lubricants; for example, they may boost existing properties, suppress undesirable properties, and introduce new

properties in the base fluids. Currently, additives account for about 5% of total lubricants, and can be classified with regards to different aspects into two types:

- Those that influence the physical and chemical properties of the base fluids. The physical effects include V - T characteristics, demulsibility and low-temperature properties, while the chemical effects include oxidation stability.
- Those that affect primarily the metal surfaces by modifying their physico-chemical properties. Examples include reducing friction, and improving EP behavior, wear protection, and corrosion inhibition.

7.5.1

Antioxidants

Industrial lubricants must fulfill many different functions, such as power transmission and wear protection, to name only two. The function of a lubricant is very much limited by the aging of the lubricant base stock, the typical characteristics of aged lubricants being discoloration and a characteristic burned odor. In the advanced stages of aging, the viscosity will begin to rise significantly, as acidic oxidation products are built up that, in turn, may induce corrosion and lubricant problems. Yet, this aging process can be delayed significantly by the use of antioxidants.

The aging of lubricants can be differentiated into two processes: (i) an oxidation, by reaction of the lubricant molecules with oxygen; and (ii) thermal decomposition (cracking) at high temperatures. In practice, oxidative aging of the lubricant is the dominant process that has a significant influence on the lifetime of the lubricant. As a result of the steadily increased power density and reduced lubricant volumes (higher load-to-oil ratio), as well as an extended service life during the later years, the thermal stress on the die lubricant molecules grows constantly. The oxidation of hydrocarbons may occur via the well-documented free radical mechanism, through the actions of alkyl and peroxy radicals [49].

The typical oxidation products to be formed via these oxidation processes include alkyhydroperoxides (ROOH), dialkyl peroxides (ROOR'), alcohols (ROH), aldehydes (RCHO), ketones (RR'C=O), carboxylic acids (RCOOH), and esters (RCOOR'). High-molecular-weight oxidation products, formed via polycondensation processes, are responsible for the typical viscosity increase of an aged oil. The subsequent polycondensation and polymerization of these still oil-soluble oxidation products lead to the creation of oil-insoluble polymers that are observed as sludge and varnish-like deposits.

Because of the acidic character of most of these oxidation products, the danger of corrosion is increased, although attacks from alkylperoxy radicals on the metal surface may also be responsible for corrosive wear. These dissolved metals can also form salts which will precipitate as sludge.

Non-hydrocarbon-based lubricants may behave in a totally different manner, however. Typically, the aging of polyalkylene glycols will lead to a reduction in viscosity as a result of decomposition of the polymeric structure.

Antioxidants may be differentiated as either *primary* antioxidants (radical scavengers) or *secondary* antioxidants (peroxide decomposers). The radical scavengers compete successfully with the lubricant molecules in the reaction with reactive radicals of the propagation process. In fact, they react preferably with the radical oxidation products to form resonance-stabilized radicals that are so unreactive that they block any propagation of the atomization. The peroxide decomposers convert hydroperoxides into nonradical products, thus also preventing the chain propagation reaction. Consequently, the combination of an optimum synergistic antioxidant with a metal deactivator would provide the maximum delay of oil oxidation.

7.5.1.1 Phenolic Antioxidants

Sterically hindered mono-, di-, and polynuclear phenol derivatives belong to the most effective antioxidants that act as radical scavengers, and these are used in many applications. Typically, the phenols are substituted in the 2 and 6 positions with tertiary alkyl groups, the most common substituent being the tertiary butyl group. The most simple derivatives are 2,6-di-*tert*-butylphenol (2,6-DTB) and butylated hydroxytoluene (BHT; 2,6-di-*tert*-butyl-4-methylphenol).

7.5.1.2 Aromatic Amines

Oil-soluble secondary aromatic amines represent another important class of antioxidants that act as radical scavengers. Typical products are a large number of alkylated diphenylamines.

7.5.1.3 Compounds Containing Sulfur and Phosphorus

The most famous representatives of this additive group are the zinc dithiophosphates, which mainly act as radical scavengers [50]. Because of their multifunctional properties (antioxidant, antiwear additive, EP additive, corrosion inhibitor), the zinc dithiophosphates have retained their dominant role as standard additives since the early days of modern tribology.

Beside the well-established group of metal dithiophosphates, a large number of ashless dithiophosphoric acid derivatives, the so-called *O,O,S*-triesters, have also been developed. These are the reaction products of dithiophosphoric acid with olefins, cyclopentadiene, norbornadiene, α -pinene, polybutene, unsaturated esters such as acrylic acid esters, maleic acid esters, and other chemicals with activated double bonds. Although these additives all demonstrate both antiwear and antioxidant properties, their antioxidant performance is generally less effective than that of the metal dithiophosphates.

7.5.1.4 Organosulfur Compounds

These products are typical peroxide decomposers, with numerous types of organosulfur compound having been proposed as antioxidants. These include dialkyl sulfides, diaryl sulfides, polysulfides, modified thiols, thiophene derivatives, xanthates, thioglycols, thioaldehydes, sulfur-containing carboxylic acids, heterocyclic sulfur–nitrogen compounds such as dialkyldimercaptothiadiazoles, 2-mercaptoben-

zimidazoles, and others. Both, zinc- and methylenebis(dialkyldithiocarbamates) have been found to be highly efficient.

7.5.1.5 Organophosphorus Compounds

Among this group, the triaryl- and trialkylphosphites are the most common types; such compounds serve not only as peroxide decomposers, but also limit photodegradation. Because of their relatively poor hydrolytic stability, however, their application is restricted to sterically hindered derivatives.

7.5.1.6 Synergistic Mixtures

In general, several types and combinations of antioxidants may be used, the most well-known effect being the synergism between aminic and phenolic antioxidants; this is based on the ability of a phenol to regenerate a more efficient aminic antioxidant. Such a combination of radical scavengers and peroxide decomposers is termed *heterosynergism*. A combination of phenolic antioxidants with phosphites is regarded as being highly efficient, especially in a hydrotreated base stock [51]. As metals may serve as catalysts in the oxidation process, typical rust inhibitors and metal passivators may also be used as synergistic compounds.

7.5.1.7 Testing the Oxidation Stability

Several bench tests have been established for the evaluation of antioxidants, including the turbine oil oxidation stability test (TOST; DIN 51 587, ASTM-D 943, ASTM-D 4310), the rotary bomb test (ASTM-D 2272), and also the IP 48 test. A detailed list of methods is available in Ref. [52]. All of these tests are conducted under severe conditions by increasing the temperature, using catalysts (iron, copper) and a high exposure to oxygen in order to shorten the time required to decompose the lubricant. Depending on the given set of oxidation conditions, the antioxidants will exhibit different performances in different tests. Consequently, a variety of different oxidation tests is necessary to obtain an actual description of the lubricant's oxidation stability and, respectively, the performance of the antioxidants. More recently, high-pressure differential scanning calorimetry (HPDSC) and sealed capsule differential scanning calorimetry (SCDSC) have been more widely applied to monitor the stability of different antioxidants and formulations [53, 54].

7.5.2

Viscosity Modifiers

The basic concepts of viscosity and the viscosity index (VI) are provided in Section 7.4. Although, in the simplest of cases, a desired VI can be achieved by mixing fluids with corresponding VI-values, the viscosity requirements of modern lubricant specifications can usually be met only by the addition of viscosity modifiers (VMs), which are also referred to as viscosity index improvers (VIIs). In contrast to those present in low-molecular base fluids, VMs have a polymer nature, and are generally described as being chain-like molecules, the solubility of which depends on the chain length,

structure, and chemical composition [55]. The absolute increase in viscosity and the VI depends on the type, the molecular weight, and the concentration of the VM in the formulation [56] (see Table 7.5). In practice, and depending on the projected application, molecular weights of 15 000 to 250 000 Da for PAMAs and 2000 to 5000 for PIBs (to name just two) are used, at concentrations usually between 3% and 30% (w/w). Because of their high molecular weight, VMs must always be dissolved in a base fluid. Apart from their thickening effect, their shear stability serves as a second characteristic, as an increasing molecular weight will reduce shear stability if the polymer concentration remains constant. The reason for this effect is either mechanically or thermally induced chain degradation. As opposed to Newtonian fluids—the viscosity of which is independent of the rate of shear or the velocity gradient—long-chain compounds that are subject to high shearing will be mechanically broken such that, depending on the type and duration of the load, a number of different molecular sizes will be created. The resultant reduction in viscosity is described by the permanent shear stability index (PSSI), which indicates the percentage loss of the contribution of the polymer to the viscosity (i.e., the viscosity increase by the VM compared to the base oil viscosity). Under conditions of high shear stress, however, and if the relaxation time for the polymer chains is short, then the high-molecular-weight molecules will adopt a temporary alignment. This causes the polymer coils to deform in the direction of the shear force, such that part of their original contribution to the viscosity is lost. This reversible fall in viscosity is described by the temporary shear stability index (TSSI). Both, the PSSI and TSSI are of major importance for automotive applications, and especially for engine, gear, and hydraulic oils, because the specified characteristics of these oils should not only apply to the fresh oil but also persist throughout the drain interval. Although the reduction in molecular weight is, in practice, overshadowed by oxidation and other effects, a series of laboratory tests has been established to characterize the shear stability [57].

The most important monomers for VMs are shown in Table 7.6, as structural formulas in the typical nomenclature for homo- and copolymers. Depending on the polarity of the monomer, the VMs are either dispersing or nondispersing. Dispersing VMs are, in principle, the link to ashless dispersants.

7.5.3

Pour point Depressants

With the exception of polyalkylated naphthalenes, pour point depressants (PPDs) are closely linked to a series of VMs. The major differences among these polymers are their application concentrations, and the selection of monomer building blocks. Both, molecular weight and thickening efficiency play only subordinate roles in a band, from 0.1% to a maximum of 2%. Whilst an additional thickening effect is always welcome, it is usually limited by solubility thresholds.

As is generally the case with flow improvers, although paraffin crystallization cannot be suppressed, the crystalline lattice—and thus the morphology of the paraffin crystals—can be significantly altered.

Table 7.5 Types of polymeric viscosity modifier.

Viscosity modifier type	Description	Main applications
$\text{OCP} \left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2 - \text{CH}_2\text{A} - \text{CH}_2 - \text{CH})\text{B} \end{array} \right]_x$	Olefin copolymers	Engine and hydraulic oils
$\text{PAMA} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 - \text{C} \\ \quad \\ \text{C=O} \quad \text{O} \\ \\ \text{C}_n\text{H}_{2n+1} \end{array} \right]_x$	Polyalkyl(meth)acrylates	Gear and hydraulic oils
$\text{PIB} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 - \text{CH} \\ \\ \text{CH}_3 \end{array} \right]_x$	Polysisobutylene	Gear oils, raw material for ashless dispersants
$\text{SIP} \left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2 - \text{CH}_2 - \text{CH} - \text{CH}_2\text{A} - (\text{CH}_2 - \text{CH})\text{B}) \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_x$	Hydrogenated styrene-isoprene copolymers	Engine oils
$\text{SBR} \left[\begin{array}{c} \text{CH}_2 \\ \\ (\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{A} - (\text{CH}_2 - \text{CH})\text{B} - (\text{CH}_2 - \text{CH})\text{C}) \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_x$	Hydrogenated styrene-butadiene	Engine oils

Table 7.6 Engine oil viscosity classification SAE J 300 (July 2001).

SAE viscosity grade	Low-temperature cranking viscosity (mPa·s) at temp. in °C (CCS)	Low-temperature pumping viscosity (mPa·s) at temp. in °C (MRV)	Low shear-rate kinematic viscosity at 100 °C (mm ² s ⁻¹)		High shear-rate viscosity at 150 °C and 10 ⁶ s ⁻¹ (mPa·s)
	Maximum	Maximum	Minimum	Maximum	Minimum
0 W	6200 at -35	60 000 at -40	3.8	—	—
5 W	6600 at -30	60 000 at -35	3.8	—	—
10 W	7000 at -25	60 000 at -30	4.1	—	—
15 W	7000 at -20	60 000 at -25	5.6	—	—
20 W	9500 at -15	60 000 at -20	5.6	—	—
25 W	13 000 at -10	60 000 at -15	9.3	—	—
20	—	—	5.6	<9.3	2.6
30	—	—	9.3	<12.5	2.9
40	—	—	12.5	<16.3	2.9 ^{a)}
40	—	—	12.5	<16.3	3.7 ^{b)}
50	—	—	16.3	<21.9	3.7
60	—	—	21.9	<26.1	3.7

a) For 0 W, 5 W, 10 W.

b) For 15 W, 20 W, 25 W and Monogrades.

7.5.4

Detergents and Dispersants

Detergents and dispersants, which often are referred to as DD or HD (heavy-duty) additives, have in the past been indispensable for the development of modern engine oils for gasoline and diesel combustion motors. These lubricants are especially severely stressed due to the high temperatures to which they are exposed, and the additional influence of aggressive blow-by gases of the combustion process. Notably, DD additives keep oil-insoluble combustion products in suspension, and also prevent resinous and asphalt-like oxidation products from agglomerating into solid particles. The overbased metal-containing compounds are also capable of neutralizing acidic combustion products and oxidation products, on the basis of their alkaline reserve. Thus, DD additives will prevent oil thickening, sludge formation and varnish deposition on metal surfaces, and also corrosive wear. The original definition of detergents refers to their cleaning properties; this is similar to the detergents in washing agents, although their function appears more related to the dispersal of particulate matter such as abrasive wear and soot particles, rather than the removal and clearing up of existing dirt. Historically, these types of additives have been metal-containing compounds, often with a high alkaline reserve, although in order to meet the dramatically increased requirements of modern high-performance engine oils, new ashless dispersants with improved dispersing properties have been developed. As these ashless compounds also possess cleaning properties, there is in fact no clear

difference between detergents and dispersants; rather, it is more of an arbitrary definition to refer to the metal-containing compounds as detergents, and to the ashless types as dispersants. It seems more appropriate, therefore, to speak of metal-containing and ashless DD or HD additives [58].

As molecules, detergents and dispersants generally have a large oleophilic hydrocarbon “tail” and a polar hydrophilic head group. The tail section serves as a solubilizer in the base fluid, while the polar group becomes attracted to contaminants in the lubricant. A multitude of dispersant molecules are capable of enveloping solid contaminants and to form micelles; in this case, the nonpolar tails will prevent not only the adhesion of polar soot particles on metal surfaces, but also their agglomeration into larger particles.

7.5.4.1 Phenates

Phenates represent an important class of detergents which are synthesized by the reaction of alkylated phenols with elemental sulfur or sulfur chloride, followed by neutralization with metal (calcium, magnesium, barium) oxides or hydroxides. Calcium phenates are currently the most widely used types. Basic calcium phenates may be produced by using an excess of the metal base; in addition to their good dispersant properties, these materials also possess a greater acid-neutralization potential.

7.5.4.2 Salicylates

Salicylates are generally prepared by the carboxylation of alkylated phenols, with subsequent metathesis into divalent metal salts. Typically, these products are also overbased by an excess of metal carbonate (calcium and magnesium) to form highly basic detergents that are stabilized by micelle formation. Salicylates exhibit additional antioxidant properties, and have proven efficacy in diesel engine oil formulations.

7.5.4.3 Thiophosphonates

These representatives of the detergents are produced by the reaction of polybutene (molecular weight 500–1000 Da) with phosphorus pentasulfide, followed by hydrolysis and the formation of metal (calcium, formerly also barium) salts. The reaction products consist mainly of thiopyrophosphonates combined with thiophosphonates and phosphonates. Today, overbased products are virtually unused.

7.5.4.4 Sulfonates

Sulfonates are metal salts of long-chain alkylarylsulfonic acids, and can be categorized as petroleum and synthetic types (for more detail, see Section 7.5.9). Besides their excellent anticorrosion properties, the neutral (and especially the so-called overbased) sulfonates that form with colloiddally dispersed metal oxides or hydroxides also exhibit an excellent detergent and neutralization potential; this renders them very cost-effective multifunctional DD additives for engine oils. Calcium sulfonates are relatively cheap products with a good general performance; magnesium sulfonates show excellent anticorrosion properties but, after thermal decomposition, tend

to form deposits of hard ash that may lead to bore polishing. Currently, barium sulfonates are very rarely used due to their toxic properties.

7.5.4.5 Ashless Dispersants

As opposed to detergents containing metals, ashless dispersants (ADs) are—by definition—free from metals. The ADs are generally derived from hydrocarbon polymers, the best-known and economically most interesting raw material group being polybutenes with molecular weights of 500 to 3000 Da. As a result of the cationic polymerization of a C₄ cut, polybutenes (PIBs) with double bonds are formed, which can be thermally coupled with maleic anhydride (MA), to produce polyisobutene succinic acid anhydride (PIBSA). In addition to the thermal synthesis of PIBSA, a chlorine-catalyzed production process is also still in use. In a further reaction step, oligomeric aminoalkylenes are added to the anhydride to form thermally stable imides. Hence, by using suitable raw materials and reaction control, this two-stage, single-vessel reaction can provide a variety of products.

Because advanced passenger car motor oil (PCMO) formulations contain almost twice the amount of ADs as in the past, the search is on for highly efficient alternatives. The dispersion of oxidation, nitration, and soot particles can be controlled by the selection of an appropriate product mixture, and by the use of components of adequate purity.

7.5.5

Antifoam Agents

The foaming of lubricants is a very undesirable effect that can cause enhanced oxidation by the intensive mixture with air, cavitation damage, and also an insufficient oil transport in circulation systems that may even lead to a lack of lubrication. Besides negative mechanical influences, the foaming tendency depends very much on the lubricant itself, and is influenced by the surface tension of the base oil, and especially by the presence of surface-active substances such as detergents, corrosion inhibitors, and other ionic compounds.

One very important point to appreciate in order to understand foaming effects is the difference between the so-called “surface foaming” and “inner foaming”:

- *Surface foaming* can be controlled by the use of antifoam agents; effective defoamers possess a lower surface tension compared to the lubricant base oil, are usually not soluble in the base oil, and therefore must be finely dispersed in order to be sufficiently stable, even after long-term storage or use. The particle size of the dispersed defoamers should be less than 100 μm, or even less than 10 μm.
- *Inner foaming* refers to the presence of finely dispersed air bubbles in the lubricant, that can form very stable dispersions.

Unfortunately, the common defoamers that are dedicated to controlling a surface foam tend to stabilize the inner foam. Generally, the air-release properties of lubricants cannot be improved on by using additives; in fact, many additives have a negative influence on air-release. Those lubricants which need excellent air-release

properties (e.g., turbine oils) must be formulated using specially selected base oils and additives. Air is present in the lubricants not only in the form of dispersed air bubbles (surface and inner foam), but may also be truly physically dissolved up to 9% (v/v) in mineral oil. This air may also cause severe problems such as cavitation (“diesel effect”), an effect which cannot be controlled by additives.

7.5.5.1 Silicon Defoamers

Liquid silicones, especially linear and cyclic polydimethylsiloxanes, are the most efficient antifoam agents at very low concentrations of 1% to a maximum of 100 mg kg⁻¹. To guarantee a stable dispersion, the silicones usually are predissolved in aromatic solvents. Compared to other additives, silicone defoamers have two major disadvantages: (i) they are very easily carried out of the lubricant due to their insolubility; and (ii) they have a strong affinity towards polar metal surfaces.

7.5.5.2 Silicone-Free Defoamers

Nowadays, silicone-free defoamers are used increasingly in many applications. Notably, in metalworking processes both the cutting fluids and any hydraulic fluids used in close proximity must be silicone-free to guarantee the subsequent application of paints or lacquers on the workpieces. In the past, silicones have caused major problems in this respect. The most frequently used silicone-free defoamers are poly(ethylene glycol)s (PEGs) (polyethers), polymethacrylates, and miscellaneous organic copolymers. Tributylphosphate has also been proposed for use as an antifoam agent.

7.5.6

Demulsifiers and Emulsifiers

7.5.6.1 Demulsifiers

Most of the industrial oils used in circulation systems (hydraulic, gear, turbine and compressor oils) require good or excellent demulsification properties in order to separate any water contamination from the lubricating system. Without demulsifiers, lubricating oils can form relatively stable water-in-oil emulsions. In principle, all surface-active substances are suitable demulsifiers, the first-known types having been the alkaline-earth metal salts of organic sulfonic acids, particularly barium and calcium dinonylnaphthenesulfonates. Nowadays, special PEGs and other ethoxylated substances have proven to be highly efficient demulsifiers, and form part of many additive packages. Surprisingly, the same class of chemical substances is used as emulsifiers, although in this case the molecular weight, the degree of ethoxylation and the treatment rate are all very important to guarantee the demulsifying properties.

7.5.6.2 Emulsifiers

Emulsifiers are especially important in the formulation of water-based metal-working fluids; hence, their types and mechanism(s) of emulsification are described in detail elsewhere [59, 60, 66].

7.5.7

Antiwear (AW) and Extreme Pressure (EP) Additives

When two contacting parts of a machinery first start to move, and the hydrodynamic lubrication has not yet built up, or severe stress and strong forces are involved, the lubricating system will run in the area of *mixed friction*. In this case, the application of antiwear (AW) and extreme pressure (EP) additives will be necessary in any metal-working fluid, engine oil, hydraulic fluid or lubricating grease, in order not only to prevent welding of the moving parts but also to reduce any respective wear. Because of their polar structures, these additives form layers on the metal surface by adsorption or chemisorption; this guarantees their immediate availability in the case of mixed-friction conditions. However, when the hydrodynamic lubricating film is either not yet or no longer present, the temperature will increase such that the AW and EP additives can react with the metal surface to form tribochemical reaction layers (iron phosphides, sulfides, sulfates, oxides and carbides, depending on the chemistry of the additive) that will prevent direct contact between the sliding metals. These friction-reducing, slideable reaction layers can smooth the asperity of the metal surface by plastic deformation, and reduce wear that otherwise would occur due to microwelding processes. It also avoids any real welding of the moving parts under EP conditions. The layers formed by only physically adsorbed polar substances, such as fatty oils and fatty acids, exhibit only poor or moderate high-pressure properties; these types of additive are termed *friction modifiers*.

More effective and more stable than friction modifiers are the chemically reactive products (AW and EP additives) that can form tribochemical reaction layers. The AW additives are mainly designed to reduce wear when the running system is exposed to moderate stress, whereas EP additives are much more reactive and used when the stress of the system is very high, the aim being to prevent welding of the moving parts that otherwise would lead to severe damage. Although, typically, EP additives increase wear effects due to their high reactivity, this differentiation cannot be precise, there being many additives that may be related to either group.

7.5.7.1 Phosphorus Compounds

Organic phosphorus compounds function excellently as AW additives under conditions of medium stress. Whilst some of these additives are highly efficient FZG boosters, most are neutral and acidic phosphoric acid ester derivatives, their metal or amine salts, or amides. As the acidic form of these compounds is the most reactive, the reactivity decreases with the degree of neutralization. Trialkyl- and triarylphosphates represent the neutral phosphoric acid triesters, where tricresylphosphate (TCP) is the most well-known species (for toxicological reasons, TCP should be free of *o*-cresol). Amine-neutralized mixtures of mono- and dialkyl phosphoric acid partial esters are highly efficient FZG boosters, and are used widely in ashless hydraulic oil formulations. Some types also exhibit anticorrosion properties. Ethoxylated mono- and dialkylphosphoric acids are even more polar as a result of their hydrophilic structure, which renders them more efficient. Recently, the use of *phosphites* has also generated much interest, although due to the inherent hydrolytic instability of this

chemical group in practice, only sterically hindered derivatives such as triarylphosphites and long-chain trialkylphosphites have been used, and for very few applications. Besides their AW properties, phosphites are capable of scavenging free sulfur via the formation of thiophosphates, on which reaction their use in gear oils is based.

7.5.7.2 Compounds Containing Sulfur and Phosphorus

The most important and well-known additives of the sulfur–phosphorus compounds are the zinc dialkyldithiophosphates (ZnDTP) [61]. These are synthesized by the reaction of primary and secondary alcohols (C4–C12), as well as alkylated phenols with phosphorus(V) sulfide, followed by neutralization of the resulting dialkyldithiophosphoric acids with zinc oxide. Usually, this last reaction step is carried out in a mineral oil solution, but it is also possible to make mineral oil-free compounds by using solvents that can subsequently be removed by distillation. In addition to the neutral species, basic ZnDTPs can also be obtained by conducting the neutralization with an excess of zinc oxide. ZnDTPs based on isopropanol or *n*-butanol are solids, whereas mixtures of short- and long-chain alcohols are liquid. The thermal and hydrolytic stability of ZnDTPs—and thus their reactivity (i.e., AW/EP-performance)—can be influenced by the structure of the alkyl groups. Hence, their thermal stability will increase not only with the chain length of the alkyl groups, but also with their structure in the sequence secondary, primary, and aromatic. Yet, by carefully directing the alcohol composition, the specific requirements of different applications can be adjusted on a selective basis. Besides excellent AW and EP properties, the ZnDTPs also serve as efficient antioxidants and metal passivators. Taken together, the multifunctional properties of the ZnDTPs lead to them being currently the most widely used and cost-effective additive group, with huge quantities employed in engine oils, shock absorber oils, and hydraulic fluids.

Ashless dialkyldithiophosphoric acid-*O,O,S*-triesters are distinguished by their improved hydrolytic stability in comparison with metal salts of the dithiophosphoric acids, although unfortunately, their antioxidant properties are reduced. As with the ZnDTPs, the reactivity of the dialkyldithiophosphoric acid-*O,O,S*-triesters can be influenced by a variation in the organic substituents.

7.5.7.3 Compounds Containing Sulfur and Nitrogen

Zinc-bis(diaryldithiocarbamate) and the ashless methylene-bis(di-*n*-butyldithiocarbamate) are highly effective EP additives and excellent antioxidants. Besides these main species, antimony and tungsten derivatives have also been prepared. The dithiocarbamates are used predominantly in lubricating greases, and to some extent also in gear oil formulations. Although the dialkyl-2,5-dimercapto-1,3,4-thiadiazole (DMTD) derivatives are usually known as metal passivators and sulfur scavengers, they also exhibit excellent EP properties. Unfortunately, the use of thiadiazoles and dithiocarbamates is limited by their relatively high price level.

7.5.7.4 Sulfur Compounds

From the early days of lubrication until the present time, elemental sulfur has been added directly to mineral oil (up to 1.5%) to improve the EP properties of

metal-working fluids. The oil-soluble organic sulfur compounds, the so-called “sulfur carriers” (general formula $R-S_x-R$) offer improved solubility and better control over the reactivity of the sulfur. Fundamentally, it is possible to differentiate between inactive and active sulfur carriers:

- The *inactive* types with predominantly disulfide bridges ($x = 2$) possess relatively stable C–S bonds which will react only at elevated temperatures.
- The *active* forms, with x between 3 and 5 (so-called pentasulfides), are much more reactive, as the sulfur of the relatively labile polysulfide bridges can easily be made available, even at low temperatures.

Numerous sulfur carriers with specific distribution of the different polysulfide bridges ($x = 1-5$) are used to cover the whole field of application, with its varying stress requirements. The mechanism of sulfur carriers under EP conditions begins with a physical adsorption, followed by chemisorption and finally cleavage of the sulfur and its reaction with the metal surface. Generally, this reaction takes place at temperatures above 600 °C [62]. Active sulfur carriers are excellent EP additives that will prevent welding via a form of controlled wear, when the slideable reaction layers are removed continuously under severe loads. Because of the high reactivity with nonferrous metals, active sulfur carriers cannot be used in the machining of these materials, especially when nonferrous metals are incorporated into an engine or other aggregates. Inactive sulfur carriers require higher temperatures to set the sulfur free; they are therefore much more compatible with nonferrous metals, and demonstrate AW properties to some degree. Contrary to this well-known behavior, active sulfur carriers exhibit surprisingly good AW properties in unsaturated esters or fatty oils, such as trimethylolpropanetrioleate or rapeseed oil [63]. The polarity, and thus the affinity to the metal surface, is determined by the organic substituents. The polarity increases in sequence-sulfurized hydrocarbons, esters, alcohols and fatty acids, whereas the solubility in mineral oil decreases in the same order.

7.5.7.5 Chlorine Compounds

The excellent AW/EP properties of chlorine compounds have been conventionally explained by their ability to coat the metal surface with a slideable metal chloride film, under the influence of high pressure and in the presence of traces of moisture. Because of the formation of hydrogen chloride, alkaline buffers must be added to avoid severe corrosion. Another approach refers to the formation of high-pressure stable adsorption layers due to the affinity of the additive's heteroatom (Cl) showing outstanding lubricity at low machining speed and moderate temperature, but a reduced efficiency with increasing temperature (speed). For environmental and toxicological reasons concerning disposal of the chlorinated fluids used, chlorine compounds are being increasingly replaced, despite this additive technology having been extremely successful in metal-working fluids. Typical additives have included chlorinated paraffins (with a chlorine content of 35–70%), and a hydrocarbon base of 10–20 carbon atoms, as well as chlorinated sulfur carriers.

7.5.7.6 Solid Lubricating Compounds

In general, finely ground powders of graphite and molybdenum disulfide, and also of their dispersions, are used as solid additives. Further detailed information on this subject is provided in Section 7.13.

7.5.8

Friction Modifiers (FM)s

In the case of fluid (hydrodynamic) lubrication, friction can be reduced only by the use of base oils with lower friction coefficients and a lower viscosity (and, in turn, a high VI). In the area of low slide velocities, moderately increased loads and low viscosities at higher temperatures, a liquid lubrication can easily proceed to mixed-friction conditions. In this case, so-called “friction modifiers” must be used to prevent stick–slip oscillations and noises, by reducing the frictional forces. These modifiers function at temperatures where AW and EP additives are not yet reactive, by forming thin monomolecular layers of physically adsorbed polar oil-soluble products or tribochemical friction-reducing reaction layers that exhibit a significantly lower friction behavior compared to typical AW and EP additives. Thus, friction modifiers can be regarded as mild AW or EP additives working at moderate temperatures and loads in the area of beginning mixed friction.

Friction modifiers can be classified into different groups on the basis of their function [64]: (i) mechanically working FM)s (solid lubricating compounds, e.g., molybdenum disulfide, graphite, PTFE, polyamide, polyimide, fluorinated graphite); (ii) adsorption layers forming FM)s (e.g., long-chain carboxylic acids, fatty acid esters, ethers, alcohols, amines, amides, imides); (iii) tribochemical reaction layers forming FM)s (saturated fatty acids, phosphoric and thiophosphoric acid esters, xanthogenates, sulfurized fatty acids); (iv) friction polymer-forming FM)s (glycol dicarboxylic acid partial esters, dialkylphthalic acid esters, methacrylates, unsaturated fatty acids, sulfurized olefins); and (v) organometallic compounds (molybdenum compounds such as molybdenum dithiophosphates, molybdenum dithiocarbamates, their synergistic combination with ZnDTPs, copper-containing organic compounds).

One widespread group of FM)s is that of the adsorption-forming agents, the effects of which increase with increasing molecular mass in the order alcohol < ester < unsaturated acid < saturated acid. The main products are carboxylic acids with 12 to 18 carbon atoms, fatty alcohols and synthetic (methyl, butyl) or natural esters of fatty acids (glycerides). Typical applications of FM)s are modern fuel economy oils, slide-way oils, automatic transmission fluids (ATFs) that contain so-called “anti-squawk” additives, and lubricants for limited-slip axles that contain so-called “anti-chatter” additives.

7.5.9

Corrosion Inhibitors

Corrosion inhibitors are used in almost every lubricant to protect the metal surface of any machinery, metal-working tool or workpiece from the attack of oxygen, moisture, and aggressive products. These mostly acidic products may be formed by the thermal

and oxidative decomposition of the lubricant (base oil and additives), brought in directly from the environment (acid atmosphere), or caused by the specific application (aggressive blow-by gases in internal combustion engines). The base oil itself forms a type of protective layer on the metal surface, although this will generally not be sufficient, especially when highly refined oils without natural inhibitors are used. The use of a highly efficient anticorrosion additive is then necessary. Corrosion inhibitors can be divided into two main groups: (i) antirust additives for the protection of ferrous metals; and (ii) metal passivators for nonferrous metals.

7.5.9.1 Antirust Additives (Ferrous Metals)

Sulfonates Petroleum sulfonates (mahogany sulfonates) are byproducts of the production of white oils by treatment with oleum, when the resulting acid tar contains long-chain alkylarylsulfonic acids. Sodium sulfonates of low molecular weight (below ca. 450 Da) are typically used as low-priced emulsifiers and detergents, but with additional anticorrosion properties, in water-based metal-working fluids, engine oils, and rust preventatives. Sulfonates with higher molecular weights are distinguished as highly efficient corrosion inhibitors, especially when based on divalent cations such as calcium, magnesium, and barium (though the use of barium compounds is steadily decreasing for toxicological and ecotoxicological reasons). Nowadays, despite their greater cost, synthetic alkylbenzene sulfonates are used preferably, based on their superior and more consistent quality. These are the reaction products of specifically designed monoalkylbenzenesulfonic acids (typically C-24 alkyl groups) and dialkylbenzenesulfonic acids (typically two C-12 alkyl groups) with alkaline and earth alkaline metal hydroxides. One special group of synthetic sulfonates is that of the dinonylnaphthenesulfonates, of which the neutral calcium and barium salts may be distinguished due to their additional demulsifying properties and high compatibility with EP additives. In addition to the neutral or only slightly basic sulfonates, overbased sulfonates with a high alkaline reserve [total base number (TBN) 100–400 mg KOH g⁻¹] play an important role, especially in the formulation of engine oils where they exhibit detergent properties and also neutralize acidic oxidation products. Moreover, in metal-working fluids they act as so-called “passive” EP additives.

Carboxylic Acid Derivatives Many different long-chain carboxylic acid derivatives have been proposed as corrosion inhibitors, where the carboxylic group acts as a polar moiety that can easily be adsorbed onto the metal surface. Lanolin (wool fat) and salts of the lanolin fatty acids, mostly in combination with sulfonates, have long been known as corrosion inhibitors in rust preventatives. Oxidized paraffins, with their high polarity due to a high content of hydroxyl-oxo-carboxylic acids, are still used for that purpose. Zinc naphthenates are used especially in lubricating greases, but lead naphthenates are no longer used for toxicological reasons. Alkylated succinic acids, their partial esters and half amides, are known as “highly efficient” rather than emulsifying antirust additives, even at very low treatment rates of 0.01–0.05%, and consequently are used preferably in turbine oils and hydraulic fluids. Another

widespread group are the amides and imides, as reaction products of saturated and unsaturated fatty acids with alkylamines and alkanolamines; the best-known of these is *N*-acylsarcosine.

Amine-Neutralized Alkylphosphoric Acid Partial Esters Some special amine salts of mono- or dialkylphosphoric acid partial esters exhibit excellent anticorrosion properties, in addition to highly efficient AW properties.

Vapor-Phase Corrosion Inhibitors Vapor-phase corrosion inhibitors (VCIs) for closed systems are substances with a high affinity to metal surfaces and a relatively high vapor pressure that guarantees their availability on parts that are not consistently in direct contact with a corrosion-inhibited lubricant. The most frequently used product group for this application are amines.

7.5.9.2 Metal Passivators (Nonferrous Metals)

The metal passivators can be classified into three groups: film-forming compounds; complex-forming chelating agents; and sulfur scavengers. The fundamental function of the film-forming types consists of building passivating protective layers on the nonferrous metal surface, thus preventing the solubilization of metal ions that would function as pro-oxidants. The complex-forming agents are able to build oil-soluble complexes with significantly reduced catalytic activity with regards to the influence of nonferrous metal ions on the oxidative aging process of lubricants. Sulfur scavengers are capable of capturing corrosive sulfur by integrating it into their molecular structure.

Metal passivators, in combination with antioxidants, demonstrate strong synergistic effects, as they not only prevent the formation of copper ions but also in turn suppress their behavior as pro-oxidants. Consequently, these metal-passivating additives are used in almost every formulation of modern lubricants, the most often being benzotriazole and tolyltriazole, as well as their alkylated liquid derivatives.

7.6

Lubricants for Internal Combustion Engines

Within the global lubricants market, engine lubricants account a greater than 60% segment. While, today, demand in Europe is effectively stagnating and is expected to decline slightly in the foreseeable future (despite increasing vehicle registrations), there is still considerable growth potential in Southeast Asia and third-world threshold countries.

In 2007, Haperscheid [67] presented a 40-pages report covering the subject of lubricants for internal combustion engines, including their formulation, classifications, specifications, and testing. Although the following text is mainly related to Haperscheid's report, it also includes updates from 2008.

Historically, the development of engine oils over the past 50 years has been focused on specifications issued by the international automobile industry. Starting with the

first specifications published by the US Army (MIL specs), today there are three internationally recognized sets of minimum requirements. In Europe, these are the Association des Constructeurs Européen d'Automobiles (ACEA), in the USA, the API, and in Asia The International Lubricant Standardization and Approval Committee (ILSAC). Details of these specifications are provided in Section 7.6.8. In principle, all specifications reflect the successive adaptation of oil qualities to developments in engine design.

7.6.1

Function of Engine Oils in Four-Stroke Engines

Engine oils have to fulfill a wide range of functions in engines. The purely tribological task consists of guaranteeing the functional reliability of all friction points in all operating conditions. Apart from this classical tribological task, engine oils have to perform a number of additional functions. This begins with the sealing of the cylinder, and ends with the transport of sludge, soot, and abraded particles to the oil filter. Starting with the tribological functions, the three classic sections of the Stribeck graph are satisfied, from hydrodynamic full lubrication to the EHD area in bearings to the boundary friction conditions at top dead center (TDC) and bottom dead center (BDC) [68]. All friction pairings, and a whole series of parameters, are covered. The sliding friction speeds range from the simple linear up-and-down movement of the piston in the cylinder through to extreme rotational movements in the floating-needle roller bearings found in advanced turbochargers rotating at speeds of up to 200 000 rpm, with micron tolerances. The temperatures encountered range from ambient in the Arctic (-40°C) to sump temperatures of 100°C to peak values of over 300°C under the piston crown. During the combustion process, the engine oil helps to seal the piston and cylinder whilst, at the same time, burning off from the cylinder wall without leaving any residue. As for the piston itself, the engine oil dissipates heat from the piston, causing it to be cooled. Both, the blow-by gases formed when fuel is burned, and their reaction byproducts, must be neutralized and held in suspension; the same applies to the soot and sludge particles resulting from any incomplete combustion. The oil also transports dirt and any abraded particles to the oil filter, and ensures its filterability. In addition, any water formed during the combustion process should be emulsified; moreover, even when higher concentrations of water are present and when the phases separate as the temperature falls, the oil should protect against corrosion.

Engine oils should reduce friction and wear during extreme, low-temperature start-ups, as well as when the lubricating film is subject to high temperatures and pressures in bearings and around the piston rings. While the oil should still flow well and be pumpable without aeration at low temperatures (down to 40°C) to avoid metal-to-metal contact during cold start-ups, the die lubricating film must perform satisfactorily in the bearings and hydraulic tappets. At low temperatures, the additives must not precipitate, and neither must the oil gel. At the upper end of the temperature scale, the oil must offer far-reaching resistance to thermal and mechanical aging.

And finally, the stability of the lubricating film should not be diminished by fuel dilution of up to 10%.

7.6.2

Viscosity Grades

The viscosity of an engine oil is an indicator of how readily a load-carrying film can be formed at all lubrication points in an engine. As viscosity is a function of temperature, this applies to all potential ambient and operating temperatures (see Section 7.4). The adequate and rapid circulation of the oil at low temperatures which is provided by a low viscosity [69] must also be achieved at cold-start cranking speeds. On the other hand, viscosity must not fall too much at high temperatures, so that an adequate lubricating film stability is provided at high thermal loads. A comparison of mono-grade and multigrade oils is listed in Table 7.6.

7.6.3

Performance Specifications

As a result of the continuing increase in specified oil performance, the leading automobile manufacturers (original equipment manufacturers; OEMs) have identified lubricants as constructional elements, and have adopted their quality philosophy. The result has been a qualitative shift in the engine oil market, away from conventional products to semi-synthetic and synthetic formulations. Along with their higher price, the economic and ecological demands on these oils have also risen. Detailed demands include: a longer life in spite of higher thermal and mechanical loads; improved emission characteristics by cutting fuel consumption; lower oil-related particulate emissions; and improved wear protection, even under severe conditions. Put simply, engine oils must offer significant potential with regards to reduction in fuel consumption and extensions in oil-change intervals [70]. At present, the oil-change intervals range between 10 000 and 50 000 km for cars, and 30 000 and 100 000 km for trucks. In the future, these figures are expected to increase even further. Oil consumption per energy unit has fallen eightfold during the past 50 years (Figure 7.21).

7.6.4

Formulation of Engine Oils

Engine oils are complex mixtures which are best described as formulations containing base oils and additives. Compared to other groups of lubricants, the base oils play an important role (see Sections 7.2 and 7.3). Without going into the characteristics and manufacturing in detail, mixtures of base oils are selected which have the necessary viscosity and performance to correspond to a rough classification. The final products are then marketed as conventional mineral oil-based, unconventional semi-synthetic (hydrocracked), and synthetic engine oils. Precise international nomenclature divides base oils into six groups (see Section 7.2)

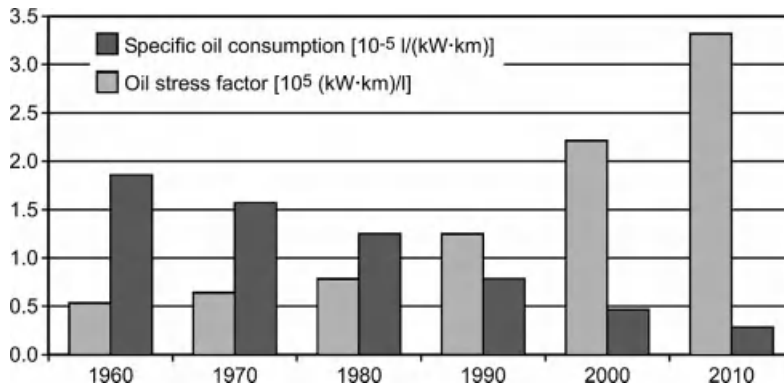


Figure 7.21 The history of oil stress.

Depending on the base oil used and the required engine performance, engine oils can contain up to thirty different additives, the percentage contents of which can range from 5% to 25% in total. In the oil industry, a differentiation is made between performance additives [71], VIs and flow improvers with, as a rule, the performance additives making up the largest group.

Performance Additives The following species of chemical components are summarized under the general term of performance additives (Section 7.5):

- **Antioxidants:** Phenols, amines, phosphites, sulfurized substances
- **Antiwear agents:** Metal dithiophosphate, carbamate
- **Detergents:** Ca and Mg sulfonates, phenolates, salicylates
- **Dispersants:** Polyisobutylene and ethylene-propylene oligomers with nitrogen and or oxygen as a functional group
- **Friction modifiers:** MoS compounds, alcohols, esters, fatty acid amides, etc.
- **Antimisting agents:** Silicone and acrylate.

7.6.5

Engine Oil Testing

Because realistic engine oil tests cannot be performed only over longlasting field trials, a number of international committees have created methods of testing engine oils in defined test engines, operated under reproducible and practically relevant conditions. In Europe, the CEC (Coordinating European Council for the Development of Performance Tests for Lubricants and Fuels) is responsible for testing, approval, and standardization [72]. Performance requirements are set-up in the form of ACEA oil sequences, which are decided together with the additive and lubricant industries. In the USA, this task is performed by the automobile industry and the API, which lays down test procedures and limits. The Asian ILSAC has largely adopted the American specifications for automobiles.

In principle, the test procedures focus on the following general performance criteria: oxidation and thermal stability; dispersion of soot and sludge particles; protection against wear and corrosion; foaming; and shear stability.

In detail, the specification of the tests differentiate between gasoline- and diesel-powered car engines and truck engines, whereby every test engine is characterized by one criterion or a group of criteria. The relevant criteria for gasoline and diesel engines are detailed in Chapter 8.

7.6.6

Passenger Car Engine Oils

Car engines include all gasoline and light diesel engines with direct or indirect injection. To ensure that the minimum requirements are met, the performance of the oils must be proven in the listed test engines, irrespective of viscosity grade or the base oil used (see Chapter 8).

7.6.7

Engine Oil for Commercial Vehicles

Commercial vehicles include trucks, buses, tractors, harvesters, construction machines, and stationary machinery powered by diesel engines. Apart from the prechamber diesels engines which have largely been superseded in Europe, the engines are usually highly turbocharged, direct injection motors. Economic and ecological aspects, along with high injection pressures, have improved combustion and thus have reduced emissions. As an initiative of the ACEA, oil-change intervals have been extended to 100 000 km for long haulage. In total, all characteristics can be found in HD oils, whereby these are allocated to the following categories with increasing performance: Heavy duty (HD); severe heavy duty (SHPD); and extreme heavy duty (XHPD).

7.6.8

Classification and Specification

As mentioned above, physical and chemical properties are not enough to select the best lubricant for an engine. Rather, complex and expensive practical and bench engine tests are performed to test and understand the performance of a lubricant. These requirements reappear in delivery conditions, in-house standards and general specifications. Haperscheid [67] has provided details of the following specifications.

7.6.8.1 MIL Specifications

These specifications originate from the US Forces, which set the minimum requirements for their engine oils, and are based on certain physical and chemical data, along with some standardized engine tests. In the past, these classifications were also used in the civilian sector to define engine oil quality. In recent years, this specification has become almost irrelevant for the German market:

- **MIL-L-46 152 A to MIL-L-46 152 E:** These military specifications have now been discarded. Engine oils which meet these specifications are suitable for use in US gasoline and diesel engines. MIL-L-46 152 E (discarded in 1991) corresponds to API SG/CC.
- **MIL-L-2104 C:** Classifies high-additive engine oils for US gasoline and normally aspirated and turbocharged diesel engines.
- **MIL-L-2104 D:** Covers MIL-L-2104 C and requires an additional engine test in a highly-charged Detroit two-stroke diesel engine. In addition, Caterpillar TO-2 and Allison C-3 specifications are fulfilled.
- **MIL-L-2104 E:** Similar in content to MIL-L-2104 C. The gasoline engine tests have been up-dated and include more stringent test procedures (Seq. III E/Seq. V E).

7.6.8.2 API and ILSAC Classifications

The API, together with the ASTM and the SAE, have created a system in which engine oils are classified according to the demands made on them, bearing in mind the varying conditions in which they operate and the different engine designs in use (Table 7.7). The tests are standard engine tests. The API has defined a class for gasoline engines (S = service oils) and for diesel engines (C = commercial). Although, at present, diesel engines in passenger cars are outnumbered by gasoline-powered engines, their numbers have increased in recent years and they are finding more acceptance in the USA. In addition, a number of fuel economy stages have been determined (EC = energy-conserving).

7.6.8.3 ACEA Specifications

As a result of persistent internal differences, the Comité des Constructeurs du Marché Commun (CCMC) was disbanded and succeeded by the ACEA, although the CCMC specifications remained valid during the interim period. The first ACEA classifications came into force on 1 January 1996, were revised in 1996, and subsequently replaced by 1998 versions, which became valid on 1 March 1998. Additional foaming tests were introduced for all categories, and the elastomer tests were modified. A-categories referred to gasoline engines, B-categories to passenger car diesel engines, and E-categories to heavy-duty diesel engines. On 1 September 1999, the 1998 specifications were replaced by the 1999 version, and these remained valid until 1 February 2004. Categories E2, E3, and E4 for heavy-duty diesel oils were updated, and a new category, E5, was introduced; these were specifically aimed at the new demands for Euro 3 engines and the often higher soot content of such oils. The A and B categories remained identical with the 1998 version. On 1 February 2002, the ACEA 2002 oil sequences were issued to replace the 1999 sequences; these were to remain valid until 1 November 2006. Updates in cleanliness and sludge for gasoline engines (categories A1, A2, and A3) and a new category A5, with the engine performance of A3 but a higher fuel economy, were introduced. Tests for cleanliness, wear, and soot handling were updated for diesel passenger cars, and a new category B5, with outstanding cleanliness and increased fuel economy, was introduced for category E5 oils. For category E5 oils, the wear performance in respect of ring, liner, and bearings was tightened. The ACEA 2004 oil sequences have been in use since

Table 7.7 Engine oil classification according to API SAE J 183.

Gasoline engines	Service classes
API-SA	Regular engine oils possibly containing pour point improvers and/or foam inhibitors.
API-SB	Low-additive engine oils, low-power gasoline engines. Include additives to combat aging, corrosion and wear. Issued in 1930.
API-SC	Engine oils for average operating conditions. Contain additives against coking, black sludge, aging, corrosion, and wear. Fulfill the specifications issued by US automobile manufacturers for vehicles built between 1964 and 1967.
API-SD	Gasoline engine oils for more difficult operating conditions than API-SC. Fulfill the specifications issued by US automobile manufacturers for vehicles built between 1968 and 1971.
API-SE	Gasoline engine oils for very severe demands and highly stressed operating conditions (stop-and-go traffic). Fulfill the specifications issued by US automobile manufacturers for vehicles built between 1971 and 1979. Covers API-SD; corresponds approximately to Ford M2C-9001-AA, GM6136M, and MIL-L46 152A.
API-SF	Gasoline engine oils for very severe demands and highly stressed operating conditions (stop-and-go traffic) and some trucks. Fulfill the specifications issued by US automobile manufacturers for vehicles built between 1980 and 1987. Surpasses API-SE with regard to oxidation stability, wear protection, and sludge transportation. Corresponds to Ford SSM-2C-9011 A (M2C-153-B), GM 6048-M, and MIL-L46 152 B
API-SG	Engine oils for the severest of conditions. Include special oxidation stability and sludge formation tests. Fulfill the specifications issued by US automobile manufacturers for vehicles built between 1987 and 1993. Specifications similar to MIL-L 46 152 D
API-SH	Specification for engines built after 1993. API-SH must be tested according to the CMA's Code of Practice. API-SH largely corresponds to API-SG with additional demands regarding HTHS, evaporation losses (ASTM and Noack tests), filterability, foaming, and flashpoint. Furthermore, API-SH corresponds to ILSAC GF-1 without the Fuel Economy test, but with the difference that 15W-X multigrade oils are also permissible.
API-SJ	Supersedes API-SH. Greater demands regarding evaporation losses. Valid since October 1996.
API-SL	For 2004 and older automotive engines. Designed to provide better high-temperature deposit control and lower oil consumption. May also meet the ILSAC GF-3 specification and qualify as energy-conserving. Introduced in July 2001.
API-SM	For all automotive engines currently in use. Designed to provide improved oxidation resistance, improved deposit protection, better wear protection, and better low-temperature performance. May also meet the ILSAC GF-4 specification and qualify as energy conserving. Introduced in November 2004.

(Continued)

Table 7.7 (Continued)

Diesel engines	Commercial classes
API-CA	Engine oils for low-power gasoline and normally aspirated diesel engines run on low-sulfur fuels. Corresponds to MIL-L 2104 A. Suitable for engines built into the 1950s.
API-CB	Engine oils for low-to-medium power gasoline and normally aspirated diesel engines run on low-sulfur fuels. Corresponds to DEF 2101 D and MIL-L 2104 A Suppl. 1 (S1). Suitable for engines built from 1949 onwards. Offer protection against high-temperature deposits and bearing corrosion.
API-CC	Gasoline and diesel engine oils for average to difficult operating conditions. Corresponds to MIL-L 2104 C. Offer protection against black sludge, corrosion and high-temperature deposits. For engines built after 1961.
API-CD	Engine oils for heavy-duty, normally aspirated and turbocharged diesel engines. Covers MIL-L 45 199 B (S3) and corresponds to MIL-L 2104 C. Satisfies the requirements of Caterpillar Series 3.
API-CD II	Corresponds to API-CD. Additionally fulfils the requirements of US two-stroke diesel engines. Increased protection against wear and deposits.
API-CE	Engine oils for heavy-duty and high-speed diesel engines with or without turbocharging, subject to fluctuating loads. Greater protection against oil thickening and wear. Improved piston cleanliness. In addition to API-CD, Cummins NTC 400 and Mack EO-K/2 specifications must be fulfilled. For US engines built after 1983.
API-CF	Replaced API-CD for highly turbocharged diesel engines in 1994. High ash. Suitable for sulfur contents >0.5%.
API-CF-2	Only for two-stroke diesel engines. Replaced API-CD II in 1994.
API-CF-4	Engine oil specification for high-speed, four-stroke diesel engines since 1990. Meets the requirements of API-CE, plus additional demands regarding oil consumption and piston cleanliness. Lower ash content.
API-CG-4	For heavy-duty truck engines. Complies with EPA's emission thresholds introduced in 1994. Replaced API-CF-4 in June 1994.
API-CH-4	Replaces API-CG-4. Suitable for sulfur contents >0.5%.
API-Cl4	For high-speed, four-stroke engines designed to meet 2004 exhaust emission standards. Formulated to sustain engine durability where exhaust gas recirculation (EGR) is used, and intended for use with diesel fuels ranging in sulfur content up to 0.5% weight. Replaces oils with API CD,CE,CF-4, CG-4 and CH-4.
All engines (API-EC I)	Energy-conserving (Minimum 1.5% less fuel consumption than an SAE 20W-30 reference oil in a 1982, 3.8 liter, Buick V6 gasoline engine. Sequence VI test.)
(API-EC II)	Same as API-EC I, but with minimum 2.7% lower fuel consumption
API-EC	Replaces API-EC I and II. Only together with API SJ, SL, SM. Cuts in fuel consumption: 0W-20, 5W-20 > 1.4%, 0W-XX, 5W-XX > 1.1%, 10W-XX, others > 0.5%, Sequence VI A test: In a 1993, 4.6-liter Ford V8 engine. Reference oil 5W-30

1 November 2004, and can be claimed by oil marketers. Oils in these categories are backwards-compatible with all other issues. Categories A and B are now combined and can only be claimed together, while categories C1, C2, and C3 are new and refer to engine oils for use in cars with exhaust after treatment systems such as diesel particulate filters (DPF). Such oils are characterized by an especially low content of ash-forming components and reduced sulfur and phosphorus levels to minimize the impact on filter systems and catalysts.

A complete list of the ACEA engine oil classification (2002/2003) is provided in Table 7.8. Apart from these specifications, Haperscheid provides extensive information relating to the OEM oil specifications of the most important manufacturers [67].

7.6.9

Future Trends (see also Section 8.5.8)

New generations of engines using optimized technologies advance the concept of tailor-made, special oils. The continuing optimization of the combustion process to increase the efficiency of gasoline engines has led to the development of gasoline direct-injection (GDI) engines which may offer fuel savings of about 20%. On the diesel side, direct injection with unit pumps or common rail technology using pressures of up to 3000 bar, have become the norm. These designs, which originated in truck engines, offer power increases of up to 50% at almost constant fuel consumption. For both trucks and for passenger cars, reducing exhaust emissions has the highest priority. The thresholds of Euro 2 and Euro 3 (from 2001) could easily be surpassed by use of special exhaust recycling and catalytic converter systems. Euro 4 for passenger car vehicles (since 2005) has required many light-duty diesel engines to implement DPFs, to meet the rigorously tightened threshold for particle emission (maximum 0.025 g km^{-1}). The introduction of Euro 4 for trucks and buses (October 2006) requires further reductions of nitrogen oxides (and particulate matter), which require a further optimized burning process and/or more advanced exhaust gas-purification equipment. An example of this is the selective catalytic reduction (SCR) of nitrogen oxides, or the use of additional soot-filter systems in most vehicles. Because these new engines and exhaust gas-purification systems require low sulfur and, most suitably, sulfur-free diesel fuels (below 10 ppm S), new demands will be made of the lubricants used. Furthermore, the surface treatment of pistons and cylinders has improved to such an extent that topology-specific oil consumption is steadily falling. As illustrated in Figure 7.21, the sum of these measures has led to a permanent increase in oil temperatures and specific oil loading, while oil-change intervals have also been constantly increased. All in all, three factors will characterize the engine oils of the future: fuel efficiency; long oil drain intervals; and low emissions.

7.6.10

Fuel Efficiency

As a result of strict limits to fuel consumption in the USA (e.g., CAFE = Californian Act for Fuel Emissions) and the proven fuel economy effect of low-viscosity engine

Table 7.8 Engine oil classification according to ACEA 2002 and 2004.

Passenger car engines category	Application area
ACEA 2002:	
A1-02	Low-viscosity (HTHSV max 3.5 mPa·s) oils with extra high fuel economy. Preferred SAE grades are xW-20 and xW-30
A2-96 issue 3	Multigrade fuel-economy oils, HTHSV min. 3.51 mPa·s, performance higher than API SH
A3-02/	Multigrade fuel-economy oils, HTHSV min. 3.51 mPa·s, performance higher than A2 especially with regard to high-temperature stability and evaporative loss
A5-02	Low-viscosity (HTHSV max. 3.5 mPa·s) oils with extra high fuel economy, engine performance similar to ACEA A3-02
B1-02	Similar to A1-02 low viscosity (HTHSV max. 3.5 mPa·s) oils with extra high fuel economy. Preferred SAE grades are xW-20 and xW-30
B2-98 issue 2	Similar to A2 multigrade fuel-economy oils, HTHSV min. 3.51 mPa·s, performance above API CG-4
B3-98 issue 2	Similar to A3-02 multigrade fuel-economy oils. HTHSV min. 3.51 mPa·s, performance higher than B2 especially with regard to piston cleanliness, soot handling, and shear stability
B4-02	Multigrade fuel-economy oils, HTHSV min. 3.51 mPa·s, additionally tested in turbocharged DI-Diesel (85 kW-“VW-“Pumpe-Düse” engine”) with regard to piston cleanliness and ring sticking
B5-02	Similar to A5-02 low viscosity oils with extra-high fuel economy. Also tested in turbocharged DI-Diesel (85 kW-“VW-“Pumpe-Düse” engine”). Extra-high piston cleanliness limit
ACEA 2004:	
A1/B1-04	Combines A1-02 and B1-02. Engine performance unchanged
A3/B3-04	Combines A3-02 and B3-98. Engine performance unchanged
A3/B4-04	Combines A3-02 and B4-02. Engine performance unchanged
A5/B5-04	Combines A5-02 and B5-02. Engine performance unchanged
C1-04	New category for multigrade oils with extra fuel economy (HTHSV max. 3.5 mPa·s), but extra low ash, phosphorus, and sulfur content (0.5, 0.05, and 0.2% w/w, respectively), in particular for use in Euro 4-type engines with advanced exhaust-treatment systems (e.g., DPF). The oils meet the performance level of A5/B5-04
C2-04	New category for multigrade oils with extra fuel economy (HTHSV max. 3.5 mPa·s), but lower ash, phosphorus, and sulfur content (0.8, 0.09, and 0.3% w/w, respectively), in particular for use in Euro 4 engines with advanced exhaust-treatment systems (e.g., DPF). The oils meet the performance level of A5/B5-04
C3-04	New category for multigrade fuel-economy oils (HTHSV min. 3.51 mPa·s), but lower ash, phosphorus, and sulfur content (0.8, 0.09, and 0.3% w/w, respectively), in particular for use in Euro 4 engines with advanced exhaust-treatment systems (e.g., DPF). The oils meet the performance level of A3/B4-04
Heavy-duty engines category	Application area

Table 7.8 (Continued)

Passenger car engines category	Application area
ACEA 2002: E2-96 issue 4	Multigrade general-purpose oils for naturally aspirated and turbocharged heavy-duty diesel engines, medium to heavy-duty cycles and usually normal oil-drain intervals. (MB 228.1 level and additional Mack T8 test.)
E3-96 issue 4	Multigrade oils with advanced performance of wear, piston cleanliness, bore polish and soot handling. Mostly recommended for diesel engines meeting Euro 1 and Euro 2 emission requirements and running under severe conditions, often with extended oil-drain intervals according to manufacturer's recommendations. (MB 228.3 level and additional Mack T8 test.)
E4-99 issue 2	Multigrade oils mostly recommended for diesel engines meeting Euro 1, Euro 2, and Euro 3 emission requirements and running under severe conditions, often with extended oil-drain intervals according to manufacturer's recommendations. (MB 228.5 level and additional Mack T8 and T8E test). Provides further control of piston cleanliness, wear, and soot-handling compared to E3
E5-02	Multigrade oils with performance level between E3 and E4. Recommended for diesel engines meeting Euro 1, Euro 2, and Euro 3 emission requirements and running under severe conditions. Advanced soot handling compared with E4, for use in engines with high EGR
ACEA 2004: E2-96 issue 5	Similar to E2-96 issue 4. Engine performance unchanged
E4-99 issue 3	Similar to E4-99 issue 2. Engine performance unchanged
E6-04	New category of multigrade oils for latest-generation diesel engines with advanced exhaust-treatment systems. Lower ash, phosphorus, and sulfur content (max. 1.0, 0.08, and 0.3% w/w, respectively) compared to E4. Engine performance similar to E4 plus Mack T10 test for additional control of liner, ring, and bearing wear
E7-04	New category for multigrade oils with extended performance of E4 with regard to soot-handling and wear (additional Cummins M11 and Mack T10 tests), including former E5 demands

oils [73], this topic is attracting attention in Europe and Asia. As a rule, engine-based savings can reach a theoretical 8–10% [74]. As engine oils cannot totally eliminate frictional losses, fuel-saving potentials of 4–5% present an enormous challenge; nonetheless, values of 3–4% are already possible today. According to the opinion of various experts, reductions in car fuel consumption in urban conditions are achieved by lowering frictional losses during cold start-ups, which simultaneously results in less wear and a lowering of viscosity under constant-throttle conditions. As the data in Figure 7.22 show, there is a plateau-like optimum for the correlative fuel savings in engines, with HTHS values between 2.5 and 2.9 mPa·s. The critical boundary to high wear conditions is seen by some to be different viscosities. Figure 7.22 shows piston ring wear under boundary to static friction conditions between 2.6 and 2.7 mPa·s [75],

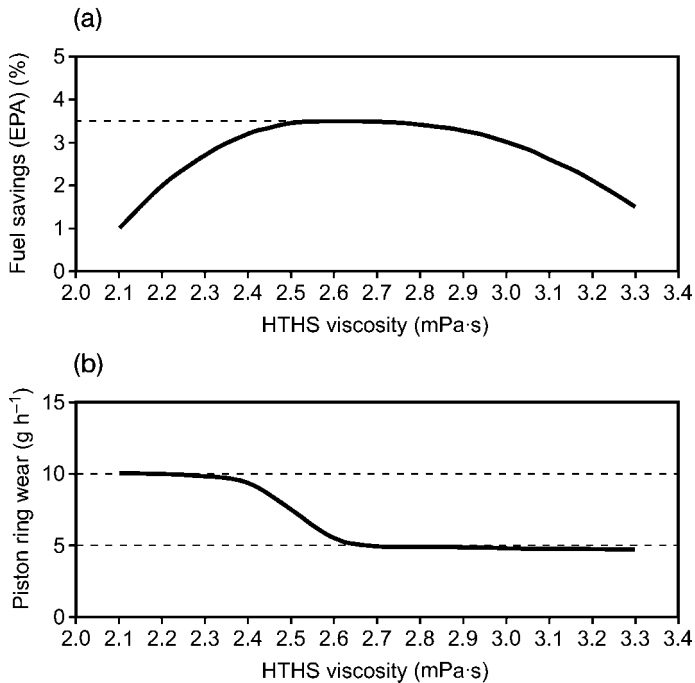


Figure 7.22 (a) Fuel efficiency and (b) piston wear versus high-temperature high-shear (HTHS) [266].

a this threshold which is viewed critically by different OEMs and is set individually. The European specification for fuel economy oils contains a span of 2.9 to 3.5 mPa·s, whereby the fuel savings in the M 111 FE test must be at least 2.5% compared to the reference oil. It must be remembered that absolute fuel savings figures depend largely on the test method and the reference oil used. Standardized dynamometer tests—which more accurately reflect driving conditions—provide more realistic values than the established bench tests, which cannot reproduce all operating conditions.

This is well illustrated by Figure 7.23, which shows graphically the correlation between evaporation tendency (Noack) and oil consumption. Evaporation losses, illustrated with the example of ILSAC thresholds for GF-2 and GF-3, serve as a generally recognized and reproducible value. A technically realized milestone for fully synthetic engine oils based on present synthetic base oils is a threshold of 5–6%.

7.6.11

Low Emission

Compared with car engine oils, HD engine oils already achieve drain intervals of 100 000 km. Because of the ever-increasing number of trucks on roads, this is a useful contribution to improving environmental compatibility. Apart from the CO, hydrocarbon (HC) and SO₂ emissions, which are seen to be caused by the fuel, particulate

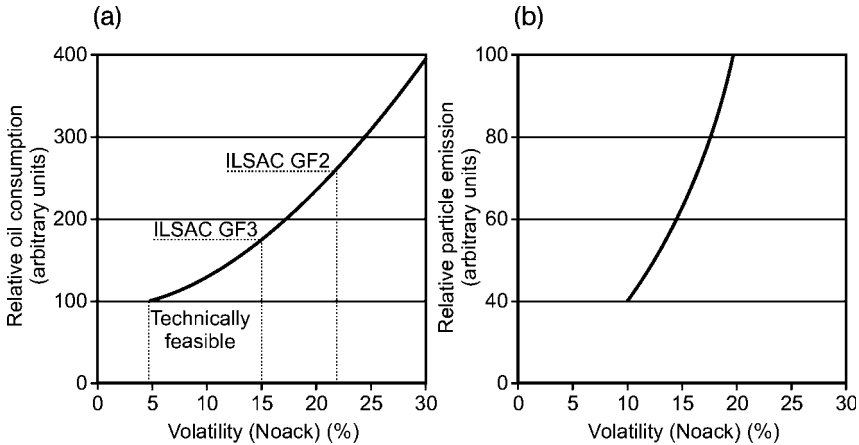


Figure 7.23 (a) Oil consumption and (b) relative oil-generated particulate emissions versus evaporation loss.

emissions play a significant role in HD engines. These particulates result from incomplete combustion, and are a mixture of fuel- and lubricant-based components. As the oil-based particles are largely caused by highly volatile elements in the formulation, evaporation losses have a direct effect on cutting pollutant output (see Figure 7.23). Figure 7.24 shows an analysis of the composition of such diesel particulate pollution and the role of lubricants. Furthermore, it can be assumed that sulfur compounds in diesel fuels will poison the catalytic converters of future Euro 4 and Euro 5 engines. The introduction of 10 ppm sulfur in fuels places the sulfur content of HD engine oils in a new light. Low-sulfur (and most probably low-phosphorus) will not lead simply to a rethink with regards to additives, but also to the rejection of solvent-neutral oils which, as a rule, contain between 0.2% and 1.0% sulfur. As occurs already with cars, unconventional and synthetic base oils are preferred, so that the trend towards low-viscosity, fuel-economic oils will spread definitively to the HD sector.

7.6.12

Two-Stroke Oils

Two-stroke engines are mostly used when high specific power, low weight and low price are key parameters. These engines are thus often used in motorcycles, boats (outboard engines), jet-skis, lawn-mowers, chain-saws and small vans, with the vast majority being found in motorcycles and boats (see Sections 8.5.2, 8.5.3 and 8.5.4 for more information). Almost all two-stroke engines use total-loss lubrication, where the oil is not circulated, as in the case of four-stroke engines, but is added to the fuel. Although a large part of the oil is burned in the combustion process, about one-fourth is exhausted as an unburned oil mist. Simple engines, as are found in older mopeds, still use the premix method which involves the operator manually adding a suitable

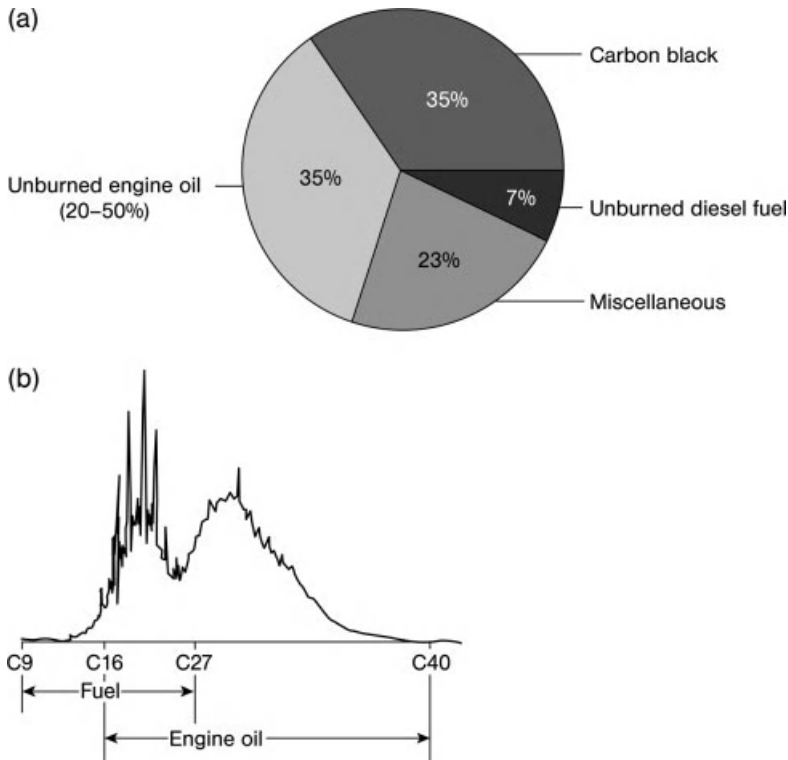


Figure 7.24 The role of engine oil in diesel particulate emissions. (a) The composition of nongaseous diesel emissions; (b) Gas chromatogram of the soluble part of diesel particulate emissions.

two-stroke oil to the fuel tank at a ratio of about 1 : 20 to 1 : 100. More advanced designs use an automatic oil-metering system, which either add a constant amount of oil to the fuel, or add oil according to the engine loading. Typical oil : fuel ratios for such systems range between 1 : 50 and 1 : 400. The majority of simple two-stroke engines breathe through a classic carburetor system and, in contrast to a four-stroke engine, the fresh fuel–air mixture in a two-stroke engine scavenges the cylinder after combustion. This simultaneous charging and emptying causes about 30% of the fresh mixture to be exhausted without burning and this, together with an only partial burning of the oil, causes many two-stroke engines to generate comparatively high emissions. In highly populated areas where there are large numbers of small motorcycles, such as in many Asian cities, this leads to severe odor, smoke, and noise pollution.

During recent years, however, these problems have been countered by a number of advances in two-stroke technology. For example, the development of direct or indirect fuel injection has led to significantly reduced emissions and improved fuel efficiency. Today's two-stroke engines require correspondingly high-quality oils for reliable operation and long life. The principal criteria for the quality of two-stroke oils are:

lubricity and antiwear properties; cleaning function (detergent/dispersant properties); avoidance of deposits in the exhaust system; low smoke; spark plug cleanliness and the avoidance of preignition; good fuel miscibility, even at low temperatures; corrosion protection; and good flowing properties.

Two-stroke oils are classified according to API service groups (TA, TB, and TC), while the Japanese Automotive Standard Organization (JASO) classifies such oils in three groups (FA, FB, and FC).

The ISO classification defines two-stroke oils in three categories: ISO-L-EGB; ISO-L-EGC; and ISO-L-EGD. For two-stroke outboard engine oils, the most important requirements are given by the NMA (National Marine Manufacturers, TEW-Specifications). Environmentally friendly two-stroke oils are mainly based on rapidly biodegradable synthetic esters. The requirements of this group of lubricants are harmonized by the International Council of Marine Industry Association (ICOMIA).

7.6.13

Tractor Oils

Two different oil technologies are used which are characterized by their application area. These are universal tractor transmission oils (UTTOS) and super tractor oils universal (STOU). The demands made on tractor oils have increased sharply in line with advances in vehicle technology and ease of operation. Whilst earlier generations of tractors had manual shift gearboxes and relatively simple rear axle designs, today's state of the art includes complex hydraulic systems, hydrodynamic drive units (retarders/power splitting), or wet (oil) braking systems. In the past, simple engine oils or low-additive gear oils were used for general lubrication, as well as for the hydraulic circuits, but today all-season use is as much a standard requirement for tractor oils as it is in the automotive area. As a result, the viscosity grades (defined according to SAE J 300) and thus the temperature ranges have been extended from SAE 15W-30 and 10W-30 to 15W-40, 10W-40, and 5W-40. The performance of such universal oils as hydraulic fluids corresponds to, at least, HLP and HVLP levels (see Table 7.12), because of the additives included to guarantee universal use.

7.6.14

Marine Diesel Engine Oils

These lubricants are heavily influenced by the type of fuel used, and the design of the engines themselves. A number of similar engines are also used in stationary applications to generate electricity, with either conventional fuels or with steam power.

7.6.14.1 Low-Speed Crosshead Engines

Low-speed diesel engines generating up to 1000 kW per cylinder at 50 to 120 rpm use the crosshead principle (large engines with over 900 mm bores and 3000 mm strokes, with 20 000 kW outputs). In crosshead designs, the cylinder block and crankcase are separate units, with sealing being provided by stuffing boxes and the liners lubricated

with cylinder oils by means of dosing devices. Depending on the bore and stroke of the cylinder, up to 16 dosing devices may be fitted. The crankcase bearings are lubricated with crankcase oils, which sometimes are called “system oils”; these oils also lubricate the crosshead bearings and guides. As opposed to cylinder oiling, which is a form of total-loss lubrication, the crankcase oil is recirculated.

7.6.14.2 Medium-Speed Engines

Medium-speed engines run at around 200 to 100 rpm. The overall design of these engines is similar to that of a vehicle internal combustion engine; they do not use the crosshead design, and the crankshaft is connected to the pistons and thus the cylinders with connecting rods. In such designs, the same oil is used to lubricate the cylinder walls and the crankshaft bearings, and forms part of a circulation system. These engines are sometimes called “trunk piston engines.”

Today, marine diesel engines are fueled by the worst and heaviest crude oil fuel cuts, with residues being gathered from all areas of refining to produce low-cost fuels. These include vacuum residues, propane de-asphalting residues, heavy solvent extracts from lube refining, and other byproducts. Unfortunately, these refining residues, as well as the major share of high-molecular-weight substances, provide poor combustion characteristics and create large amounts of deposits. In addition, a high sulfur content of up to 3% will lead to oil acidification. The formulation of marine diesel lubricants is considerably influenced by these fuel characteristics since, although the fuel is filtered in centrifuges, the high ash and asphalt levels in the fuels lead to significant quantities of solid impurities being formed during combustion.

7.6.14.3 Lubricants

Cylinder oils in crosshead engines are total-loss products which lubricate the sliding motion of the piston rings in the cylinder liner. To avoid the deposit of combustion residues, these oils must have good dispersant properties. In addition, they must be capable of neutralizing the corrosive acids which result from the high sulfur levels in the fuels. To satisfy these requirements, cylinder oils have a large proportion of over-based components (up to 30% over-based calcium sulfonates or other over-based components). The alkalinity required for neutralization leads to TBNs of up to 100. When additives for such oils are being selected, special attention must be given to the good colloidal solubility of the additives in the base oil, so as to avoid precipitation. The large surface areas of cylinders in crosshead engines requires the applied oil to disperse rapidly and reliably, and this is achieved by good spreadability. The stuffing boxes fitted to crosshead engines ensure that the crankcase oils are hardly contaminated by combustion chamber residues, and consequently these oils contain relatively few additives. Additives to combat thermal oxidation are essential, and the neutralizing capacity can be relatively low, with a TBN of 5. Contamination of the crankcase oil with cylinder oil will lead to an increased emulsifying capacity, which is undesirable; hence, water separation is another vital characteristic of crankcase oils. An increase in dispersant and detergent properties caused by the ingress of cylinder oil can also lead to wear problems, as the effect of typical AW and EP additives such as

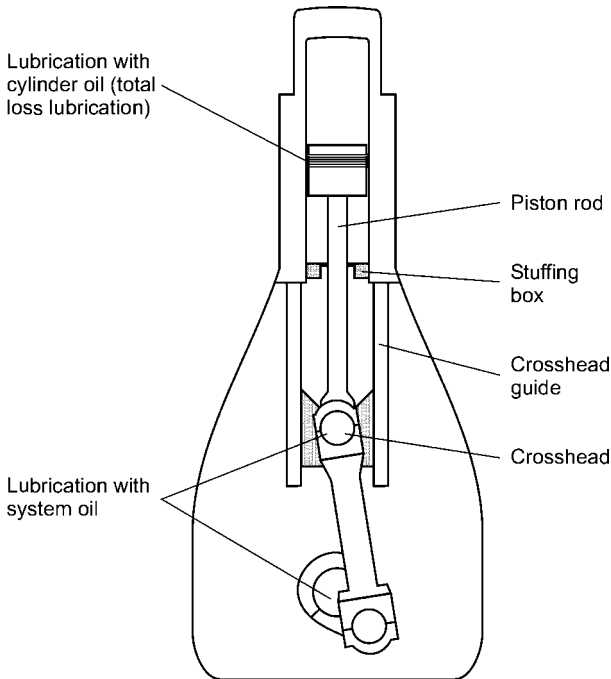


Figure 7.25 Schematic representation of a low-speed crosshead engine.

zinc dialkyldithiophosphate is thus diminished. The type of oil used to lubricate trunk piston engines (combined crankcase and piston lubrication) is also largely determined by the sulfur content of the fuel. Oils with TBNs of 12 to 40 are common, and the neutralizing capacity of the oils is very soon exhausted in some cases, so that the TBN of used oils can be much lower. During the development of these oils, tests are carried out on one- or three-cylinder Bolnes engines, although the final results only become available after very time-consuming onboard trials that last for at least a year. Today, it is certain that significant restrictions on the sulfur content of marine diesel fuels will be imposed in the coming years, and this will result in a lowering of the high proportion of over-based components necessary for such oils at present [76]. A low-speed crosshead engine, together with its lubrication system, is shown schematically in Figure 7.25.

7.6.15

Other Combustion Engines

The fact that natural gas-powered engines generate significantly less emissions than gasoline-powered units has led to their increasing use, especially in the mobile sector.

Gas engines for stationary applications are particularly interesting in areas where gas is cheaply available (apart from natural gas landfill gas).

Currently, there is no universal specification for passenger car gas engine oil, and gas-powered cars normally use the same conventional oils as are used in gasoline-powered engines. The large variation in operating conditions between mobile and stationary engines generally requires oils with different additive packages.

7.7

Gear Lubrication Oils

In principle, any type of lubricant that is currently available on the market (including engine oils) can be used in any gear and transmission, thus ensuring—for the moment—their functionality. However, at this point it might be pertinent to issue a warning about the risks involved in this scenario, when a “next-best” lubricant is used without knowing the operating and environmental conditions of the application. The operating conditions include the switching periods and the forces to be transferred, the so-called specific loads of each single machine component which result from operational speed, and the transferred torque. The operation of a transmission causes friction losses in all sliding rolling contacts, which in turn leads to the generation of heat. In this case, an insufficient or inappropriate lubrication, often combined with inadequate cooling of the friction contact points, will lead to a short-term failure of the system. The most frequent failure criteria for gears and transmissions include: extreme abrasive wear; early endurance failure; fatigue of components; and scuffing and scoring of the friction contacts. The selection of a lubricant which is not adapted to the respective construction components, nor to the operating and environmental conditions of gears and transmissions, can—given an early failure of the machine—lead to maximum consecutive damages up to the breakdown of a complete system. Although this situation will invariably have resulted from attempts to save on relatively low lubricant costs, the resulting repair and standstill times of the system will lead to unforeseen, and generally very high, financial loss. More importantly, it highlights the significance of the lubricant as a machine element in modern-day gears and transmissions.

7.7.1

Requirements of Gear Lubrication Oils

In many designs of machinery, *torque transfer* plays a decisive role, with the various types of transmission forming two basic groups: (i) gears with a constant ratio; and (ii) gears with a variable ratio. Each of the above-mentioned types of torque transfer makes specific requirements on the lubricant that must be met to ensure the reliable function of both machinery and plant. Thus, the heavily loaded lubricants in hypoid gears require a high oxidation stability, together with a very good scuffing and scoring and wear load capacity, due to the high load of the tooth contacts. At the same time, the formation of a load-capable and separating film thickness for sufficient

lubrication and cooling of the sliding rolling contacts in hypoid gears, requires a lubricant with an adequately high viscosity at the operating temperature. On the other hand, lubricants used in hydrodynamic gears, such as torque converters, hydrodynamic wet clutches or retarders, do not require a good scuffing and scoring load capacity, but must have a high oxidation stability. Due to viscosity-dependent losses, those lubricants used in hydrodynamic gears must therefore have a clearly lower viscosity at operating temperature when compared to lubricants used in hypoid gears.

The above-mentioned gear types are used in machine and plant constructions with variable exposure times. The requirements made on these gears, which are closely connected to the requirements made on the gear lubrication oils, should be viewed in an industry-wide manner with regards to service life and oil-drain intervals. The main differences in the required service lives, which range from 100 to 500 operating hours for gears in household machines to more than 100 000 h service life for gears used in paper-producing machinery, are important in terms of lubrication.

The development of heat in a gear causes the temperatures of both the oil sump and the oil tank to rise. This effect is highly significant for a lubricant's service life, as it accelerates the oil's aging process and, consequently, will reduce its service life. The development of heat and subsequent rise in oil temperature is determined by the type of gear, the transferred torque, the specific load, the switching periods (permanent or intermittent operation), and also the environmental conditions—whether the gear is used in a warm or cold climate, or in a mobile or stationary application. For gears that require extended service lives, as used in paper-producing machines or printing presses, the lubricant must be exchanged according to the mechanical and thermal claims, in compliance with the oil producer's recommendations. Assuming that the average oil sump temperature in such transmissions is approximately 90 °C, the oil should be exchanged at intervals of 2500 h of operation. An increase of the oil sump temperature by 10 K will lead to a 50% reduction in the service life; hence, reducing the temperature by the same amount will double the oil's service life in general. Today, gears for which short or medium service lives are required, such as in passenger cars or mobile hydraulic systems, are often lubricated with "life-time" fluids. As the oil sump temperatures in these transmissions often rise to 130 °C, the use of synthetic lubricants is recommended in these applications. Suitable synthetic lubricants, such as polyalkyleneglycols or synthetic hydrocarbons, will reduce the friction losses and, in turn, the temperature of the transmissions. In general, whilst the service life—and, therefore, the oil-drain interval of synthetic lubricants—is three-fold longer than that of mineral oils, the current prices for synthetic lubricants are much higher than those of mineral oils. According to the market share of mobile and stationary gears, it is important to differentiate between gears for industrial applications and gears for automotive applications. With regards to the gear lubricant, household and craftsman machinery play only a minor role, and so will require only a relatively short service life. Hence, in most cases these machines are lubricated not with oil, but with grease.

7.7.2

Tribology of Gears

There significant differences between the tribology of gear drives [77] on the one hand, and of journal and roller bearings on the other hand, as the lubrication conditions that characterize the sliding rolling contacts in toothed wheels differ from those in journal or roller bearings. As noted in Chapter 3, the lubrication conditions in the tooth contacts are the most difficult (see Figure 3.5b); consequently, the toothed wheels in a gear very often control the main requirements of the lubricant.

7.7.2.1 Toothed Wheels

Toothed wheels differ in their gear types [78], which appear in gears very often in mixed form. In general, the various gear types or arrangements of the toothed wheels and axles in a gear are decisive for the classification of the gears.

7.7.2.2 Load and Speed Conditions During Tooth Engagement

The different gear types comply with the “toothing law.” According to its specifically different geometric ratios and operating conditions, each gear type is limited to a maximum transferable torque that results from the maximum admissible tooth flank load. This provides a basis for the maximum transferable torque on the one hand, and from the rolling and sliding speed ratio within the tooth contact (which leads to the maximum transferable rotational speed of the gear) on the other hand. The product of the maximum transferable torque and rotational speed provides the maximum transferable power of a gear. Thus, the key factors are the sliding rolling contact pressure, the specific load in the tooth contact, and the gear’s rotational speed, in addition to the currently effective rolling and sliding speed ratio in the tooth contact.

The load and surface velocity of the tooth flanks are characterized by continuously changing conditions alongside the entire tooth engagement line. The sum of the normal velocity of the tooth flanks equals the effective hydrodynamic velocity, while the difference of the sliding velocity of the tooth flanks equals the sliding velocity. Together with the locally effective contact pressure (the so-called “sliding rolling contact pressure”), this sliding speed causes friction losses tangential to the tooth flank and, thus, an increase in temperature in the sliding rolling contact. Only in the pitch point contact C, can a pure rolling movement be observed without sliding speed in the whole tooth engagement at that point (see Chapter 3 and Section 8.4)

7.7.2.3 Static and Dynamic Load Distribution Within Tooth Engagement

For the tooth contact shown in Chapter 8, a static load distribution alongside the tooth engagement distance can be assumed. In the single-tooth engagement, the entire load is transferred via one pair of toothed wheels, whereas in a double-tooth engagement area this is ensured by two pairs. Due to the elasticity of the teeth, the transition from a double- to a single-tooth engagement and back to a double-tooth engagement does not take place abruptly, but almost linearly. The tooth engagement is a vibrating system which, according to the geometry and the operational, shows a dynamic load distribution which differs and sometimes clearly exceeds the static

load distribution. In this vibrating system, the lubricant—and especially the viscosity of the lubricant—have an absorbing effect. In this context, it must be noted that a larger absorption in the tooth contact which, for example, is achieved by using a lubricant with a higher viscosity, leads to a clearly measurable reduction in the operational noise level, while converting the absorbed energy into heat and, thus, increasing the surface contact and gear temperature.

7.7.2.4 Lubrication Film Generation Within Tooth Contact

Given a known local tooth geometry, load and speed in the tooth contact alongside the tooth flanks in the tooth engagement, the characteristic of the Hertzian pressure is obtained as the decisive mechanical normal force for a no-lubricated, sliding rolling contact in each tooth engagement point (see Figure 7.26). If a separating EHD film has been generated (see Chapter 3) in the highly loaded tooth contact (see Ref. [79]), a pressure, temperature, and lubricant distribution according to Figure 7.26 can be assumed.

One key factor when assessing the correct lubrication and condition is the minimum lubricant film thickness, which must be sufficient in order to avoid the metal surface contact of the tooth flanks and to direct the generated heat away from the contact zone, by means of friction and/or absorption. If the minimum lubricant film thickness is first determined according to Refs [79, 80], the current lubrication condition in the tooth contact can then be assessed. The nonstationary sliding rolling contact is the reason why there are different lubrication conditions at each contact point of the tooth engagement line. At pitch point C (see Chapter 8) of a tooth engagement where – as in a roller bearing – a pure roll-off or rolling movement without sliding speed is generated, relatively optimal lubrication conditions can be assessed. The lubrication conditions during the tooth engagement and disengagement, however, are more unfavorable due to the relatively high slide speed proportions. Another factor will also have a negative impact on the generation of

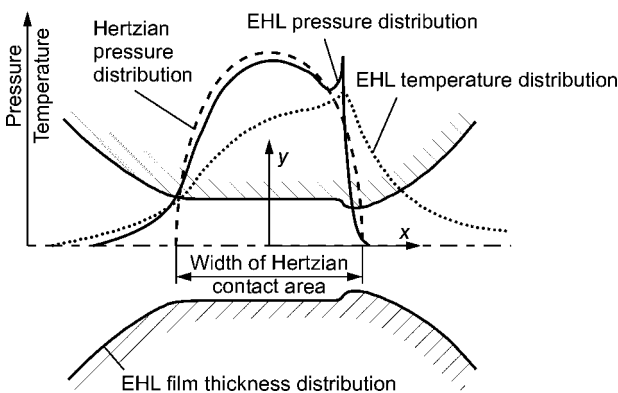


Figure 7.26 Distribution of pressure and temperature and lubricating film thickness in the elastohydrodynamic nonconforming tooth contact (according to Ref. [78]).

a lubrication film in a tooth contact, namely that during the new tooth engagement, the film can be stripped off by the tooth tip of the engaging toothed wheel. The geometry of a tooth tip is of particular interest, as the lubrication film must be regenerated on the tip with each new tooth engagement, but break with each disengagement. Consequently, tooth contact will be characterized by highly discontinuous operational conditions that will, in general, aggravate the generation of lubricating films.

When a gear is characterized by a more lubrication-unfavorable toothing geometry due to the relatively large slide–speed proportions along the tooth engagement line (e.g., in a hypoid or cylindrical worm gear), it will be subject to significantly larger friction losses and higher sliding rolling contact temperatures than would a simple spur gear with a comparable or equivalent transfer performance and with relatively low slide–speed proportions. During operation, hypoid and cylindrical worm gears, in comparison to spur gears, show a relatively faster increase in temperature, and this is correlated with higher oil sump temperatures. This leads, in turn, to a lower gear efficiency level and, with regards to the lubricant required for these gear types, a need for special requirements. For example, in hypoid gears there is a need for an increased scuffing load capacity, whereas in worm gears low-friction lubricants will have a particularly positive effect on tooth wear and the gear's service life.

7.7.2.5 Lubrication Conditions

In order to avoid tooth damage, and to ensure the long-term smooth and functional operation of a gear, a detailed observation and assessment of the lubrication conditions in the tooth contacts, made during the design stage of gears, is particularly important. Depending on the local force, contact pressure and temperature, and based on the material values of the toothed wheels and lubrication values of the lubricant, [81], it is possible to calculate a film thickness over the tooth engagement line in a gear. This calculation integrates the lubricant film thickness calculation according to Ref. [79], and also the dynamic lubricant viscosity and pressure coefficient α at the mass temperature of the toothed wheel's surface. According to Ref. [82], the above-mentioned procedure provides valuable information concerning the effective lubricant film thickness in the tooth contact. Today, when using this method, attention is generally focused on observing the pitch point C. The rapid development of this procedure, combined with currently available electronic data processing, has led to a more complex evaluation of tooth engagement being only a matter of time; indeed, it has already been established as a standard method.

The lubrication condition determined in the tooth contact can be assessed from knowledge of the effective surface roughness of the tooth flanks, with the value according to Ref. [83], while the specific film thickness is assessed according to Eq. (7.10):

$$\lambda = h_{\min}/R_a = 2h_{\min}/(R_{a1} + R_{a2}) \quad (7.10)$$

where λ is the specific film thickness according to Ref. [83], h_{\min} is the minimum film thickness, and R_a is the arithmetic average mean roughness of the tooth flanks

surface of the pinion (R_{a1}) and wheel (R_{a2}), according to Ref. [84]. Many examinations carried out in Ref. [83] have used the specific film thickness as a guide value for the qualitative assessment of the damage behavior of the tooth flanks. According to the evaluation of numerous observations, it is possible to differentiate between two lubrication regimes [83]: (i) specific film thickness where $\lambda > 2$ (hydro- or elastohydrodynamic lubrication); and (ii) specific film thickness where $\lambda > 0.7$ (boundary lubrication; see Chapters 2 and 3)

Besides continuous material wear, typical surface damages on gears may also occur, such as scuffing and scoring as a result of sudden metal-on-metal contact, and pitting and micropitting caused by fatigue. A suitable lubricant which has a positive influence on micropitting must have a sufficiently high viscosity, as well as a suitable lubricant additive system. When selecting the latter, the operational viscosity or temperature of a gear is of major significance. Experience has shown that some lubricant additive systems, such as a gear oil sump temperature of 90 °C, have a very high micropitting load capacity, whereas this is very low at an oil sump temperature of 60–120 °C. Clearly, this point must be taken into consideration when selecting a suitable lubricant.

7.7.3

Gear Lubrication Oils for Motor Vehicles

Gear lubrication oils for motor vehicles must meet the specific requirements of the gear drives. The gear drive, which transfers torque from the engine to the drive gears, consists of a gearbox and a drive axle that uses differential gears to transmit power to the wheels. In Europe, the majority of gearboxes that serve to change the gear ratios are manual transmissions, with synchronization, whereas in the Americas and in the Asian Pacific they are mostly automatic or semi-automatic transmissions (often termed constantly variable transmissions, CVTs). In the case of automatic or CVTs, the lubricant is responsible not only for the gear drive lubrication but also for the function-related operation of wet clutches, wet brakes, torque converters, retarders, and dual clutches. Today, however, it is impossible to meet the requirements of all these types of transmission with a single fluid; consequently, due to increasing technological developments and the specific component design of new gear components (e.g., sensorics), the trend is increasingly oriented towards individualization. Today, an ever-increasing number of tailor-made individual lubricant solutions are being developed for specific applications, transmissions and different types of transmission. As with new engine oils, the development of gear lubrication oils for motor vehicles is ongoing, and driven by several factors:

- Vehicle operators welcome an improving reliability of the vehicles and increasing oil-drain intervals to reduce the operative costs incurred.
- The requirements and specifications issued by the motor, transmission, and vehicle manufacturers intend to considerably extend the oil-drain intervals. Today's trend is to supply all transmissions with so-called "fill-for-life" fluids

(>300 000 km), and most manual transmissions and axle gears in passenger cars now fit into this category. With regards to automatic transmissions in passenger cars, long oil-drain intervals will soon be achieved, and for commercial vehicles the oil-drain intervals required by the manufacturers will be extended. The plan is to achieve transmission service lives of 500 000 km, 750 000 km, and eventually up to 1 000 000 km without draining.

- The legislation in industrialized countries influences the lubricant formulation, mainly for reasons of environment-friendly fluids and disposal; hence, the use of mineral-based oils is decreasing. Today, environment-friendly, synthetic, and ester-based base oils are often used for reasons of environmental protection. Due to their better thermal oxidation stability, ester-based oils are used together with PAO and hydrocracked base oils (see Sections 7.3 and 7.4). Attempts are also being made to reduce lubricant toxicity, especially in conventional components of commonly used additives. In this respect, reduction of the chlorine content is of major importance, due to disposal of the used lubricants. In order to reduce particles emission, the discharge of oils into the environment and, thus, oil consumption, future gear lubricants for vehicles must be tested accurately with respect to the elastomers used in seal production.
- Drivers of modern motor vehicles expect improved performance, and reductions in both noise emission and fuel consumption. This trend is reflected by the increasing use of low-viscosity lubricants and reduced fill volumes. Multigrade oils that are currently used on a large scale should appreciably reduce fuel consumption.

7.7.4

Driveline Lubricants for Commercial Vehicles

The most important current specifications issued by transmission manufacturers and automotive companies, are categorized as manual transmission and rear axle gears, as detailed above. With respect to specifications, the new and modified SAE classes must be taken into account; notably, the new SAE J2360 should be mentioned, as this will replace the former MIL-PRF-2105E. The new SAE “Automotive Gear Lubricant Viscosity Classification, J 306” must also be included. In this specification, the limitation of shear loss after shearing (stay-in-grade) has gained much importance:

- **Gear oil viscosity classification and gear oil performance level:** ISO 3448, SAE J300, SAE J306, MIL-L-2105, AGMA, MIL-L-2105E, SAE J2360.
- **Heavy-duty axle applications (commercial vehicles, trucks, buses):** Chrysler MS-9020, Daimler Chrysler DC 235.8, API GL-5, GM 886 337 0, Ford 5QM-2C9002-AA, Volvo STD 1273.12, Scania STO 1:0, Renault RVI TDL, MAN 342, MAN M3343, VW TL727, ZF Ecofluid X.
- **Light-duty axle applications (passenger cars):** Chrysler MS-9763, API GL4, Ford M2C-119A, CM 998 547 6, Clak MS-8 Rev. 1, Volvo STD 1273.10, Volvo STD 1273.13.

- **Heavy-duty synchronized transmissions and transaxle applications (commercial vehicles, trucks, buses):** Daimler Chrysler DC 235.11 API GL-1, API GL-3, MACK GO-J, MACK GO-J PLUS, MAN MAN 341 Volvo STD 1273.07, ZF ZF Ecofluid M.
- **Heavy-duty nonsynchronized manual transmissions (commercial vehicles, trucks):** API MT-1, Eaton PS-164, Eaton Bulletin 2053.

This trend in the development of lubricants for commercial vehicles has led to a significant change in the current ratio between service fill and factory fill. Currently, the share between service fill and drain is 75%, with factory fill 25%, but during the next ten years this will be reduced to 20% service fill and 80% factory fill. From today's point of view, the above-mentioned specifications all constitute a challenge for the development of gear lubrication oils for commercial vehicles. Apart from the very high chemical and physical requirements included in these specifications with regards to oxidation stability (tested at 150–160 °C), corrosion, filterability, and foaming, the specifications include a large number of mechanical–dynamic tests, as well as very high safety levels with respect to scuffing and scoring, pitting, and wear resistance of the toothings, by using different, standardized, nonstandardized, and company-internal test procedures. Unfortunately, this will decelerate the development of new oils by making the process increasingly complicated and expensive. One particular obstacle in the development of oils for commercial vehicles is the improvement and optimization of synchronization behavior during gear-shifting operations.

The main problem in fluid development is to adjust the same friction or friction constancy during a required gear service life of approximately 100 000 gearshift operations, by using different material–lubricant combinations and without making any significant alterations to the other chemical–physical and dynamic–mechanical properties.

7.7.5

Driveline Lubricants for Passenger Cars

The development trends, and the requirements on gear lubrication oils for passenger cars connected with these, are reflected in the specifications issued by leading automotive companies, which continuously determine an increasing number of requirements for screening and approval tests. Today, some vehicle and gear manufacturers have developed systems by which fresh oils can be synthetically aged or oxidized, such that they can be re-tested while using conventional test methods. Several important specifications for manual transmission fluids and axle fluids for the gears of passenger cars include the following:

- **Synchronized manual transmission and transaxles (passenger cars):** Volvo STD 1273, 08, DaimlerChrysler DC 235,10. VW TL726.
- **Light-duty synchronized manual transmission (light trucks, passenger cars):** API PM-1, Ford SM-2C-1O11A, Ford M2C 200C, VW TL52 512, VW TL52 171, TL52 178, BMW 602.00.0.

7.7.6

Lubricants for Automatic Transmissions and CVTs

The most important consumers of fluids for automatic transmission and drive systems, the so-called ATFs, include off-highway vehicles and machines, and commercial vehicles such as buses (e.g., city and inter-city buses, coaches, and mini/midi buses). In addition, ATFs are used to fill power steering systems in trucks, commercial vehicles, and passenger cars. Today, 90% of all passenger cars on the North American and Asian vehicle markets use automatic transmission systems; hence, the total estimated ATF volume worldwide for the year 2007 amounted to approximately 1.2 million tons (market shares: North America 61%, Asian Pacific 15.5%, Europe 12.5%, Latin America 8.8%, Middle East 2.2%). Most manufacturers of automatic transmission systems require fluids for application, which meet listed specifications:

- **Heavy-duty automatic transmissions (commercial vehicles, trucks, buses):** Allison C-4, Allison TES-295, Chrysler MS-9602, ZF TE-ML 02, ZF ZFN 13 015.
These specifications refer to the Asian, North American and European markets, and to the business for service fill and relubrication of vehicles. Currently, the factory fill is subject to enhanced specifications:
- **Light-duty automatic transmissions (light trucks, passenger cars):** SAE J311, TASA ATF, Chrysler MS-7176, DaimlerChrysler DC 236.12, DaimlerChrysler DC 236.20, DaimlerChrysler Mopar4 + , Ford M2C 202 B, Ford Mercon V, Ford Mercon 5 P, GM CM 6418-M, GM Dexron IIIH, GM Dexron VI, GM Opel B 040 1068, GM Opel B040 107 3, GM Opel B 040 2030, VW TL52 162, VW TL52 182, Porsche 040 204, ZF ZFN 13 026, ZF ZFN 13 014, ZF ZFN 904.

The European manufacturers of vehicles and, especially, of transmission systems, have issued particular specifications mainly for off-highway construction machines and commercial vehicles (e.g., Caterpillar, Terex, Komatsu Dresser, Voith, Allison, ZF) Automatic transmissions (wet clutches) require hydrodynamic clutches, torque converters and wet brakes. A series of wet friction-clutches and brakes, as well as their shifting and friction characteristics, play a major role during the automatic gearshift operation, and this fact is taken into account in the mentioned specifications. With regards to friction characteristics, the lubricant (other than the toothing requirements not described here in detail) is probably the most significant element.

A detailed description of the fluid requirements for hydrodynamic transmissions, wet clutches and brakes, CVT applications, T-CVT traction drives and H-CVT hydrostatic dynamic powershift drives has been provided by T. Bartels [89].

7.7.7

Multifunctional Fluids in Vehicle Gears

Special gear lubricants (termed “multipurpose fluids”) are used in agricultural and working machines, such as tractors and harvesters, in which the long-term and perfect function of wet clutches and wet brakes must be ensured. The scuffing

load capacity of the hypoid gears must also be guaranteed, by using a suitable fluid, while friction, hydraulic and wear requirements must also be met. In order to ensure effective driving and working operations at low temperatures, the torque converters must function adequately and safely, even under conditions of permanent slip for the wet clutches. Consequently, multipurpose oils will almost always have a low viscosity and an excellent viscosity–temperature behavior. The presence of water and dirt has a significant impact on these oils, especially in terms of their foaming and air-release properties. This situation is aggravated by the fact that the above-mentioned requirements often must function within only one system. In addition to the complex requirements that are made on multipurpose oils [which are referred to as UTTOs (universal tractor transmission oils, not usable for tractor engines), another engine-related performance is normally required, whereby the oils can also be used as engine oils [they are then termed STOUs (super tractor oils universal)]. Against the background of these requirements, it is easy to understand why the major manufacturers of tractors and agricultural machines, such as Ford, John Deere and Massey Ferguson, have each developed their own specifications for UTTOs and STOUs, the most important of which are as follows:

- **Off-highway vehicles and construction machines (railway, excavators, cranes):** Caterpillar TO-4, Terex EMS 19 003, Komatsu Dresser B22-0003, Komatsu Dresser B22-0005, Voith G607, Voith G1363, ALLISON TES-353, ZF Powerfluid, ZF ZFN 130 031.
- **UTTO multifunctional farm and tractor, agricultural machines (hypoid gears, synchronizers, wet clutches, hydraulics):** John Deere JDM 11 D, John Deere JDM 11 E, John Deere JDM J20 C, John Deere JDM J20 D, Massey Ferguson CMS M1127, Massey Ferguson CMS M113 Massey Ferguson CMS M1143, Ford ESN-M2C-86-C, Case JI Case 1316, New Holland STD 200 HYD OIL, New Holland NHA-2-C-200, New Holland NI-IA-2-C-201, New Holland M2C134.D.
- **STOU multifunctional farm and tractor, agricultural machines (engine hypoid gears, synchronizers, wet clutches, hydraulics):** Massey Ferguson CMS M1139, Massey Ferguson CMS M1143, Ford ESN-M2C-159-C, John Deere JDM J27, Renk 530 BW, ZF TE-ML 06.

7.7.8

Gear Lubricants for Industrial Gears

From the lubricant producer's point of view, industrial gear applications differ from vehicle transmissions, due mainly to their wider variety and greater number of combinations of toothing types and sizes available. In particular, worm gears, planetary gears and helical spur gears with crossed axes are worthy of mention. Gears for industrial applications are also different, due to their much wider variety of possible operating and ambient conditions. Notably, these gears will have a much higher torque and performance, as well as a much larger housing dimensions, such that they will also require much larger volumes of lubricant. Based on the conditions of industrial gears usage, the service life demands are clearly greater than those made

on vehicle transmissions. With few exceptions, modern-day gear lubricants for industrial applications include a low-additive treat, there being no high-performance lifetime lubricants. When compared to vehicle gear lubricants, these fluids meet fewer requirements. For industrial applications, the user should regularly and punctually drain the lubricant, in accordance with the gear manufacturer's recommendation, and in this respect it is important to take into account the environmental compatibility of the lubricants used. In contrast to vehicle gears, the type of lubrication used for industrial gears may be very different, and vehicle gears will invariably be equipped with an oil-immersion or injection-lubrication system. However, according to their operating conditions, industrial gears can be lubricated manually either by dripping or pouring, by lubrication via an oil sump, an oil mist, or through an oil injection system. Very often, much larger oil lubrication systems may be encountered (e.g., in printing presses or paper-producing machines) which have lubricant filling capacities of several hundreds of liters. A schematic overview of a lubrication system used commonly today is shown in Figure 7.27.

When using an oil lubrication system, the total volume of the oil must not be held too low, in order that air release from the oil can be achieved. In this respect, the air separation and foaming properties of the oil play very important roles, as air will serve as a load lubricant. The purity of the lubricant during the operation of these systems is another central factor with regards to the gears' service life and, in turn, the oil's filtration and filterability. The viscosity-dependent pumpability of the oil, especially at cold temperatures and also during the start-up of such systems, must be taken precisely into account, as an incorrect viscosity selection for a lubricant can lead to standstill of the entire system. A guideline for adequate viscosity selection as a function of load and speed for spur gears and worm gears in industrial applications is given in Ref [85].

Clearly, the different gear lubricants for industrial applications should meet as many technical requirements as possible although, at the same time, it is essential to meet the demands of the system operators with regards to longer oil drain intervals. In comparison to the lubrication oils used for vehicles transmissions, the worldwide number of specifications relating to the properties of lubricants used for industrial applications is quite small. The important specifications issued by gear manufacturers and end consumers are listed in the following.

7.7.8.1 Industrial Gear Oil Specifications

- API GL-2, AMAA 520 Part 6, 7, AMAA 520 Part 9
- AGMA 9005-E02, AGMA 250.04,251.02, David Brown S1.53 101, US Steel 224
- Cincinnati Milacron P-47,50,53,63,74, GM LS2 Part 1,2,3,4, Rockwell International 0-76, DIN 51 517, Flender Sheet A, Winergy 02.05.2003.

These specifications cover both simple mechanical–dynamic test procedures and common component testers and test standards with roller bearings and toothed wheels (cf. Chapter 8). Apart from these specifications, which are used worldwide, many gear and system manufacturers currently issue their own more sophisticated specifications for their industrial gears, with increasing requirements. The majority

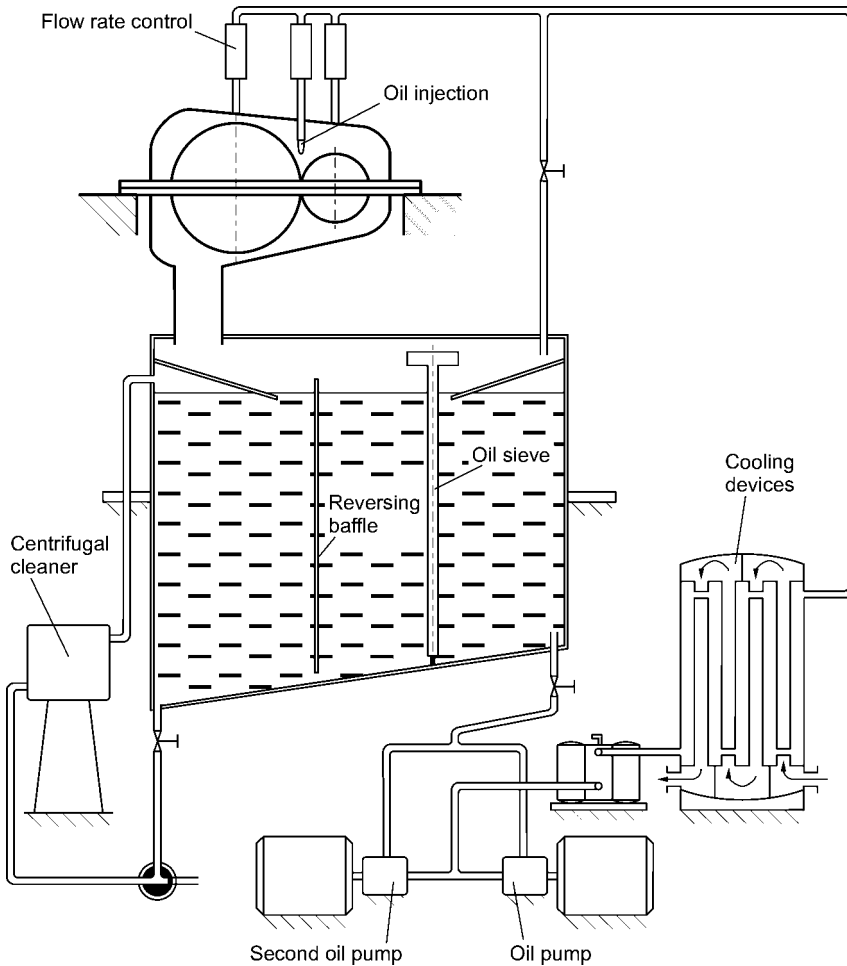


Figure 7.27 Schematic representation of a lubrication system for large industrial gears.

of these specifications include stricter limits in chemical–physical and mechanical–dynamic test standards. Detailed information regarding the properties required by the lubricants are described in the following subsections.

7.7.8.2 Important Requirements of Lubricants for Industrial Gears

Viscosity–Temperature Characteristics

According to the ambient and operating conditions, the required viscosity–temperature behavior of gear lubrication oils constitutes a very important requirement during application. In this case, the base oil’s properties according to the viscosity range is of great importance. Worldwide, lubrication oils for industrial gears are subject to the ISO viscosity grade conversions, whilst in the Americas, and also in a large part of the automotive industry, the SAE gear viscosity numbers apply. In the Americas and,

mainly, in the Asian Pacific regions, the viscosity ranges for AGMA lubricants are used most often. A fluid with a high VI can be used all year round, thus eliminating seasonal fluid changes. For example, a high-VI fluid will enable cooler operating temperatures, thus avoiding any unscheduled shut-downs because of overheating; it will also enable an efficient and smooth operation at higher temperatures, and enable start-up at lower temperatures. Consequently, the temperature operating range of the gear equipment will be increased. High-VI fluids have better low-temperature properties than do standard gear or hydraulic fluids, which means that, at low temperatures, a fluid of a given grade (ISO VG) will have a viscosity less than that of a lower-grade (thinner) fluid. Yet, it is still possible to identify a fluid that meets high-VI (multigrade oil) performance levels by matching the characteristics.

Fluid Shear Stability Another important aspect of fluid performance is viscosity and VI stability under the operating conditions used. Fluids can be prepared with high-VI oils (e.g., expensive synthetic oils) and/or by adding polymers known as VIIs to the formulation (see Section 7.5). Although, in the majority of cases, the base oil and most other additives will not be affected by shear forces, under certain circumstances the VII might be affected, causing it to be broken into smaller pieces, with subsequent reductions in both the fluid viscosity and VI. As a result, the benefits of a high-VI fluid might be lost in operation. However, low-molecular-weight VIIs are now commercially available that are resistant to breaking (shearing), such that this problem is eliminated.

Corrosion and Rust Protection In particular, corrosion and corrosion protection play very important roles with respect to lubrication oils for industrial gears. Due to the required extended drain for industrial gears, severe corrosion can facilitate an unexpectedly quick failure of the bearings, toothed wheels, and other important gear components; however, this can be avoided by using a protecting lubricant combined with a suitable additive. Hence, modern-day specifications will include a variety of tests to determine the corrosion-protection properties of lubricants for iron-steel, copper, and other yellow metals. Some industrial applications, notably offshore applications where the presence of salt water in the gears may aggravate the situation, will require the use of special test methods.

Oxidation Stability Oxidation stability will reduce the aging of a lubricant, which may in turn be connected with a change in viscosity and an increase in the acid number. By using specific test methods, it is possible to determine the aging behavior of the oil by altering the acid number (this number indicates how many milligrams of KOH are required to neutralize the acids in the oil). Today, sensitive gears are often tested on a regular basis; should the acid number change noticeably, the oil producers would recommend that the oil be drained.

Demulsibility and Water Separation Water is a poor lubricant that facilitates corrosion and which should, therefore, be kept away from the oil-based lubricant. Unfortunately, water cannot be prevented from penetrating the lubricant, and when

the proportion of water in the oil has exceeded a certain limit, the only possibility remaining is to drain the oil or to physically separate the oil and water. In large lubrication systems, the water will sink to the bottom of the oil tank due to its greater specific weight, and be released through a drain cock. However, this requires the lubricant to have a good water-separation behavior.

Other requirements important for lubricating oils include air release, paint compatibility, seal compatibility, foaming, and environmental and skin compatibilities.

7.7.8.3 Open Gear Drives

Open gear drives are often found in the cement industry, as so-called “milling gears,” in rotary kilns in the iron and steel industry, in coal-burning plants, or in open-cast mines. These open large gears are often lubricated with sprayable, adhesion lubricants. In this case, apart from the requirements made on load capacity and wear protection, priority must also be given to the adhesion properties, sprayability, pumpability and corrosion protection. In the above-mentioned systems, solid-matter so-called “compounded lubricants” have proved to be successful additives for the adhesion lubricants. Unfortunately, the oil mist and spray lubrication systems used may not only cause health and environmental problems but also lead to a direct loss of oil through the waste air. Open gears may also be lubricated either manually, or at regular intervals by using dosing pumps and high-viscosity oils.

7.7.8.4 Comparison of Various Types of Industrial Gear Oils

From the very outset, the design and component selection of gears was focused on cost, and on cost-effective engineering. The objective of a study, and an evaluation of the results obtained [90], was to compare the performance of synthetic industrial gear oils with conventional, mineral oil-based gear lubricants of CLP standard (DIN 51 517) in terms of their oxidation stability (oil-aging stability) and friction characteristics. This could ultimately lead to a significant increase in the service life of the lubricant, as the extended drain intervals correlated with a much higher mechanical–dynamic performance level.

Examples of industrial gear oils blended from different types of base oils are listed in Table 7.9. The expected lifetimes of gear oils, notably with regards to oxidation stability, can be compared by using the rotary bomb oxidation test. In this test, which is conducted in a pressurized autoclave, the time is measured over which the oxygen in a gear oil is utilized. Whilst synthetic long-life oil (long-drain in accordance with lifetime factor) has a good oxidation stability, comparative tests have indicated that some synthetic industrial gear oils have a much greater oxidation stability than do mineral oil-based products. Typically, the performance of synthetic gear oils in application-related mechanical–dynamic tests with regard to micropitting, frictional torque and persistent oil sump temperatures, in gears and roller bearings, has been shown far superior to that of standard mineral oil-based gear lubricants. These findings are shown in Figure 7.28, for scuffing load stage and oil sump temperature on the FZG Gear Test Rig (see Chapter 8). The test results of the lubricants provide vital information concerning oil-related friction reduction in gearboxes and roller

Table 7.9 Industrial gear oils, a comparison of base fluid data.

Characteristic	Gear oil				
	CLP-M	CLP-PLUS	CLP-PAO	CLP-PC	CLP-E
Type of fluid	Mineral	Mineral	Synthetic	Synthetic	Synthetic biodegradable
Base oil of the fluid	Mineral oil	Mineral oil	Polyalphaolefins	Polyglycols	Synthetic ester
Viscosity at 40 °C (mm ² s ⁻¹)	220	220	220	220	220
Viscosity at 100 °C (mm ² s ⁻¹)	18.4	18.4	25.7	34.7	28.0
Viscosity index	95	95	150	200	160
Flash point (°C)	230	230	260	230	280
Pour point (°C)	18	18	54	33	48
Water- soluble	No	No	No	Partly	No

bearings, and also emphasize their overall performance. This level of performance from synthetic fluids results in increased power and improved productivity. Compared to standard mineral oils of types CLP-M and CLP-PLUS, the prices of the synthetic base fluids of types CLP-PAO, CLP-E, and CLP-PG are much higher. However, the longer lifetime of the synthetic base oil more than compensates for the higher product price, and also reduces the sump temperatures by 10–30 °C. Each of these aspects must be considered when the overall cost–benefit of a product is

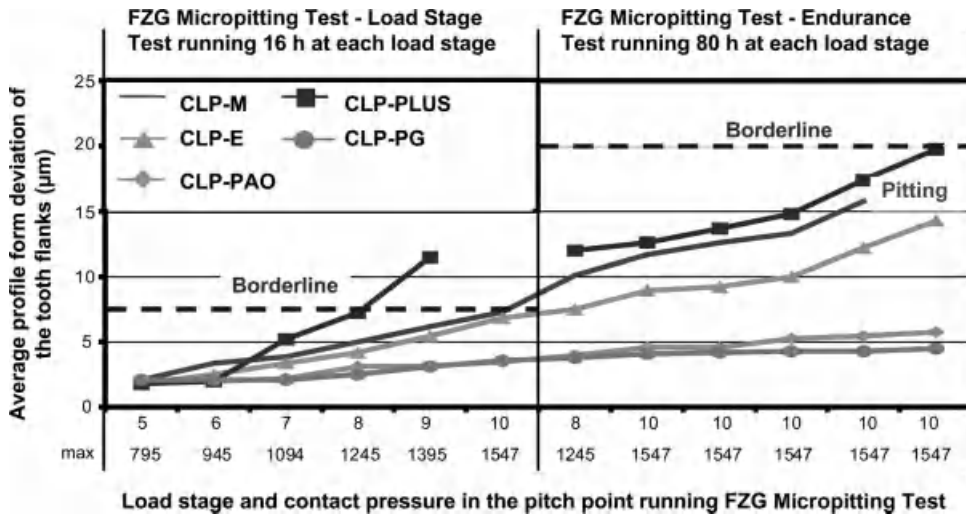


Figure 7.28 Industrial gear oils. A comparison of micro-pitting test results from the FZG Gear Test Rig.

evaluated. Hence, the higher cost of a synthetic gear oil must be set against the savings generated by its longer life (compared to mineral oils) and reductions in service costs. By considering all of these aspects, the use of synthetic base fluids may substantially reduce the total lubricant-related system costs. In real-life applications, however, it is worth performing a cost–benefit analysis while considering the excellent tribological characteristics of synthetic gear oils. The higher initial price for synthetic products may be compensated by savings generated by significantly longer drain intervals compared to mineral oils, as well as to an overall reduction in total operating costs.

7.8 Hydraulic Oils

Today, the manufacturers of hydraulic components supply the very large majority of industries, including the agriculture and construction machinery sectors, conveyor technology, foodstuffs and packaging industries, woodworking and machine tools, ship-building, mining and steel industries, aviation and aerospace, medicine, environmental technology, and the chemical industry. Today, fluid technologies are essential to the point where many applications are economical only when fluid technology can be used; indeed, fluid technology is omnipresent, whether in stationary or mobile applications.

In 2009, W. Bock produced the book *Hydraulic Fluids – A Liquid Machine Element* [90], on which the following elaboration is based, in addition to a lecture by T. Mang at the University of Aachen (RWTH) [91] and the updated Chapter 11 of Ref. [92].

The field of fluid technology—and, therefore, of hydraulics—is divided into *hydrostatics* and *hydrodynamics*. In hydrostatic systems, the transfer of energy requires static pressure, and so pressures are high but flow rates are low [93]. In hydrodynamic systems, the kinetic energy of the flowing fluid is used, so the pressures are low but the flow rates high. Fluids designed for hydrodynamic applications are known as “power-transmission oils,” while fluids for hydrostatic applications are known as “hydraulic oils” or “hydraulic fluids” [94, 95]. After engine oils, hydraulic oils are the second most important group of lubricants, accounting for approximately 13–14% of total lubricant consumption [95, 96]. In 2007, mineral-based hydraulic oils accounted for approximately 80–85% of all hydraulic oils in Germany. Fire-resistant fluids had a market share of approximately 7%, rapidly biodegradable hydraulic fluids about 9%, and synthetic PAO and other synthetic hydrocarbon fluids about 1%. In recent years, the performance of hydraulic systems has increased significantly, this being reflected in higher pressures, higher system temperatures, and lower system volumes, all of which increase the circulation and thus the stress on the medium. Hydraulic fluid developments, both to date and in the future, and their correct application, are of enormous economic significance as optimum applications conserve energy, reduce maintenance intervals, reduce wear, increase machine life, and thus enable worthwhile savings.

7.8.1

Elements of a Hydraulic System

The most important elements of a hydraulic system are: pumps and motors (e.g., gear, rotary vane and piston pumps); hydraulic cylinders (e.g., single- and double-action); valves (e.g., pressure limiters and control valves); circuit components (e.g., fluid tanks, filter systems, pressure tanks, pipework, etc.); and seals, gaskets and elastomers. The function and tribology of these elements are described in Section 8.6.

7.8.2

Composition of Hydraulic Fluids (Base Fluids, Additives)

The quality and performance of a hydraulic fluid depends on the quality of the base fluid and the combination of the additives or additive systems used. Additives improve certain characteristics which the base fluid cannot provide, or cannot provide to a sufficient extent. Bearing in mind the technical and ecological aspects, the type of base fluid and types of additive ultimately decide the classification of hydraulic oil (see Sections 7.2, 7.3 and 7.5). Mineral oils account for 88% (mainly paraffinic Group 1 Oils), while synthetic oils account for 12% (of which 80% are esters, 15% polyglycols, and 5% other synthetic oils). The additive components can either complement or counter each other. Those characteristics that can be improved by the use of additives include mainly aging stability, corrosion protection, wear protection, EP behavior, viscosity–temperature behavior, foaming, detergency, water separation, and friction coefficient. The most important additives for hydraulic fluids are surface-active additives such as rust inhibitors, metal deactivators, wear inhibitors, friction modifiers, and detergents/dispersants, while the important base oil active additives include antioxidants, defoamers, VI improvers, and pour point improvers. A basic classification of hydraulic fluid additive systems can be made by differentiating between additive systems that contain zinc and ash and those that are zinc- and ash-free (ZAF) (see Section 7.5) [95, 97]. On average, zinc-containing hydraulic oils account for 70–80% of the total volume, and ZAF fluids for 20–30%.

7.8.3

Characteristics of a Hydraulic Fluid

The primary functions and properties of a hydraulic fluid include: transferring pressure and motion energy; transferring forces and moments when used as a lubricant; minimization of wear to sliding surfaces under boundary friction conditions; minimization of friction; protection of components against corrosion (ferrous and nonferrous metals); dissipation of heat; suitability for a wide range of temperatures; good viscosity–temperature behavior; and prolonging the life of the machinery.

The most important secondary characteristics include: high aging stability; good thermal stability; inactive to materials; compatibility with metals and elastomers; good air separation; low foaming; good filterability; good water release; good shear stability in the case of non-Newtonian fluids, and many more.

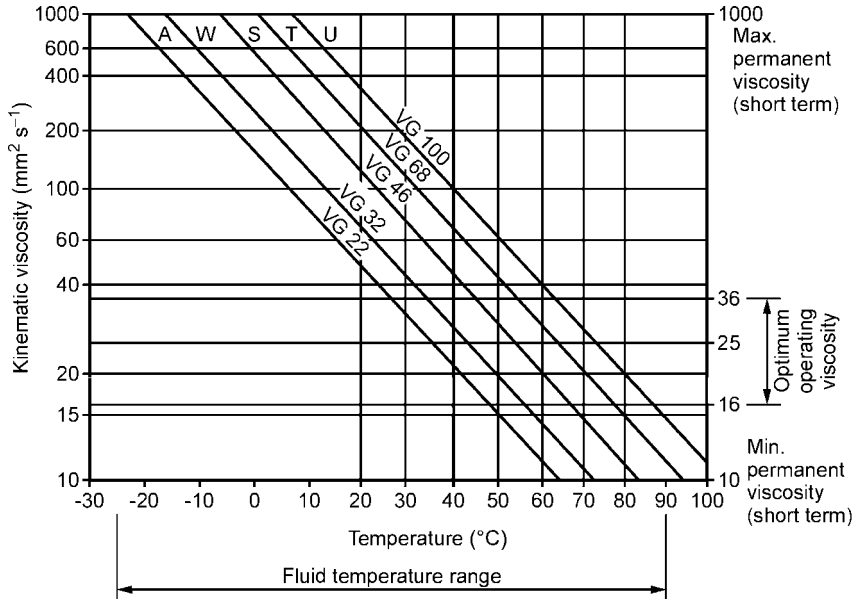
The tertiary characteristics include: low evaporation as a result of low vapor pressure; toxicologically inert; ecologically safe, and low flammability (fire-resistance). The wide variety of different characteristics required of hydraulic fluids necessitates special performance which cannot be satisfied by just one base oil. Consequently, special chemical substances (additives) will improve and complement the technical performance of hydraulic fluids. Synthetic base fluids can satisfy specific performance requirements such as environmental compatibility, high thermal stability, fire-resistance, and use in food-grade applications [95].

7.8.4

Selection Criteria for Hydraulic Fluids

Fluid selection depends on the application, such as the working temperature range, design of the hydraulic system, type of pump, working pressure, and environmental considerations. The required fluid life, availability, and economic and ecological factors also determine the type of hydraulic oil used. From a rheological standpoint, the viscosity of the fluid selected should be as low as possible; this guarantees an instant hydraulic response when the die system is activated. On the other hand, a minimum viscosity is required to reduce leakages and to guarantee adequate lubrication of the pump and other moving parts. Any change in hydraulic fluid temperature has a direct effect on viscosity, and for this reason the working-temperature range of a hydraulic system should be kept relatively narrow in order to make any viscosity fluctuations as small as possible. For accurate fluid selection, it is assumed that the working and ambient temperatures are known. In sealed systems this is the circuit temperature, and in open systems the tank temperature. The viscosity of the fluid selected should be in the optimum range, between 16 and 36 mm² s⁻¹. The normal operating temperature depends on the ambient temperature, pressure, and other factors. Typically, in low- and medium-pressure stationary hydraulic systems, the operating temperature should be ca. 40–50 °C (tank temperature), whereas for systems which operate at higher pressures (>400 bar) the average temperature can be 10–20 °C higher [93]. It must be remembered that the fluid temperature at the pump outlet and downstream of any motors or valves is higher than in the tank or than the system's average temperature. The leakage temperature, which is influenced by pressure and pump speed, is always above the system or tank temperature. The fluid temperature should never exceed 90 °C (max. 100 °C) in any part of the system. If these conditions cannot be met, owing to extreme circumstances, then at lower ambient temperatures it is recommended that the pumps and motors are flushed [94]. For the various hydraulic fluid applications, Brueninghaus-Hydromatic provides a recommendation, as shown in Figure 7.29.

The average temperature of mineral-based hydraulic oils in stationary systems should not exceed 50–60 °C, and 80–90 °C in mobile systems. Fluids containing water (e.g., HFC fluids) should be kept down to 35–50 °C (i.e., the vapor pressure of water). The volume of fluid in stationary systems should be three- to fivefold the volume that is pumped per minute. In mobile systems, the tank volume should be



A = for arctic conditions or for extremely long pipelines
 W = for winter conditions in Central Europe
 S = for summer conditions in Central Europe or for enclosed areas
 T = for tropical conditions or for areas with high temperatures
 U = for excessively high temperatures (e.g. due to internal combustion engines)

Depending on the construction of the pumps (axial piston units) and the operating conditions the following viscosity ranges are valid:

$10 \text{ mm}^2 \text{ s}^{-1}$ ($t_{\text{max}} = +90^\circ\text{C}$) $1000 \text{ mm}^2 \text{ s}^{-1}$ ($t_{\text{min}} = -25^\circ\text{C}$)

$[5 \text{ mm}^2 \text{ s}^{-1}$ ($t_{\text{max}} = +115^\circ\text{C}$) $1600 \text{ mm}^2 \text{ s}^{-1}$ ($t_{\text{min}} = -40^\circ\text{C}$)] special components

Figure 7.29 Selection diagram for hydraulic fluids.

either equal to or twofold the pumped volume, although under special circumstances it can be less.

7.8.5

Classification of Hydraulic Fluids

Hydrostatic applications can be divided into subgroups with regard to ISO, CETOP and national (e.g., DIN) classifications. The different categories of hydraulic fluids and their principle uses are shown in Figure 7.30, while the classifications and minimum requirements of hydraulic fluids, according to DIN, are listed in Tables 7.10–7.13.

The details of ATF's, and of fluids for tractors and agricultural machinery are described in Section 7.7.

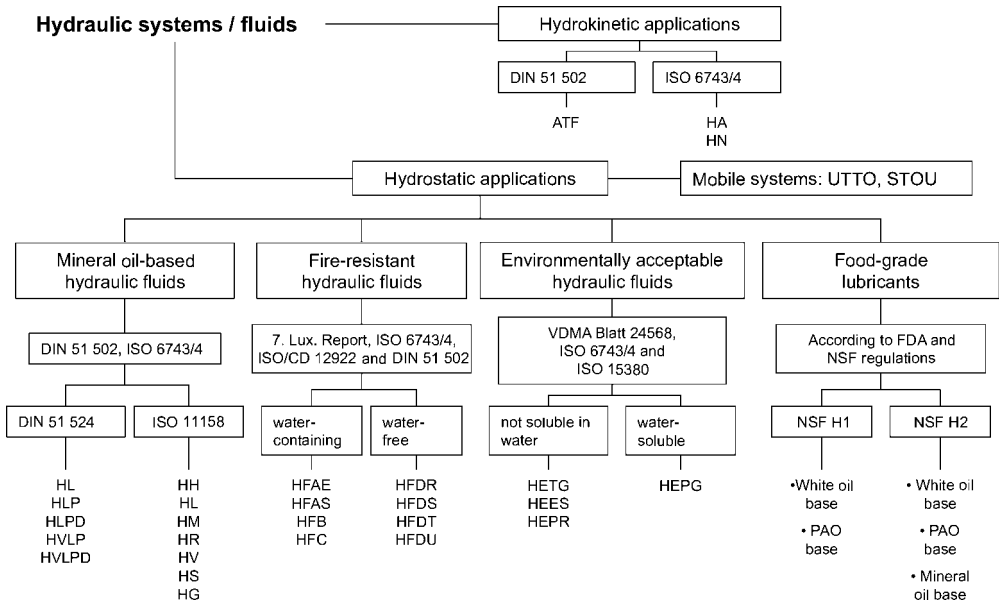


Figure 7.30 Classification of hydraulic fluids; an overview.

7.8.6

Fire-Resistant Hydraulic Fluids

Fire-resistant fluids have been developed for mining, die-casting, steel mill, and aviation applications. These fluids have significantly higher ignition temperatures or fire-resistant properties, and thus afford better fire protection than mineral oils. The use of these fluids is compulsory for some applications, for example underground coal mining. Fire-resistant hydraulic fluids are classified according to the Luxembourg Report [98], ISO 6743/4, VDMA sheets [99, 100], CETOP RP97H [101], DIN 51 502 and Factory Mutual (FM-USA). Evaluated factors include the physical characteristics of the different types of fluid and their fire-resistance and technical specifications. The grading of the different types of fluid are identical in DIN 51 502, ISO 6743/4 and the Luxembourg Report: HFAE, Oil-in-water emulsions (mineral oil-based); HFAS, synthetic, water-based solutions (ester or/and polyglycol-based); HFB, water-in-oil emulsions (mineral oil-based); HFC, water-based monomer and polymer solutions (polyglycol-based); and HFD, water-free fluids (ester-based).

- HFA Fluids:** These are seldom used in industrial applications because of their poor antiwear characteristics and very low viscosity. The additives used in HFA fluids usually improve corrosion protection for steels and nonferrous metals, guarantee the biostability of the fluid, and ensure compatibility with sealing materials (seal wear reduction). HFA fluids also contain friction-reducing additives, but these only provide limited protection against wear. Their principal use is in mining hydraulics and in some non-European steel mills. The practical

Table 7.10 Classification of mineral oil-based hydraulic fluids (categories according to DIN 51 502 and ISO 6743/4H and ISO 11 158).

Category (Symbol)		Composition/Typical characteristics	Field of application/Operating temperatures
DIN	ISO-L		
—	HH	Noninhibited refined mineral oils	Hydraulic systems without specific requirements (rarely used nowadays)/ –10 to 90 °C
HL	HL	Refined mineral oils with improved anti-rust and anti-oxidation properties	Hydrostatic drive systems with high thermal stress; need for good water separation/–10 to 90 °C
HLP	HM	Oils of HL-type with improved antiwear properties	General hydraulic systems which include highly loaded components, need for good water separation/–20 to 90 °C
—	HR	Oils of HL-type with additives to improve viscosity–temperature behavior	Enlarged range of operating temperatures compared with HL oils/–35 to 120 °C
HVLP	HV	Oils of HM-type with additives to improve viscosity–temperature behavior	For example, hydrostatic power units in construction and marine equipment –35 to 120 °C
—	HS	Synthetic fluids with no specific inflammability characteristics and no specific fire-resistance properties	Special applications in hydrostatic systems, special properties/–35 to 120 °C
—	HG	Oils of HM-type with additives to improve stick-slip-behavior, and anti-stick-slip properties	Machines with combined hydraulic and plain bearing way lubrication systems where vibration or intermittent sliding (stick/slip) at low speed must be minimized/–30 to 120 °C
(HLPD)	—	Oils of HM-type with detergent/dispersant (DD) additives DD additives reduce friction	Hydrostatic drive units with high thermal stress, which require EP/AW additives, DD additives keep contaminants in suspension, e.g., machine tools and mobile hydraulic equipment

Category L: Lubricants, Industrial oils and related products.

Category H: Hydrostatic hydraulic systems.

concentration of mineral oil-based HFAE (emulsions) or synthetic HFAS (solutions) is between 1 and 5% in water (depending on the water quality).

- **HFB Fluids:** These are water-in-oil emulsions with a (flammable) mineral oil content of ca. 60%. HFB fluids are used almost only in the UK mining industry and in other UK-influenced countries (Commonwealth countries). Because of their high mineral oil content, these fluids do not pass spray-ignition tests in Germany and several other countries.

Table 7.11 Minimum requirements of hydraulic fluids: DIN 51 524, Part 1, HL (Revised Version 2006 – April).

DIN 51 524 Part 1 – Hydraulic fluids with improved anti-rust and anti-oxidant properties										
	HL 10	HL 15	HL 22	HL 32	HL 46	HL 68	HL 100	HL 150		
Grade (DIN 51 502)	HL 10	HL 15	HL 22	HL 32	HL 46	HL 68	HL 100	HL 150		
ISO viscosity grade (DIN 51 519)	VG 10	VG 15	VG 22	VG 32	VG 46	VG 68	VG 100	VG 150		
Viscosity at 0 °C and (mm ² s ⁻¹ , max. (DIN 51 562-1)	90 (600)	150	300	420	780	1400	2560	4500		
Viscosity at 40 °C, mm ² s ⁻¹ min.–max. (DIN 51 562-1)	9.0–11.0	13.5–16.5	19.8–24.2	28.8–35.2	41.4–50.6	61.2–74.8	90.0–110	135–165		
Viscosity at 100 °C, mm ² s ⁻¹ , min. (DIN 51 562-1)	2.5	3.2	4.1	5.0	6.1	7.8	9.9	14.0		
Pour point, °C, max. (DIN ISO 3016)	-30	-27	-21	-18	-15	-12	-12	-12		
Flash point (COC), °C, min. (DIN EN ISO 2592)	125	140	165	175	185	195	205	215		
Purity class (ISO 4406:1999)	21/19/16 (defined requirements depend on the system)									
Contamination with solid particles (mg kg ⁻¹ , max.) (DIN ISO 5884 or ISO 4405:1991)	50									
Filterability without H ₂ O, Stage I F ₁ /Stage II F ₁₁ , min. % (E DIN ISO 13 357-2)	80/60									
Filterability with H ₂ O, Stage I F ₁ /Stage II F ₁₁ , min. % (E DIN ISO 13 357-1)	70/50									
Demulsibility, 54 °C, minutes, max. (DIN ISO 6614)	20				30					
Demulsibility, 82 °C, minutes, max.	—				—				30	(Continued)

Table 7.11 (Continued)

DIN 51 524 Part 1 – Hydraulic fluids with improved anti-rust and anti-oxidant properties	
Water content in % m/m, max. (DIN EN ISO 12 937 – method A)	0.05
Steel corrosion, method A (DIN ISO 7120)	Pass
Copper corrosion, 100 °C, 3 h, degree of corrosion, max. (DIN EN ISO 2160)	2
Aging properties (maximum increase in neutralization number after 1000 h) in mg KOH g ⁻¹ , max. (DIN 51 587 or DIN EN ISO 4263-1)	≤2.0
Behavior toward the SRE-NBR 1 sealant after 7 days ± 2 h at 100 ± 1 °C (DIN 53 538-1, DIN ISO 1817, and DIN 53 505)	0 to 18
Relative change in volume, %	0 to 15
Change in Shore A hardness	0 to -10
Air release, 50 °C, minutes, max. (DIN ISO 9120)	5
Foam volume in ml, max. (ISO 6247:1998, incl. Corr. 1: 1999) at 24 °C	5
at 93.5 °C	5
at 25 °C after 95 °C	5
	10
	13
	21
	28
	0 to 12
	0 to -7
	0 to -6
	150/0
	75/0
	150/0

Table 7.12 Antiwear hydraulic fluids, Minimum requirements of hydraulic fluids: DIN 51 524, Part 2, HLP – April 2006, DIN 51 524 Part 3 HVLP.

Grade (DIN 51 502)	HLP 10	HLP 15	HLP 22	HLP 32	HLP 46	HLP 68	HLP 100	HLP 150
ISO viscosity grade (DIN 51 519)	VG 10	VG 15	VG 22	VG 32	VG 46	VG 68	VG 100	VG 150
Viscosity at 0 °C/(–20 °C, mm ² s ^{–1} , max. (DIN 51 562-1)	90 (600)	150	300	420	780	1400	2560	4500
Viscosity at 40 °C, mm ² s ^{–1} , min.-max. (DIN 51 562-1)	9.0–11.0	13.5–16.5	19.8–24.2	28.8–35.2	41.4–50.6	61.2–74.8	90.0–110	135–165
Viscosity at 100 °C, mm ² s ^{–1} , min. (DIN 51 562-1)	2.5	3.2	4.1	5.0	6.1	7.8	9.9	14.0
Pour point, °C, max. (DIN ISO 3016)	–30	–27	–21	–18	–15	–12	–12	–12
Flash point (COC, °C, min. (DIN EN ISO 2592)	125	140	165	175	185	195	205	215
Purity class (ISO 4406:1999)				21/19/16 (defined requirements depend on the system)				
Contamination with solid particles, mg kg ^{–1} , max. (DIN ISO 5884 or ISO 4405:1991)				50				
Filterability without H ₂ O, Stage I F ₁ /Stage II F _{1r} , min. % (E DIN ISO 13 357-2)				80/60				
Filterability with H ₂ O, Stage I F ₁ /Stage II F _{1r} , min. % (E DIN ISO 13 357-1)				70/50				

(Continued)

Table 7.12 (Continued)

Grade (DIN 51 502)	HLP 10	HLP 15	HLP 22	HLP 32	HLP 46	HLP 68	HLP 100	HLP 150
Demulsibility, 54 °C, minutes, max. (DIN ISO 6614)	20	—	—	30	—	—	—	—
Demulsibility, 82 °C, minutes, max. Water content in % m/m, max. (DIN EN ISO 12 937 – method A)	—	—	—	—	—	—	30	—
Steel corrosion, method A (DIN ISO 7120)	—	—	—	Pass	—	—	—	—
Copper corrosion, 100 °C, 3 h, degree of corrosion, max. (DIN EN ISO 2160)	—	—	—	2	—	—	—	—
Aging properties (maximum increase in neutralization number after 1000 h) in mg KOH g ⁻¹ , max. (DIN 51 587 or DIN EN ISO 4263-1)	—	—	—	≤2.0	—	—	—	—
Behavior towards the SRE-NBR 1 sealant after 7 days ± 2 h at 100 ± 1 °C (DIN 53 538-1, DIN ISO 1817, and DIN 53 505)	—	—	—	—	—	—	—	—
Relative change in volume, %	—	0 to 18	—	0 to 15	—	0 to 12	—	0 to 10
Change in Shore A hardness	—	0 to -10	—	0 to -8	—	0 to -7	—	0 to -6
Air release, 50 °C, minutes, max. (DIN ISO 9120)	5	5	5	5	10	13	21	32
Foam volume, in ml, max. (ISO 6247:1998, incl. Corr. 1:1999) at 24 °C	—	—	—	150/0	—	—	—	—

Table 7.12 (Continued)

Grade (DIN 51 502)	HLP 10	HLP 15	HLP 22	HLP 32	HLP 46	HLP 68	HLP 100	HLP 150
Filterability without H ₂ O, Stage I F ₁ /Stage II F ₁₁ , min. % (E DIN ISO 13 357-2)			80/60					
Filterability with H ₂ O, Stage I F ₁ /Stage II F ₁₁ , min. % (E DIN ISO 13 357-1)			70/50					
Demulsibility, 54 °C, minutes, max. (DIN ISO 6614)	20			30				
Demulsibility, 82 °C, minutes, max. Water content in % m/m, max. (DIN EN ISO 12 937 -method A)			0.05				30	
Steel corrosion, method A (DIN ISO 7120)			Pass					
Copper corrosion, 100 °C, 3 h, degree of corrosion, max. (DIN EN ISO 2160)			2					
Aging properties (maximum in- crease in neutralization number after 1000 h), mg KOH g ⁻¹ max. (DIN 51 587 or DIN EN ISO 4263-1)			≤2.0					
Behavior towards the SRE-NBR 1 sealant after 7 days ± 2 h at 100 ± 1 °C (DIN 53 521, DIN ISO 1817, and DIN 53 505)	0 to 18	0 to 15	0 to 15	0 to 12	0 to 10			
	Relative change in volume, %	Change in Shore A hardness	Change in Shore A hardness	0 to -7	0 to -6			

Table 7.13 Minimum requirements of hydraulic fluids: ISO 6743, Part 4 – HM, ISO 11 158. Specification for type HM mineral oil hydraulic fluids Oils with improved anti-rust and anti-oxidant and anti-wear properties (a typical application is for general hydraulics).

Characteristics or test	Units	Specifications	Standard or Test Method
Viscosity grade		VG 10 VG 15 VG 22 VG 32 VG 46 VG 68 VG 100 VG 150	ISO 3448
Density at 15 °C	kg dm ⁻³	a) a) a) a) a) a) a) a)	ISO 3675
Color ^{b)}		a) a) a) a) a) a) a) a)	ISO 2049
Appearance at 25 °C ^{c)}		Cilbr Cilbr Cilbr Cilbr Cilbr Cilbr Cilbr Cilbr	
Flash point			
Cleveland open cup, min.	°C	100 140 140 160 180 180 180 180	ISO 2592
Pensky–Martens closed cup, min.	°C	88 128 148 168 168 168 168 168	ISO 2719
Kinematic viscosity at 40 °C, min.–max. ^{d)}	mm ² s ^{-1d)}	9.0–11.0 13.5–16.5 19.8–24.2 28.8–35.2 41.4–50.6 61.2–74.8 90.0–110 135–165	ISO 3104 and ISO 3105
Viscosity index		a) a) a) a) a) a) a) a)	ISO 2909
Pour point, max.	°C	-30 -21 -18 -15 -12 -12 -12 -12	ISO 3016
Neutralization value ^{e)}	mg KOH g ⁻¹	a) a) a) a) a) a) a) a)	ISO 6618
Water content	% (m/m)	0.05 0.05 0.05 0.05 0.05 0.05 0.05 0.05	ISO/DIS6296or DIN 51 777-2 ^{f)}
Copper corrosion, 100 °C, 3 h, max.		2 2 2 2 2 2 2 2	ISO 2160
Rust prevention, procedure A		Pass Pass Pass Pass Pass Pass Pass Pass	ISO 7120
Foam: at 24 °C, max.	ml	150/0 150/0 150/0 150/0 150/0 150/0 150/0 150/0	ISO/DIS 6247
at 93 °C, max.	ml	75/0 75/0 75/0 75/0 75/0 75/0 75/0 75/0	
at 24 °C, max.	ml	150/0 150/0 150/0 150/0 150/0 150/0 150/0 150/0	
Air release, 50 °C, max.	min.	5 5 5 5 10 13 21 32	ISO/DIS 9120
Water separation			
time to 3 ml emulsion at 54 °C	min.	30 30 30 30 30 30 30 30	ISO 6614
time to 3 ml emulsion at 82 °C	min.	— — — — — — — —	30 30

Elastomer compatibility ^{e)}	1)	1)	1)	1)	1)	1)	1)	1)	1)	ISO 6072
Oxidation stability, 1000 h:										
delta neut. number, max.	—	—	2.0	2.0	2.0	2.0	2.0	2.0	2.0	ASTM D4310
insoluble sludge	—	—	a)	a)	a)	a)	a)	a)	a)	
Wear protection,	—	—	—	10	10	10	10	10	10	DIN 51 354
FZG A/8.3/90, min. ^{h)}	—	—	—	—	—	—	—	—	—	BS 2000: part 281
Vane pump ⁱ⁾	—	—	a)	a)	a)	a)	a)	a)	a)	or ASTM D 2882

a) Report only.

b) For purposes of identification, dye may be used by agreement between supplier and end user.

c) Clear-bright is abbreviated as Clbr. Cleanliness level expressed according to ISO 4406 may be used by agreement between supplier and end user.

d) $\text{mm}^2 \text{s}^{-1}$ is equivalent to cSt.

e) Initial neutralization number is influenced by the presence of functional moieties in the total additive package.

f) DIN 51 777-2 is applied to instances where interference by certain chemicals can be avoided.

g) The type of elastomer and definition of compatibility are to be agreed between supplier and end user.

h) Applicable from ISO VG 32 to ISO VG 150.

i) Applicable from ISO VG 22 to ISO VG 68.

- **HFC Fluids:** These are normally based on a mixture of minimum 35–50% fully demineralized water with polyglycols (monomers or polymers) as thickeners. Low-molecular-weight ethylene and/or propylene glycols are used to improve the low-temperature behavior of the fluid. Carefully matched additive systems which improve wear and corrosion protection and foaming behavior ensure the required tribological properties.
- **HFD Fluids:** These are synthetic, water-free and fire-resistant hydraulic fluids. Usually, HFDR fluids based on phosphoric acid esters or HFDU fluids based on carboxylic acid esters or polyolesters are used. Today, HFDR fluids containing phosphoric acid esters are used as control and regulator fluids in turbines, and as hydraulic fluids in aviation systems. HFDU fluids based on carboxylic acids and polyolesters make up the largest segment of HFD fluids. They are normally used for hydrodynamic clutches and high-performance hydraulic systems at pressures of 250–350 bar and temperatures of 70–100 °C (and higher). HFDU fluids have tribological properties similar to those of mineral oils. They show excellent characteristics in boundary lubrication and in biodegradability.

7.8.7

Biodegradable Hydraulic Fluids

Environmentally friendly, rapidly biodegradable hydraulic fluids were originally developed to ensure ecological compatibility, and are used in stationary and mobile systems. Their market share is growing rapidly, to a point where they will most likely replace mineral oil-based hydraulic fluids within several areas. This trend has been underlined by the creation of VDMA guideline 24 568, which specifies minimum requirements for HETG, HEES, and HEPG fluids (see below) and the inclusion of these three fluid groups into ISO 6743/4, in combination with the new ISO 15 380 specification (enlarged to include HEPR). Rapidly biodegradable hydraulic fluids are allocated to several product families according to VDMA 24 568 (minimum technical requirements), VDMA 24 569 (change-over guidelines) and ISO 6743/4 and ISO 15 380:

- **HETG:** triglyceride (non-water-soluble, vegetable-oil types)
- **HEES:** synthetic ester types (non-water-soluble)
- **HEPG:** polyglycol types (water-soluble)
- **HEPR:** PAOs and related hydrocarbon products.

The classification and the fields of application for the various families of biodegradable hydraulic fluids are listed in Table 7.14. More detailed information concerning biodegradable fluids is provided in Section 7.15.

7.8.8

Food-Grade Hydraulic Fluids

The classification of foodstuff-compatible hydraulic oils is based on Food and Drug Administration (FDA) and NSF International guidelines [102]. (*Note:* NSF

Table 7.14 Classification of rapidly biodegradable hydraulic fluids.

Category according to VDMA 24 568 and ISO 15 380	Composition/Typical characteristics	Field of application/Operating temperatures
Water-free, rapidly biodegradable hydraulic fluids		
HEPG	Polyalkylene glycols soluble in water	Hydrostatic drives, e.g., locks, "water hydraulics" –30 to <90 °C (reservoir temp. –20 to 80 °C)
HETG	Triglycerides (vegetable oils) not soluble in water	Hydrostatic drives, e.g., mobile hydraulic systems –20 to <70 °C (reservoir temp. –10 to 70 °C)
HEES	Synthetic esters not soluble in water	Hydrostatic drives, mobile and industrial hydraulic systems –30 to <90 °C (reservoir temp. –20 to 80 °C)
HEPR	Polyalphaolefins and/or related hydrocarbons not soluble in water	Hydrostatic drives, mobile and industrial hydraulic systems –35 to <80 °C (reservoir temp. –30 to 100 °C)

International – The Public Health and Safety Company, is a not-for-profit, nongovernmental organization in the USA.) The NSF issue of H1 or H2 lubricant approvals depends on the FDA classification of components such as base oils and additives (FDA Code of federal regulations, 21 CFR 178.3570). The European hygiene guideline 93/43 EWG and the Hazard Analysis and Critical Control Points (HACCP) Management System, promotes the use of safe lubricants in the food-processing industries. The NSF organization has taken over the activities of the United States Department of Agriculture (USDA), which has closed its activities

7.8.9

Hydraulic Fluids for Aircraft

The principal functions of aircraft hydraulics include control of the elevator, rudder, ailerons, flaps, landing gear, doors, and brakes. The most commonly used pumps are of the axial piston type, with pressures of between 100 and 280 bar. The fluid volumes, at between 20 and 40 liters, are relatively small. The hydraulic fluids used must be free from particle contaminants because aircraft hydraulics must function under extreme climatic conditions with enormous fluctuations in temperature; hence, these hydraulic fluids must have outstanding thermal stability and good viscosity–temperature behavior, and should also be fire-resistant. A wide variety of different hydraulic fluids are currently used in aircraft; these include those based on phosphoric acid esters, PAOs, silicate esters, and special mineral oils. One standard which all such fluids must fulfill is that of US military specifications, such as MIL H 5606 or others. These specifications serve as a basis for other specifications issued by the manufacturers of aircraft and aircraft hydraulics.

7.8.10

International Requirements of Hydraulic Oils

The requirements of hydraulic fluids are normally set out in national standards or company-specific specifications. Apart from ISO 6743/4 and DIN 51 524, there are several specifications issued by leading component manufacturers. Although these specifications often overlap, there are differences in detail, normally in relation to thermal/oxidation stability, mechanical/dynamic tests, filterability tests, and in-house tests performed by some manufacturers. A summary of the most important OEM hydraulic oil specifications is listed in Table 7.15.

7.8.11

Contaminants, Oil Cleanliness Categories, and Filtration

There are several types and causes of hydraulic fluid contamination, which can be differentiated as primary and secondary contamination:

- *Primary contamination* is that which existed in the hydraulic circuit before it was commissioned. This can include machining residues, assembly residues, and fresh-oil contaminants.
- *Secondary contamination* is that formed after the system has begun to operate. Examples include mechanically abraded material, flow-related abrasion, corrosion, wear and dirt that enters the system via cylinder seal materials or via tank de-aerating units.

Sensitive problems occur as a result of greater particle sizes of the contamination, and this is related to the clearance of hydraulic component points. The known methods to define oil cleanliness are ISO 4406 and NAS 1638; cleanliness categories according these methods are listed in Table 7.16. If specific filters are used to remove impurities in hydraulic oils the mesh size must be adequate to satisfy the requirements of the specific hydraulic component, although the filterability of hydraulic oils may be different, by using various additive systems and base oils. In general, hydraulic systems use filter mesh sizes ranging from 3 to 40 μm , but for specific applications filters with 1–3 μm meshes are used. In those cases, filter blockage can occur if the additive systems are incompatible or if high-molecular-weight components (e.g., VI-improvers) are present.

7.8.12

Machine Tool Lubrication: Fluid Family

Apart from cutting fluids, hydraulic oils are volumetrically the most significant group of machine lubricants, followed by slideway oils and gear oils. The lubrication of machine tools is described in DIN 8659-1 and -2, and ISO 5169 and ISO 3498. These standards contain requirements which should be observed when manufacturers and users establish their lube plans. The standards also satisfy the requirements specified in DIN/ISO 5170 (machine tool lubrication Systems). A lubrication chart

Table 7.15 Major OEM hydraulic oil specifications.

Performance: ASTM-test	Denison HF-0 (piston and vane pump test)	Denison HF-1 (piston pump test)	Denison HF-1 (vane pump test)	Vickers/Mannes- mann Rexroth	Cincinnati Mila- cron P-68, P-69, P70	Rust and Oxida- tion Cincinnati Milacron P-38, P-54, P-55, P-57
SLUDGE AND METAL CORROSION (1000 h, D4310)						
Neutralization no. (D974)	1.0 mg KOH g ⁻¹ max. 100 mg 200 mg	1.0 mg KOH g ⁻¹ max. 100 mg 200 mg	1.0 mg KOH g ⁻¹ max. 100 mg 200 mg			
Insoluble sludge max. Total copper max.						
C.M. THERMAL STABILITY TEST						
-168 h at 135 °C, Cin. P70 (ISO VG46)				5% max. change	5% max. change	
Results after test:						
Viscosity (D445, D2161)				+50% max. change	0.15 max. increase	
Neutralization no. (D744)				25 mg 100 ml ⁻¹ max.	25 mg 100 ml ⁻¹ max.	
Sludge or precipitate	100 mg 100 ml ⁻¹ max.	100 mg 100 ml ⁻¹ max.	100 mg 100 ml ⁻¹ max.			
Conditions of steel rod						
Visual				No discoloration	No discoloration	
Deposits (per 200 ml)				3.5 mg max.	3.5 mg max.	
Metal removed (per 200 ml)				1.0 mg max.	1.0 mg max.	
Condition of copper rod	Report	Report	Report	5 max.	5 max.	
Copper rod rating Visual (CM)	10 mg max.	10 mg max.	10 mg max.	10.0 mg max.	10.0 mg max.	
Copper weight loss						

(Continued)

Table 7.15 (Continued)

Performance: ASTM-test	Denison HF-0 (piston and vane pump test)	Denison HF-1 (piston pump test)	Denison HF-1 (vane pump test)	Vickers/Mannes- mann Rexroth	Cincinnati Mila- cron P-68, P-69, P70	Rust and Oxida- tion Cincinnati Milacron P-38, P-54, P-55, P-57
HYDROLYTIC STABILITY						
(ASTM D2619)						
Copper weight loss (mg cm ⁻²)	0.2 max.	0.2 max.	0.2 max.			
H ₂ O acidity (mg KOH)	4.0 max.	4.0 max.	4.0 max.			
PUMP WEAR TEST (ASTM D2882)					50 mg max.	100 h
DENISON AXIAL PISTON AND VANE PUMP WEAR TEST	T6H20C accord- ing to TP 30 533	P-pump	T-pump			
(in cooperation with Denison when deemed necessary)				Total 90 mg max. ¹⁾		
VICKERS HP VANE PUMP TEST				In-house report ²⁾		
MANNESMANN REXROTH IN-HOUSE PUMP TEST						
FILTERABILITY (DENISON PROCEDURE)						
Filtration time w/o water	600 s max.		600 s max.			
Filtration time with water (PALL filtration)	Not to exceed two times the filtra- tion rate w/o water	Procedure A and B	Not to exceed two times the filtra- tion rate w/o water 80 min. Procedure A and B			Procedure A
RUST TEST (ASTM D665A) 24 h	Procedure A and B	Procedure A and B	Procedure A and B			
FOAM (ASTM D892) after 10 min. NEUTRALIZATION NO. (ASTM D974) mg KOH g ⁻¹	No foam	No foam	No Foam		1.5 max.	0.2 max.

Table 7.16 Cleanliness categories.

Type of system/case of application/filter size	Cleanliness category in accordance with ISO 4406	Cleanliness category in accordance with NAS 1638
Against fine soiling and mudding-up of sensitive systems; servo hydraulics	min. 13/10	3–4
Heavy-duty servo systems, high-pressure systems with long service life	min. 15/11	4–6
Proportional valves, industrial hydraulics with high operating safety	min. 16/13	7–8
Mobile hydraulics, common mechanical engineering, medium pressure systems	min. 18/14	8–10
Heavy industry, low-pressure systems, mobile hydraulics	min. 19/15	9–11

of a grinding machine with the lubrication points is provided in Ref. [91] (see Figure 7.31).

Technically similar lubricants can often be grouped to enable some lubricant rationalization, and machine manufacturers often refer to the lubricant recommendations issued by component manufacturers. The recommendations issued by the manufacturers of hydraulic components, gearboxes, slideways, and linear guides must be observed. For lubrication purposes, a machine tool can be divided into a number of major elements: hydraulic unit; gearbox; spindle; slideway; linear system; plain and roller bearings; and finally, cutting zone lubrication. In general, a different lubricant is recommended for every component—that is, at least seven different types and viscosities of lubricant (excluding the cutting fluid) are required. Some interesting new trends in machine tool lubrication are described in the following subsections. These cover the close relationship between cutting fluids and hydraulic oils and the potential of fluid rationalization, and highlight the route from water-soluble cutting fluids to neat oils with good hydraulic fluid compatibility.

7.8.12.1 Oil Instead of Emulsion

During the early 1990s, the first discussions were held about replacing conventional emulsions with neat oils, based on the concept of a total process cost analysis [102]. The background was the high cost of the machining fluids application (5–17%) compared to overall process costs caused by the expense of maintaining and disposing of water-miscible cutting fluids. A major factor of the high cost was contamination of the water-miscible cutting fluid with hydraulic fluid and other machine lubricants. Today, the “oil instead of emulsion” trend is seen as an answer to a number of problems, since not only are cost benefits realizable, but the environmental, safety-at-work and technical performances are superior. From a safety-at-work point of view, neat oils are more skin-compatible than emulsions, as they do not contain biocides and/or fungicides. Another major aspect is the almost

Lubrication Chart Cylindrical Grinding Machine

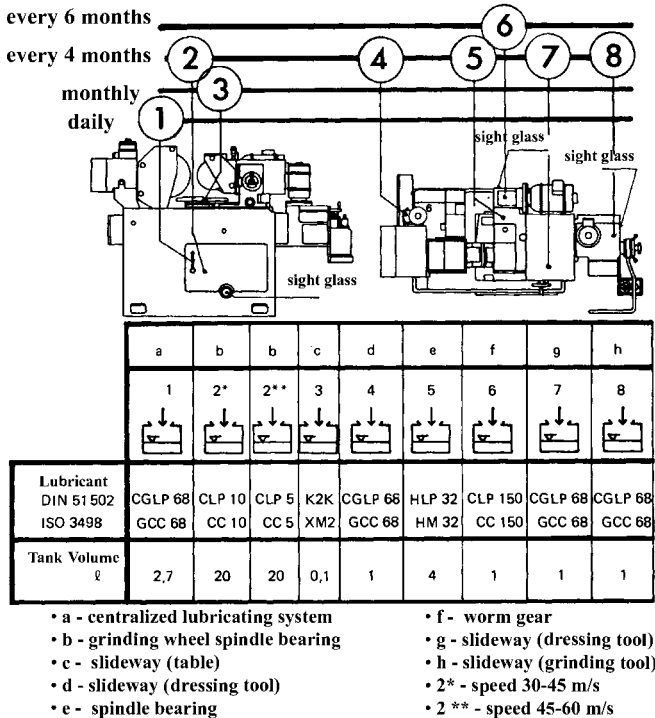


Figure 7.31 Lubricant chart for a machine tool.

unlimited life of oils compared to the fluid change cycles of water-miscible fluids (6 weeks for individually filled machines and 2–3 years maximum for central systems). Oils are also better in terms of environmental protection and protecting resources. As regards pure machining performance, oils can satisfy more than 90% of all machining operations. Replacing emulsions with oils offers a better lubricity, improved surface finishes, and a significantly longer tool life. A cost analysis performed in a gearbox plant generated the factor of 2 as an average of all machining operations [103], while between 10- and 20-fold longer tool lives were recorded in cubic boron nitride (CBN) grinding and deep-hole drilling trials. In addition, in-house corrosion protection for corrosion-prone materials such as cast iron and mild steel is normally not required. The same applies to machine tools, which are protected against corrosion even if the paint finish is damaged. The only disadvantages of machining with oils are in those processes which generate a lot of heat. For example, with a fourfold reduction in cooling, tool and machining problems can occur during critical operations which include the manufacture of carbide drills from solid stock. In order to perform these processes with oil, the viscosity must be reduced to a minimum, but this generates the first conflict between technical

performance and safety-at-work. The evaporation of conventional oils based on paraffinic solvent raffinates rises almost exponentially with falling viscosity yet, at the same time, the flashpoint falls. This problem can only be solved by the use of unconventional base oils which combine the advantages of a high flashpoint with low evaporation at very low viscosities. In response to these requirements, the first cutting oils based on hydrocracked oils with esters were developed during the late 1980s, and pure ester oils were established on the market in the early 1990s. The evaporation characteristics of the different base oils are described in Section 7.2. Of particular interest are the very low values for ester oils, which include products with different chemical structures that originate, in the main, from oleochemical products— that is, from animal and vegetable raw materials. Apart from a low evaporation, ester oils also display tribological advantages due to their significantly better friction behavior [104]. Even in the absence of any additives, ester oils also offer improved friction and wear characteristics, due to their polarity. This advantage, combined with a high viscosity index, low water-polluting hazard and good biodegradability, predestines this group of base oils for use in machine tools as cutting fluids, hydraulic fluids, and machine lubricants. Currently, a number of special oils which comprise a mixture of hydrocracked oils and ester oils have been developed, to provide a combination of the excellent tribological properties of the latter with the lower price of the former.

7.8.12.2 Fluid Families and Multifunctional Fluids for Machine Tools

The decisive step towards cost optimization by harmonizing machine lubricants was first made possible by the trend towards metalworking with oils. A much underestimated aspect of total cost analyzes is the influence of tramp oils on cutting fluids. Investigations in both Europe and the USA have shown that three- to 10-fold the entire hydraulic fluid volume becomes mixed with the total cutting fluid volume every year [105]. This effect, over a 10-year period at a European automobile manufacturer, is shown in Figure 7.32. In the case of water-miscible cutting fluids, the significant quantities of dragged-in oils caused some pronounced changes to

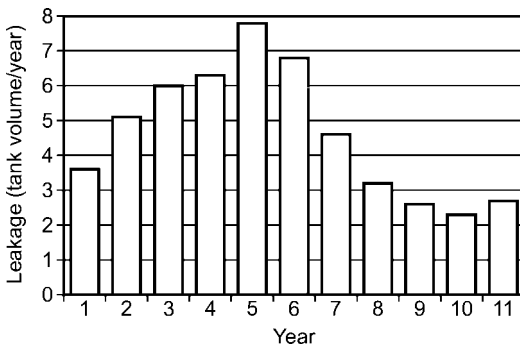


Figure 7.32 Hydraulic oil losses in machine tools. This example was taken from a mass production scheme in the European automotive industry.

the emulsion, which led in turn to machining problems, corrective actions, and considerable costs. In the case of neat oils, contamination with tramp oils cannot be seen, and can only be assumed when problems such as poor dimensional accuracy and increased tool wear become apparent. The trend towards machining with neat oils has presented a range of cost-reduction possibilities. One analysis by a leading German machine tool manufacturer showed that an average of seven different lubricants is used in every machine tool. Apart from leakage problems and the incompatibility of some lubricants, costs are also generated by the need to stock all of the necessary lubricants. The incorrect application of a lubricant, and/or confusion among the oil grades, may lead to considerable damage being caused to machines, or even to production stoppages.

One possible solution to this problem might be to introduce “multifunctional” products that would satisfy a wide range of machining operations, while simultaneously fulfilling the demands of advanced machine tool lubrication. Unfortunately, although the problems associated with a need for a range of lubricants might be solved by using a “universal fluid” for all machine lubrication points, conventional machine tools generally require ISO VG 32 or 46 hydraulic fluids, as the controls, valves and pumps are all designed around these viscosity grades. On the other hand, the current trend in metal-working fluids is towards lower viscosities that offer lower drag-out losses on chips and grinding sludge. Another reason to use low-viscosity oils is the trend towards high-speed cutting, which requires good heat dissipation to achieve good results. This divergence between the viscosity of metal-working oils, hydraulic oils and machine tool lubricants still allows process cost optimization by harmonizing the additives in all machine tool lubricants. A machine tool fluid family should contain the same, or at least compatible, additives in lubricants of different viscosities, the advantages of this being:

- the unavoidable leaks of hydraulic fluids and slideway oils have no negative effect on the cutting fluid;
- that manufacturing quality remains constant, without complex analytical measures;
- the tramp oils function as cutting fluids and thus do not create additional costs;
- a higher process reliability, good machining results, and reduced tool wear all serve to lower manufacturing costs; and
- universal application.

Moreover, users can benefit from an enormous rationalization potential with regards to lubricant grades, because a fluid family satisfies not only the lubrication requirements of the machine tools but also those of various machining processes and materials. A typical example of this is in engine manufacture, where one oil can be used for the rough machining of the block through to honing of the cylinders, offering sensational savings potential.

In process lines, water-based cleaning operations can be eliminated because undesirable mixtures will be avoided by using compatible lubricants. Both, chips and solid contaminants can be removed from the cutting fluid by using ultra-fine

filtration. Moreover, apart from the high investment costs of washing lines, the detergent, energy, water and monitoring costs will also be eliminated.

The harmonized additives in all process oils allow the economic recycling of residual oil from chips, grinding sludge, and components, such that up to 50% of the oil can be returned to the cutting fluid circuit.

7.8.12.3 Future Perspectives: “Unifluid”

In the near future, it is highly likely that only one low-viscosity oil will be available that can be used as a hydraulic oil and also for different cutting and grinding operations. This universal fluid—“Unifluid”—has been developed and tested in a German research project sponsored by the Ministry for Agriculture. “Unifluid,” which has a viscosity of $10 \text{ mm}^2 \text{ s}^{-1}$ at 40°C , has demonstrated excellent results in a German automotive engine plant for machining and lubricating a complete transfer line (including the hydraulic system).

7.8.13

Composition of Hydraulic Fluids

Today, typical hydraulic fluids are composed of 95–98% base fluids and 2–5% additives. As mentioned above, the major contributors to base fluids are refined mineral oils distillates (Section 7.2), whilst other base fluids used are, basically, fully and partially saturated esters, polyglycols, PAOs, and other synthetic oils (see Section 7.3). The most important additives for hydraulic fluids are listed in Table 7.17.

Table 7.17 Most important types of additive in hydraulic fluids, and their chemistry.

Type	Chemistry
Antioxidants (AO)	Phenolic and aminic AO, zinc dialkyldithiophosphate (ZnDTP)
Copper deactivators	Nitrogen compounds (triazoles), dimercaptothiadiazoles
Steel/iron corrosion inhibitors	Carboxylic acid derivatives, sulfonates, succinic acid compounds
Antiwear (AW) additives	Esters, ZnDTP
Extreme pressure (EP) additives	Phosphorous and sulfurous compounds, thiophosphates, sulfurized hydrocarbons (active and inactive)
Friction modifiers	Fatty acids, polar compounds, esters
Detergents/dispersants	Ca and Mg phosphates, sulfonates, phenates, polyiso-butylensuccinimide
Antifoam agents	Silicone oil, silicone oil-free, polymethylsiloxane
Viscosity index improvers (VIIs)	Polymethacrylates
Pour point depressants (PPs)	Polymethacrylates
Dyes	Azo dyes, fluorescent dyes
Tackifiers	Polyisobutylenes, polar compounds

7.9

Turbine Oils

In a steam turbine, thermal energy is extracted from pressurized steam and converted into mechanical work. Such turbines are particularly suited to drive electrical generators in power stations and, indeed, about 80% of all electricity generation worldwide is by the use of such steam turbines. These machines are produced in a very wide variety of sizes, of up to 1500 MW, in which the steam temperatures may reach about 560 °C and pressures can exceed 240 bar. The gas turbine is, in many respects, similar to the steam turbine, whereby air is compressed (using compressors) and also heated either by an outside burner or by a direct injection of the fuel. When used in power stations, the hot exhaust air of the gas turbine is often used to produce steam for a steam turbine. A combination of these two turbine types results in a higher efficiency (up to 60%). One important use of the gas turbine is in the air-breathing jet engine, where the gas turbine is optimized to produce thrust from the exhaust gases.

Additional information on gas turbines and the related tribological phenomena are provided in Section 8.5.7.

7.9.1

Demand on Turbine Oils

The demands on turbine oils are defined by the turbines themselves, and their specific operating conditions [184]. The oil in the lubricating and control circuits of steam and gas turbines must fulfill certain objectives [185]: the hydrodynamic lubrication of all bearings and the lubrication of gearboxes; heat dissipation; functional fluid for control and safety circuits; and avoidance of wear on gear tooth flanks in turbine gearboxes especially when the turbine is spooled-up. Apart from these mechanical–dynamic requirements, a number of physical–chemical specifications must also be fulfilled by the turbine oil [185], including: aging stability for long operating periods; hydrolytic stability (especially of the additives used); corrosion protection even if water, steam and/or condensation is present; reliable separation of water (vapor and separation of condensed water); rapid air release and low foaming; and good filterability and purity. These stringent demands on steam and gas turbine oils are met with carefully selected base oils and the inclusion of special additives [186–192, 194].

7.9.2

Formulation of Turbine Oils

The turbine oils used today contain special paraffinic base oils with good viscosity–temperature characteristics, as well as antioxidants and corrosion inhibitors. If geared turbines require a degree of load-bearing capacity (e.g., failure load stage FZG 8 min. DIN 51 3 54-2), some mild EP additives are included. Currently, turbine base oils are created exclusively by solvent extraction and hydrogenation. Refining and

subsequent selective high-pressure hydrogenation has a significant influence on the turbine oil's characteristics, such as oxidation stability, water separation, air release, and foaming. This applies in particular to water separation and air release, because these features cannot be subsequently improved with additives. Phenolic antioxidants combined with aminic antioxidants (synergies) are added to turbine oils to improve their oxidation stability. In order to improve corrosion protection, non-emulsifiable corrosion protection agents and nonferrous metal passivators are used (see Section 7.5), which are not negatively affected by water or steam contamination during operation, and remain in suspension. If standard turbine oils are used in geared turbines, then mild, long-life, temperature- and oxidation-stable EP/AW additives (e.g., organophosphorus and/or sulfur compounds) are included. Small quantities of silicone-free defoamers and pour point depressors are also used in turbine oils.

7.9.3

Requirements and Classification of Turbine Oils

The requirements of steam turbine oils for normal service are described in DIN 51 515 Part 1, and listed according to the viscosity grade as LTD 32 - LTD 100. The requirements for high-temperature turbine oils are given in Part 2 of this DIN 2004 (Table 7.18) [195]. The classification of lubricants for turbines according to ISO is listed in Table 7.19 [196]. The principal demands of turbine manufacture are collected in Table 7.20.

7.10

Compressor Oils

Lubricants for compressors are mainly discussed for the two main application areas, namely air compressors and refrigerants. A recent comprehensive information pack on these two areas of application has been provided by Bock [197, 198]; this is related to the following subsections, including earlier publications from T. Mang [199, 211], as well as technical information sheets from specialized suppliers of refrigerating compressor lubricants [200, 207].

7.10.1

Air Compressor Oils

Compressors may be classified as two types—displacement compressors and dynamic compressors. In displacement compressors, the gaseous medium is drawn into a chamber, compressed, and expelled by a reciprocating piston. In contrast, the principle of a dynamic compressor is that the turbine wheels accelerate a medium which is then abruptly decelerated. During the past 25 years, traditional piston compressors have increasingly been replaced by rotary compressors (and in by

Table 7.18 Requirements of high-temperature turbine oils, DIN_{51 515} Part 2, November 2004, L-TG for higher temperature service.

Lubricating oil group	Limits		Testing according to ^{d)}	Comparable ISO ^{a)} Standards
	TG 32	TG 46		
ISO viscosity grade ^{e)}	ISO VG 32	ISO VG 46	DIN 51519	ISO 3448
Kinematic viscosity at 40 °C (in mm ² s ⁻¹)	min. 28.8	41.4	DIN 51 550 in conjunction with	
	max. 35.2	50.6	DIN 51 561 or DIN 51562-1	ISO 3104
Flash point (COC) (°C)	min. 160	185	DIN ISO 2592	ISO 2592
Air release property ^{f)} at 50 °C (min)	max. 5	5	DIN 51 381	—
Density at 15 °C (g ml ⁻¹)	max. To be specified by supplier	To be specified by supplier	DIN 51 757	ISO 3675
Pour point (°C)	≤ -6		DIN ISO 3016	ISO 3016
Neutralization no.	To be specified by supplier	To be specified by supplier	DIN 51 558-1	ISO/DIS 6618
Ash (oxide ash)	% mass	To be specified by supplier	DIN EN 7	ISO 6245
Water content (mg kg ⁻¹)	max. 150		DIN 51777-1	ISO/DIS 12937
Cleanliness level	min. 20/17/14		DIN ISO 5884 with ISO 4406	ISO 5884 with ISO 4406
Foam:				
Seq. I at 24 °C	max. ml 450/0		—	ISO 6247
Seq. II at 93 °C	max. ml 100/0			
Seq. III at 24 °C after 93 °C	max. ml 450/0			
Demulsibility (min)	To be specified by supplier		DIN 51 599	ASTM-D 1401
Water separation ability (after steam treatment) (seconds)	max. 300	300	DIN 51 589	—
Copper corrosion corrosiveness	max. 2–125 A 3		Part I DIN 51 759	ISO 2160

Corrosion protection against steel corrosiveness	max.	0-A	DIN 51 585	ISO/DIS 7120
Aging behavior ^{e)}				
Time (in h) to reach delta NZ of 2.0 mg KOH g ⁻¹	min.	3.000	DIN 51 587	ISO/DIS 4263
RBOT	minute	≥800 ^{b)}	—	—
Modified RBOT (min)	% of time in unmodified test	≥85 %	—	ASTM-D 2272

a) International Organization for Standardization.

b) GE recommends only 450 min.

c) Middle point viscosity at 40 °C in mm² s⁻¹.

d) The oil sample must be stored without any contact to light before performing the test.

e) The aging behavior test must be carried out as a type test procedure because of the long testing time.

f) The test at a temperature of 25 °C must be specified by the supplier when the customer needs values at low temperatures.

Table 7.19 Principal demands of turbine manufacturers (according to W. Bock).

	Siemens TLV 901304 (July 1999)	e.g., General Electric GEK 101941 A (November 1999)	e.g., General Electric GEK 32568 E (May 1999)	Alstom HTGD 90117 V0001U 7/2005	Alstom HTGD 90117 V0001U 7/2005	Testing accord- ing to DIN ISO	Testing accord- ing to ASTM
Lubricating oil group	Steam and gas turbine oils ^{b)}	Gas turbine oils with EP/AW additives with bearing ambients above 260 °C ⁵⁾	Gas turbine oils with bearing ambients above 260 °C ^{d)}	Steam and gas turbine oils (with and without EP/AW additives), ISO VG 32/46 ^{e)}	Steam and gas turbine oils (with and without EP/AW additives), ISO VG 68 ^{e)}		
Kinematic viscosity at 40 °C (mm ² s ⁻¹)	28.8–35.2	28.8–35.2	28.8–35.2	VG 32; ± 10%	VG 68; ± 10%	DIN 51 562-1	ASTM-D 445
ISO VG 32	41.4–50.6			VG46; ± 10%			
ISO VG 46	—	29–33.5	29–33.5	—	—		ASTM-D 287
Gravity (°API)	≤ 4	5 (max.)	5 (max.)	≤ 4	≤ 7	DIN 51 381	ASTM-D 3427
Air release property at 50 °C (min)						DIN 51 558-1	ASTM-D 974
Neutralization no. (mg KOH g ⁻¹)	≤ 0.2	—	0.2 max.	0.2 max.	0.2 max.		
without EP/AW additives	≤ 0.3	0.2 max.	—	0.3 max.	0.3 max.		
with EP/AW additives	≤ 100	—	—	—	—		
Water content (mg kg ⁻¹)	≤ 400 (Seq. 1)	50/0 max.	50/0 max.	300/0	300/0	DIN 51 777-1	ASTM-D 1744
Foaming at 25 °C	≤ 450	50/0 max.	50/0 max.	50/0	50/0	—	ASTM-D 892
Tendency (ml)		50/0 max.	50/0 max.	300/0	300/0		
Stability (s)							

Water separability (s)	≤300	≤300	≤300	—	DIN 51 589-1	—
Demulsibility (min)	≤20	≤30	≤30	—	DIN 51 599	ASTM-D 1401
Density at 15 °C (kg m ⁻³)	≤900	≤880	≤900	—	DIN 51 757	ASTM-D 1298
Flash point		VG 32 and 46: ≥200	VG 68: ≥205	—	DIN ISO 2592	ASTM-D 92
ISO VG 32 (°C)	> 160	215 (min.)	215 (min.)	—	ISO 3016	ASTM-D 97
ISO VG 46 (°C)	> 185	—	—	—	ISO 4406	—
Pour point (°C)	≤-6	-12 (max.)	-12 (max.)	—	—	—
Particle distribution (ISO class)	≤17/14	—	—	—	—	—
Color	≤2	max. 2.0	max. 2.0	—	DIN ISO 2049	ASTM-D 1500
Copper corrosion, corrosiveness	≤2-100 A 3	1 B (max.)	1 B (max.)	≤2-100 A 3	DIN EN ISO 2160	ASTM-D 130
Corrosion protection against steel, corrosiveness	≤0-B	0-B (pass)	0-B (pass)	O-B (pass)	DIN 51 585	ASTM-D 665
Aging behavior: Increase of Neutralization no. (in mg KOH g ⁻¹) after h (TOST test)	≤2.0 (after 2500 h)	≤2.0 (after 3000 h)	≤2.0 (after min. 3000 h)	<1 (after 2000 h) ^a	DIN 51 587	ASTM-D 943
Additional requirements on turbine oils for use in gearboxes FZG-Test: A/8,3/90	≥8	≥8	—	8	DIN 51 354	ASTM-D 1947
Failure load stage						
Carbon residue Ramsbottom, (%)	0.1% (max.) (or equivalent)	0.1% (max.) (or equivalent)	0.1% (max.) (or equivalent)	—	—	ASTM-D 524
Oxidation stability by rotating bomb (min)	500 (min.)	500 (min.)	500 (min.)	>300 min.	—	ASTM-D 2272
Oxidation stability by rotating bomb (modified) N2-blown RBOT	85% (min.) of time in unmodified test	85% (min.) of time in unmodified test	85% (min.) of time in unmodified test	—	—	ASTM-D 2272
Viscosity index (VI)	95 (min.)	95 (min.)	95 (min.)	≥90	—	ASTM-D 2270

(Continued)

Table 7.19 (Continued)

	Siemens TLV 901304 (July 1999)	e.g., General Electric GEK 101941 A (November 1999)	e.g., General Electric GEK 32568 E (May 1999)	Alstom HTGD 90117 V0001U 7/2005	Alstom HTGD 90117 V0001U 7/2005	Testing accord- ing to DIN ISO	Testing accord- ing to ASTM
Lubricating oil group	Steam and gas turbine oils ^{b)}	Gas turbine oils with EP/AW additives with bearing ambients above 260 °C ^{c)}	Gas turbine oils with bearing ambients above 260 °C ^{d)}	Steam and gas turbine oils (with and without EP/AW additives), ISO VG 32/46 ^{e)}	Steam and gas turbine oils (with and without EP/AW additives), ISO VG 68 ^{e)}	—	—
Atomic emission spectroscopy	<5 ppm	<5 ppm	≤5ppm	≤5 ppm	—	—	ASTM-D 4951
Zinc content							
Filterability				Stage I min 93% Stage II min 85%		ISO 13 357-2	

a) Neutralization no. <1.8 mg KOH g⁻¹, sludge <0.4% according to DP 7624. Base oils:

b) Mineral oils or synthetic oils with additives to improve corrosion protection and aging stability (additionally EP/AW additives in the case of gearbox lubrication).

c) Petroleum lubricating oil – synthetic hydrocarbons with greater high-temperature, oxidation stability and R&O inhibitors, HP/AW additives.

d) Petroleum lubricating oil – synthetic hydrocarbons with greater high-temperature, oxidation stability and R&O inhibitors.

e) Refined mineral oils with additives mainly aging inhibitors and corrosion inhibitors (no EP/AW additives).

Other important specifications (examples): Westinghouse: I.L. 1250-5 312- Steam Turbines; 21 T 0591 – Gas Turbines; Solar: ES 9-224 – Gas Turbine.L.S. = Load stage.

Table 7.20 Classification of lubricants for turbines, ISO 6743-5, Draft 1999, in conjunction with ISO/CD 8068.

General application	Composition and properties	Symbol ISO-L	Typical application
(1) Steam turbines, directly coupled or geared to the load, normal service	Refined mineral oils with suitable anti-oxidants and corrosion inhibitors	TSA	Power generation and industrial drives and their associated control systems, marine drives, where improved load-carrying capacity is not required for the gearing
(2) Gas turbines, directly coupled or geared to the load, normal service		TGA	
(3) Steam turbines, directly coupled or geared to the load, high load-carrying capacity	Refined mineral oils with suitable anti-oxidants and corrosion inhibitors with additional extreme-pressure performance to lubricate gear systems.	TSE	Power generation and industrial drives and marine geared drives and their associated control systems where the gearing requires improved load-carrying capacity.
(4) Gas turbines, directly coupled or geared to the load, high load-carrying capacity		TGE	
(5) Gas turbines, directly coupled or geared to the load, higher-temperature service	Refined mineral oils with suitable anti-oxidants and corrosion inhibitors for higher temperatures.	TGB	Power generation and industrial drives and their associated control systems where high-temperature resistance is required due to hot-spot temperatures
(6) Other lubricants (according to ISO 6749-5 and ISO/CD 8068)		TGSB (=TSA + TGB)	
(a) TSC-Synthetic steam turbine fluids with no specific fire-resistant properties (e.g., PAO) (see also TGCH)			
(b) TSD-Synthetic steam turbine fluids based on phosphate esters with fire-resistant properties (alkyl phosphate ester)			
(c) TGC-Synthetic gas turbine fluids with no specific fire-resistant properties (e.g., PAO) (see also TGCH)			
(d) TGD-Synthetic gas turbine fluids based on phosphate esters with fire-resistant properties (alkyl phosphate ester)			
(e) TCD-Synthetic fluids for control systems based on phosphate esters with fire-resistant properties			

particular screw compressors), so that the market share of screw and rotary vane compressors is presently about 60%.

7.10.1.1 Lubrication of Reciprocating Piston Compressors

In a reciprocating piston compressor, the piston is connected to the crankshaft by a connecting rod, and in general, the cylinder and drive share the same splash lubrication from oil in the crankcase. In larger compressors, the pistons are driven by cross-head rods (cross-head compressors, single or double action). In this case, the drive is lubricated by crankcase splash, but separately from the cylinders [101]. The cylinders in a piston compressor represent the most difficult task for the lubricant, and ultimately decide which lubricant is chosen. The lubricant's primary tasks are to reduce friction and wear, to seal the compression chambers, and to protect against corrosion. The peak stresses occur at TDC and BDC, at which points there is a great danger of the lubricant film tearing and allowing metal-to-metal contact. The oil is also subject to enormous stress resulting from the high temperatures created when the medium is compressed (this can cause oxidation, and lead to deposits) and, in the case of air compression, an oxygen enrichment. Only the cleanest possible air or gas should be compressed, because contaminants can accelerate oxidation and wear. This applies especially to the water content of the air/gas and other contamination; for example, aggressive gases from the surroundings can influence the performance of the used lubricant in an extremely negative way. In the case of drive unit lubrication, the lubrication of the bearings is of primary importance. Piston compressors are available as either lubricated-with-oil or oil-free versions. Normally, lubricants based on mineral oil according to DIN 51 506 – VCL, VDL (or PAO- or diester-based lubricants) are used with viscosity grades of DIN VG 68 to DIN VG 150. Mobile compressors are often lubricated with monograde engine oil (SAE 20, SAE 30, and SAE 40). Small- to medium-sized piston compressors are used for pressures up to 10 bar.

7.10.1.2 Lubrication of Rotary Piston Compressors

The pressure chambers of a rotary piston compressor are cooled and lubricated by total-loss systems, or by direct oil injection. The lubrication of such compressors is similar to that of the cylinders in a reciprocating piston compressor, insofar as the lubricant is subject to high outlet temperatures in both cases. In the case of oil-injected and oil-cooled rotary piston compressors, a quantity of oil is continuously injected into the compressor chambers. such that the outlet temperature does not exceed 100–110 °C. At the same time, the oil seals the pistons against the housing and protects against wear. Cooling of the medium results in an increase in compression performance, while cooling and sealing increase the volumetric efficiency and thus the overall efficiency of the compressor. The oils used are normally VCL or VDL according to DIN 51 506 with an ISO VG between 68 and 150, or monograde SAE 20, SAE 30, SAE 40 engine oils. Rotary piston compressors are mostly used for vehicle and railroad applications (including road tankers), and the outlet pressures are mostly less than 10 bar [201]. The lubrication circuit of a rotary vane compressor (oil cooled) is shown in Figure 7.33.

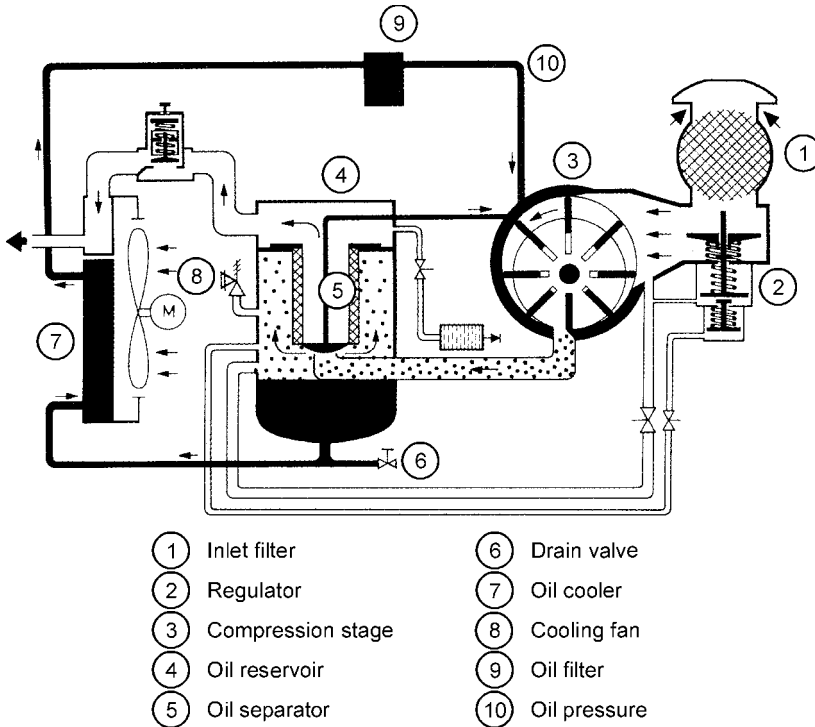


Figure 7.33 The lubrication circuit of a rotary vane compressor (oil-cooled). M, motor for cooling fan.

7.10.1.3 Lubrication of Screw Compressors

In oil-injected screw compressors, the oil has lubricating, sealing, and cooling functions. The lubricant is injected into the pressure chamber between the rotors at about 3–4 bar, and then forms a hydrostatic and hydrodynamic lubricating film. Consequently, the oil lubricates the meshing rotors and the plain and roller bearings which form part of the geared coupling, seals the gaps between the rotor and the housing, and also helps absorb heat and dissipate this via the radiators. The temperature of the compressed air, of about 80–100 °C, can be adjusted by the quantity of oil injected. Downstream oil separators (normally cartridge filters) remove the oil from the air, with residual oil quantities of 1–3 mg m⁻³ of air being achieved. The separated oil is de-aerated in tanks, and then filtered and cooled from about 80 °C to 50 °C. As the oil is on the pressure side of the screw compressor (e.g., up to 10 bar), this pressure can be used to re-inject the oil. As the viscosity of the oil is of primary importance to EHD lubrication, it must be matched to the start-up and normal running conditions. As a rule, ISO VG 46 lubricants cover most manufacturer's recommended viscosity thresholds of about >10 mm² s⁻¹ at operating temperature to about 500 mm² s⁻¹ when starting-up. Whilst this range satisfies most applications in central Europe, higher viscosity ISO VG 68 oils or synthetic ester, poly(alkylene glycol) (PAG)- or PAO-based lubricants (see Section 7.3) are used in

countries with high ambient temperatures. In recent years, lubricants based on hydrocracked oils (so-called Group III oils; see Section 7.2) have found increasing acceptance. Typically, screw compressor oils have a mild EP/AW performance.

7.10.1.4 Lubrication of Roots Compressors

Roots compressors normally consist of two symmetrical, figure-of-eight-shaped rotors in a housing; the counter-rotating rotors are driven by external gears, and do not touch. The sole task of the oil is to lubricate the rotors' gears and bearings. The benefits of this type of compressor are oil-free air, large volumes, and low vibration. The recommended lubricants include DIN 51 517 CL and CLP or HD SAE oils in the viscosity grades ISO VG 68 and ISO VG 100.

7.10.1.5 Lubrication of Turbo Compressors

The oils for this type of compressor lubricate the bearings, radial shaft seals, and possibly also the gears via a positive-feed circuit. In some cases, the bearings are lubricated with grease. Ideally, the same lubricant should be used for the compressor and its drive. Most often, DIN 51 515 TDL 32, TDL 46 and TDL 68 turbine oils or TDL-EP grades are used. Turbo compressors are used principally for creating compressed air in mines and industrial manufacturing plants.

7.10.2

Lubrication of Compressors for Oxygen and Hydrocarbons

7.10.2.1 Oxygen

Because of explosion hazards when oxygen is compressed, pressure chambers lubricants must be mineral oil-free. Both, water and water-based solutions such as glycerin can be used for cylinder lubrication, while mineral oil-based products may be used for compressor drives, as long as they do not come into contact with the pressure chambers. Oxygen compressors can be lubricated with inert lubricants based on perfluoroether oils (see Section 7.3).

7.10.2.2 Hydrocarbons

Hydrocarbons such as ethane or propane are easily soluble in mineral oil, which causes the viscosity of the lubricating oil to fall if mineral oil-based products are used. For this reason, higher-viscosity mineral oils such as ISO VG 100 and ISO VG 150 must be used in piston compressors in which the crankcases are subject to low inlet pressures (1–3 bar). In the case of screw compressors (high pressure; 10–15 bar), ISO VG 68, 100, 150, and 220 ester- or polyglycol-based lubricants with lower hydrocarbon solubility are recommended [210].

7.10.3

Specifications of Compressor Oils

DIN 51 506 describes the classification and requirements of lubricating oils which are used in reciprocating piston compressors with oil-lubricated pressure chambers

Lubricants for screw and oil-injected rotary vane and screw compressors are not included in DIN 51 506. The requirement for air compressor oils for reciprocating piston compressors and screw compressors are described in ISO/DP 621-Draft. An overview of normally used compressor oils is provided in Table 7.21.

7.10.4

Lubricants for Refrigerating Compressors (Refrigeration Oils)

The lubrication of refrigeration compressors occupies a special position in lubrication technology, as the longevity expected of refrigeration compressors is closely connected to the high quality which is required of refrigeration oil. The interaction with other substances that the refrigeration oil comes into contact with (e.g., refrigerant), and especially the extremely high and low temperatures, makes very specific demands on refrigeration oils. The principal function of a compressor oil is to lubricate the pistons or rotors, to lubricate and seal the valves and, in some cases, also the slip-ring seals [206, 208]. Furthermore, the refrigeration oil must dissipate heat away from the hot compressor components and assist in sealing the compression chambers and valves. It is vital that refrigeration oil which reaches and collects in any colder sections of the circuit in the form of oil vapor or oil mist, or as a result of splashing, is returned to the compressor by mechanical means (oil separator) or via the refrigerant flow (refrigerant solubility) under all operating conditions. The structure of a refrigeration system is shown schematically in Figure 7.34 [197, 199].

7.10.4.1 Minimum Requirements of Refrigeration Oil

The basic requirements of refrigeration oils are laid down in DIN 51 503-1. This standard defines the basic requirements of refrigeration oils according to the medium being compressed. The introduction of new chlorine-free, polar refrigerants such as HFC R 134a (to replace CFC R 12), necessitated a revision of DIN 51 503 which appeared as DIN 51 503-1 in 1997. According to this standard, refrigeration oils are classified in alphabetical groups according to the refrigerants being compressed. KAA: Refrigeration oils not soluble in ammonia; KAB: Refrigeration oils soluble in ammonia; KC: Refrigeration oils for partially and fully halogenated fluorinated and chlorinated hydrocarbons (CFC, HCFC); KD: Refrigeration oils for partially and fully fluorinated hydrocarbons (FC, HFC); KE: Refrigeration oils for hydrocarbon refrigerants such as propane or *iso*-butane. DIN 51 503-2 describes criteria for evaluating used refrigeration oils [209]. An overview of normally used refrigerator oils with various refrigerants is provided in Table 7.22.

7.10.4.2 Refrigeration Oils for CO₂

The natural refrigerant CO₂ is gaining increasing acceptance among users. Although, the properties of CO₂-oil mixtures are not fully known (under both the sub- and trans-critical conditions), it can be said, in principle, that the solubility of CO₂ in a polyolester (POE) oil is better than a PAG-polyglycol-based refrigeration oil [212]. Suitable CO₂ refrigeration oils have been developed notably during the past decade. Apart from solubility, thermal stability is also an important factor (outlet

Table 7.21 Overview of normally used compressor oils. The viscosity and the quality recommendations of the compressor manufacturers must be taken into consideration (according to W. Bock [197]).

Viscosity classification	Compressor type			
	Piston compressors ^{a)}	Screw compressors oil-injected	Sliding vane compressors ^{a),b)}	Turbo compressors (axial and radial) ^{c)}
ISO VG 32		MO		TDL 32
		HC oils		TDL 32 EP
		PAO		Synthetic oil
ISO VG 46		MO		TDL 46
		HC oils		TDL 46 EP
		PAO		Synthetic oil
		POE		
ISO VG 68 (SAE 20W-20)	MO	MO	MO	TDL, 68
	PAO	HC oils	Diester	TDL 68 EP
	Diester	PAO	HC oils	Synthetic oil
		POE		
ISO VG 100 (SAE 30)	MO		MO	
	PAO		Diester	
	Diester		HC oils	
ISO VG 150 (SAE 40)	MO			
	PAO			
	Diester			

MO = mineral oil; PAO = polyalphaolefin; HC = hydrocrack oil (so-called Group III oils); POE = biologically degradable polyolesters.

- Diester, Polyolester and PAO; for very hard-working conditions, increase of service intervals is possible.
- HC Oils (so-called Group III oils): for medium and hard working conditions.
- MO: for normal and medium working conditions.
- Lubricants for Roots-compressors: HL, CL, CLP; ISO VG 100-150, DIN 51 524, DIN 51 517
- Lubricants for vacuum pumps: ISO VG 68-150

a) Total-loss lubrication: HD-monograde motor oils HD 20W-20, HD 30, HD 40

b)

- For oil-injected compressors in mobile equipment (e.g., railways, buses): multigrade motor oils (e.g., 10 W 40, 15 W 40).
- For oil-injected compressors in stationary units: turbine oils according to DIN 51 515 TDL, air-compressor oils according to DIN 51 506 VCL, VDL.
- For hard working conditions: monograde motor oils HD 20W-20, HD 30, MIL 2104 D.

c) Turbine oils according to DIN 51 515 TDL or TDL-EP with extreme pressure additives.

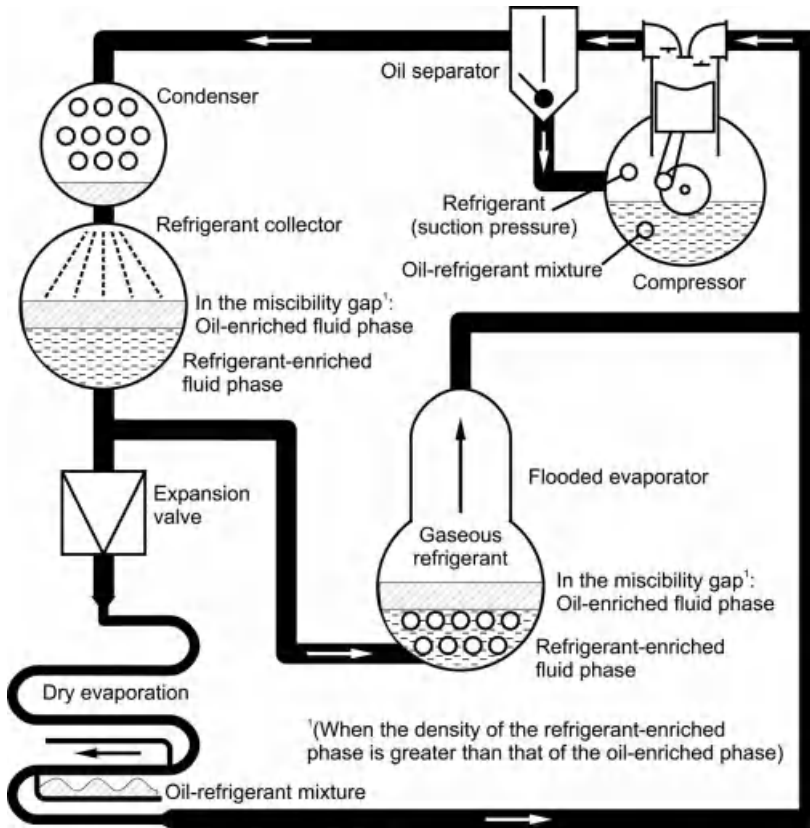


Figure 7.34 Schematic representation of a refrigeration system.

temperatures ca. 160–180 °C) [203, 204]. As a refrigerant, CO₂ is increasingly used in industrial applications, in deep-freezing systems (low-temperature cascades), for climate control, in heat-pump systems, and in container refrigeration units. These units can run transcritically and/or subcritically.

Special synthetic POE oils (ISO VG 55, 85, 130, 170) with selected AW/EP additives are used in these so-called industrial applications. The solubility of these POE oils in CO₂ is controlled (any reduction in the viscosity of the POE–CO₂ mixture must be checked), and the miscibility is excellent (this is especially important for very-low-temperature systems). This excellent miscibility (no miscibility gap down to –40 °C) guarantees oil flowability and oil return from the evaporator to the compressor. The transcritical air-conditioning systems used in buses also operate with special POEs. In the near future, CO₂ may serve as a substitute for R134a in car air-conditioning systems (phasing out is due to begin in 2011/2012). In these subcritical CO₂ car air-conditioning systems, selected and “endcapped” PAGs with AW and EP additives will be used to guarantee the lifetime of the compressor under the severe conditions of the

Table 7.22 Overview of normally used refrigerator oils. The viscosity recommendations of the compressor manufacturers must be taken into consideration (according to W. Bock [197]).

Compressor type	Refrigerant				
	Hydrocarbons ^{a)} (e.g., R 290 R 600a)	Ammonia ^{b)}	CFC, HCF, (e.g., R 12, R 22)	CFC, HCF ^{c)} (e.g., R 134a, R 404a)	Drop-In (e.g., R 402A, R 403A)
Hermetic compressors (e.g., piston compressors)	MO	—	MO	POE	MO/AB
	AB ISO VG 7-32		AB (MO/AB) ISO VG 15-46	ISO VG 10-32	ISO VG 32
Open-piston compressors	MO	MO	MO	POE	MO/AB
	AB PAO ISO VG 46-100	AB PAO, PAG ISO VG 32-68	AB MO/AB ISO VG 32-100	ISO VG 32-68	ISO VG 32-68
Semi-hermetic compressors	MO	—	MO	POE	MO/AB
	AB PAO ISO VG 46-100		AB MO/AB ISO VG 32-100	ISO VG 32-68	ISO VG 32-68
Scroll compressors	MO	—	MO	POE	MO/AB
	AB ISO VG 46-100		AB ISO VG 32-100	ISO VG 32-68	ISO VG 32-68
Screw compressors	MO	MO	MO	POE	MO/AB
	AB PAO, PAG ISO VG 68-220	AB PAO, PAG ISO VG 32-68	AB ISO VG 68-220	ISO VG 100-320	IAS VG 68
Turbo compressors	MO	— ^{d)}	MO	POE	MO/AB
	PAO, PAG ISO VG 68-100		ISO VG 68-100	ISO VG 68-150	ISO VG 68

MO = mineral oil; AB = alkylbenzene; MO/AB = mineral oil-alkylbenzene mixture;

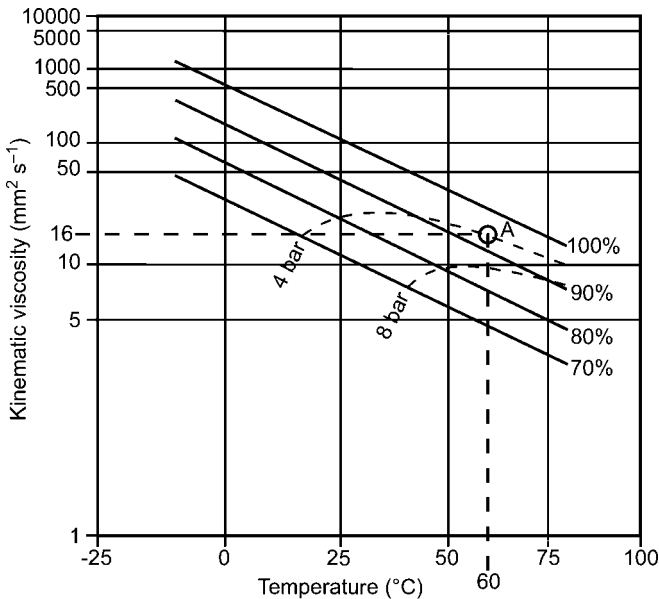
PAO = polyalphaolefin; PAG = polyalkyleneglycol; POE = polyol ester.

- PAG-lubricants are partly soluble with hydrocarbons (low-viscosity reduction); MO, AB and PAO are highly soluble with hydrocarbons (high-viscosity reduction).
- MO, AB, and PAO are not soluble with ammonia; PAG is (partly) soluble with ammonia; ISO VG 68 is used in piston compressors; up to ISO VG 220 is used in screw compressors (please use PAG-compatible components); PAG is hygroscopic.
- PAG-lubricants are used in R 134a air-conditioning systems of cars and trucks (PAG 46, PAG 100); POE and PAG lubricants are hygroscopic.
- Normally oil-free.

CO₂ transcritical process. The use of special ester oils remains the subject of discussion, however.

7.10.4.3 Mixture Viscosity in Relationship to Temperature, Pressure, and Refrigerant Concentration

The graph shown in Figure 7.35 can be used to read-off (from the y-axis) the kinematic viscosity of the oil–refrigerant mixture at a defined temperature, defined pressure, and defined refrigerant concentration. The diagram shows the viscosity in relationship to the temperature of the oil–refrigerant mixture at various concentrations. If the viscosity of the mixture (again, this is valid only when in a state of equilibrium) is required and the refrigerant concentration derived from pressure and temperature is unknown, then the diagram should be referred to. This situation results from the competing influences of viscosity gains when the temperature of the oil falls, and of the viscosity drops caused by greater quantities of dissolved refrigerant at lower temperatures. This fact is of considerable importance to the design and operation of a refrigeration compressor, and care should be taken that the oil does not reach its maximum viscosity at problematic points in the oil return circuit (e.g., upward flows, evaporators). It is also important that the conditions in the compressor crankcase do not approach those indicated by the falling left-hand part of the viscosity–temperature graph, because small temperature fluctuations can have



All %-figures represent the oil mass in the refrigerant.

Figure 7.35 Mixture viscosity in relationship to temperature, pressure, and refrigerant concentration (RENSIO Triton SE 55–R 134a). At 4 bar and 60°C, ca. 5% R 14a is dissolved, and the viscosity of the POE/R 134a mixture is 16 $\text{mm}^2 \text{s}^{-1}$.

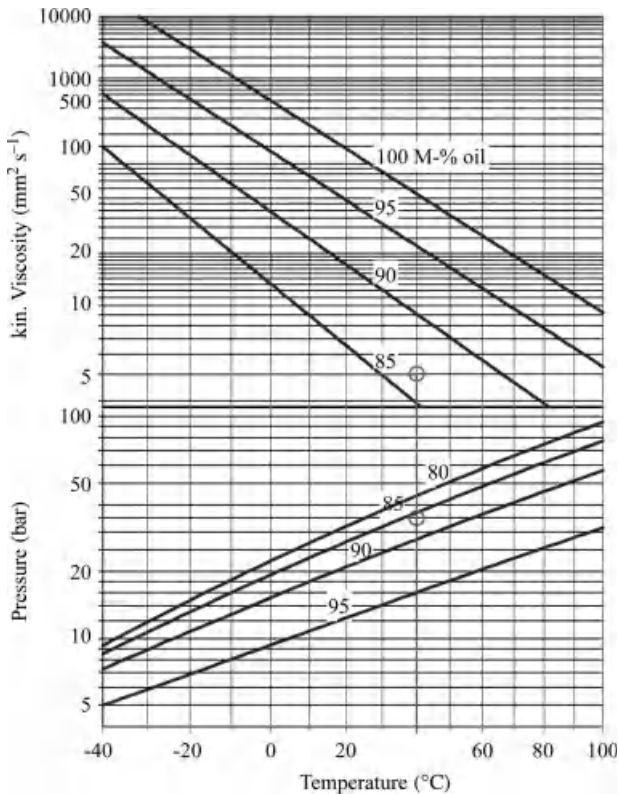


Figure 7.36 Kinematic viscosity against temperature and pressure (Reniso C 55 E – CO₂) [198, 200].

significant effects on viscosity under such conditions. Figure 7.36 shows the influence of temperature, pressure, and mass of refrigerant on the viscosity for CO₂ and polyolester-oil (RENISO C 55 E, Fuchs Petrolub) [108, 207]. In Figure 7.36, the typical working conditions for the air-conditioning in a car are marked by lines and points. From both Figures 7.35 and 7.36, it is clear that a unique tribological effect occurs, namely an increase of viscosity with increasing temperature (changing the refrigerant concentration).

7.10.4.4 Miscibility Gap and Solubility Threshold

Whilst R-refrigerants are among the most oil-soluble, not all refrigerants are miscible in refrigeration oils at all temperatures, and at all concentrations. If, for example, a fully dissolved oil–refrigerant mixture is cooled, a point will be reached when the fully dissolved mixture separates into two fluid phases; this area of partial solubility is termed the “die miscibility gap.” The miscibility gap span depends on the type of refrigerant, and also to a large extent on the type of refrigeration oil. Refrigerant solubility is defined statically in DIN 51 514. The miscibility gap is of great

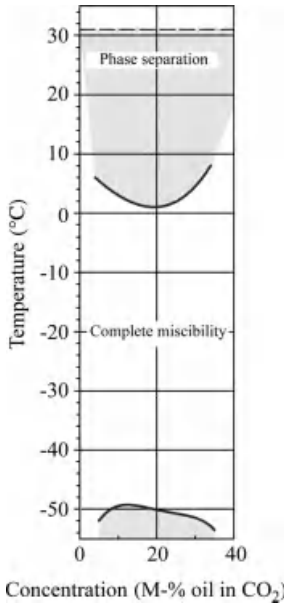


Figure 7.37 Miscibility gap (Reniso C66 E – CO₂) [200].

importance to the refrigerant circuit since, if the oil–refrigerant ratio is within the miscibility gap, problems can occur caused by oil-enriched fluid phases depositing in collectors, condensers, evaporators, and the crankcase. Flooded evaporators require the largest possible quantity of refrigerant to be dissolved at evaporating temperatures without the phases separating. An example the miscibility gap of RENISO C 55 E and CO₂ is shown in Figure 7.37.

7.10.4.5 Chemical Reactions in the Cycle

A number of investigations have been conducted concerning the chemical reactions between an oil and a refrigerant [199, 205], which can result in the creation of products containing chlorine and fluorine. A further consequence is the increased formation of carbon deposits (mostly on the valves). From this aspect, it is worth mentioning the formation of R22 from R12 (that today are no longer used), in which hydrogen is extracted from the oil and subsequently appears as a damaging reactive product in the form of hydrochloric acid. Notably, there are specific factors relating to the refrigerant and oil in order for these reactions to take place (e.g., unstable refrigerant; increase in reactions with oils having high sulfur and oil resin contents). In this case, an important role is played in the interchangeable effects between the contaminants and materials within the process (e.g., insulation materials for hermetic compressors). In addition to causing damage to the windings of motor compressors, serious consequences can arise from these chemical processes, such as oil clogging, disturbances in the lube oil circuit caused by blocked filters, carbon deposits on the valves, corrosion, and copper plating. Clearly, the chemical

compatibility for the specific plant should also be considered when selecting the type of oil to be used.

7.11

Metal-Working Fluids

Lubrication in metal-working has been described extensively by T. Mang in *Lubrication in Metalworking* [107] and in *Lubricants and Lubrications* (edited by T. Mang and W. Dresel) [108], the latter of which has been used extensively to provide information for many metal-working applications. The following section includes the key text of this 250-page chapter, and a detailed bibliography.

In terms of applications and lubricants, lubrication in metal-working is extremely complex, and normally described as two areas, namely chip-forming and non-chip-forming. The great flexibility and versatility of the many different types of machining method are particularly significant in the metal-working industries. Although, for some years now there has been a growing trend towards the use of non-cutting (forming) techniques to achieve workpiece quality and to save material and process costs, this has not had any obvious effect on the volume share of lubricants. This situation has also become apparent from machine tool statistics, where the prophesied dramatic change of the 1970s did not take place.

7.11.1

Chip-Forming Operations

7.11.1.1 Action of Machining

The lubrication and cooling, the significance of different cutting fluids with various materials, the selection of cutting fluids for different cutting methods, and the determination of cutting conditions [109, 141, 147, 246].

7.11.1.2 Friction and Wear Assessment Methods for the Use of Cutting Fluids

The tool life and the number of parts produced by the tool as practical assessment parameters, measuring cutting forces in screening tests, feed rates and constant feed forces, measuring tool life by screening methods, cutting geometry and chip flow, temperature measurement, radioactive tools, and surface finish [110].

7.11.1.3 Water-Miscible Cutting Fluids

The nomenclature and breakdown, composition, emulsifiers (anionic, cationic, nonionic) viscosity of emulsion, phase reversal, determination of the type of emulsion, degree of dispersion, emulsion stability, corrosion inhibitors and other additives, cutting fluids containing emulsifiers, coolants containing polyglycols, salt solutions, corrosion protection and corrosion test methods, concentration of water mixed cutting fluids, determination of concentration by DIN, concentration measurements using hand-held refractometers, concentration measurement through individual components, determination of concentration by titration of anionic components and by

alkali reserve, concentration after centrifuging, determination of physical emulsion stability, electrolyte stability, thermal stability, stability to metal chips, foaming properties, foam prevention, methods of determining foam behavior, metalworking fluids microbiology, hygienic and toxicological aspects of microorganisms, methods of determining microbial count, determination of the resistance of water miscible coolants towards microorganisms, reducing or avoiding microbial growth in coolants, preservations of coolants with biocides [111, 126, 127, 165, 167, 180, 181].

7.11.1.4 Neat Cutting Fluids

Classification of neat metal-working oils according to specifications, composition of neat cutting fluids, base oils and additives, significance of viscosity on the selection of neat products, oil mist and evaporation behavior, low misting oils, the creation of oil mist, toxicity of oil mist, oil mist measurements, oil mist index, oil mist concentration in practice [112].

7.11.1.5 Machining with Geometrically Defined Cutting Edges

Turning, drilling, milling, gear cutting, deep hole drilling, threading and tapping, broaching [113].

7.11.1.6 Machining with Geometrically Non-Defined Cutting Edges

Grinding, high-speed grinding, grinding wheels materials and bondings, requirements for grinding fluids, special workpiece material considerations, CBN high-speed grinding, honing, honing oils, lapping, lapping powder and carrier media [114, 135, 148–150, 179, 182].

7.11.1.7 Specific Requirements for Machining Operations

Ferrous metals, aluminum and aluminum alloys, magnesium and its alloys, cobalt, the health and safety aspects of carbides, titanium, nickel and nickel alloys [115].

7.11.1.8 Metal-Working Fluids Circulation Systems

Metalworking fluids supply, grinding, individually filled machines and central systems, tramp oil in coolants, separation of solid particles, filtration processes [116, 136–138, 178].

7.11.1.9 Monitoring and Maintenance of Neat and Water-Miscible Cutting Fluids

Storage of cutting fluids, mixing water-miscible cutting fluids, monitoring cutting fluids, the principal methods of testing the condition of neat cutting fluids, maintenance of neat cutting fluids, maintenance of water-miscible cutting fluids, corrective maintenance of neat and water-miscible cutting oils, changing cutting fluids [117, 128–131, 133, 134, 136].

7.11.1.10 Splitting and Disposal of Cutting Fluids

Evaluation criteria for cutting fluids water phases, threshold and legislation, electrolyte separation, splitting emulsions with adsorbents, separating of water-miscible cutting fluids by thermal methods, ultrafiltration [118].

7.11.1.11 Coolant Costs

Investment costs, application costs, specific costs, circulation factor, drag-out coefficient, optimization of coolant use, dependency of the specific coolant costs on the number of coolant changes [119, 139, 140, 142, 183].

7.11.1.12 New Trends in Coolant Technology

Oil instead of emulsion, fluid families and multifunctional fluids for machine tools, deoiling of chips, minimum quantity lubrication [120, 135, 143–146, 166].

7.11.2

Forming Lubricants

7.11.2.1 Sheet Metal-Working Lubricants

Processes, basic terms in forming processes, lattice structure of metals, yield strength, strain rate, flow curve, efficiency of deformation, resistance of forming and surface pressure, strain rate, anisotropy and texture, deep drawing, friction and lubrication in the different areas of deep drawing operation, Holder and die radius, tribological conditions in the flange, significance of lubrication dependent upon metal thickness, dependence of the friction share of the drawing force, assessment of the suitability of lubricants for deep drawing, deformation analysis, stretch drawing and a combination of stretch and deep drawing, shear cutting, stamping, fineblanking, material and surface microstructure, tools used in sheet metal-forming operations, lubricants for sheet metal-forming, lubricant behavior during forming, trends in sheet metal-working lubricants, temporary corrosion protection, corrosion tests, removal of forming lubricants, industrial cleaners, testing tribological characteristics in sheet metal-forming [151, 152, 235, 265].

7.11.2.2 Sheet Metal-Forming in Automobile Manufacturing

Prelubes, skin passing, coil oiling, transport and storage of sheet metal, washing of steel strips and blanks, additional lubrication, pressing, welding and bonding, cleaning and phosphating, cathoretic painting, saving potential using prelubes, dry-film lubricants [121, 153, 155, 163, 164].

7.11.2.3 Lubricants for Wire, Tube, and Profile Drawing

Forming classification, friction and lubrication, machine and tools in wire drawing, classification of wire drawing by wire thickness, drawing force and tension, drawing tool and wear, wire cracks, hydrodynamic drawing, wire friction on cone, lubricant feed in wet drawing, dry drawing, applying lubricants as pastes or high-viscosity products, drawing copper wire, lubricants for copper wire drawing, lubricant concentration in copper wire drawing, water quality and electrolyte stability in copper wire drawing, influence of the lubricant on wire enameling, drawing of steel wire, lubricant carrier layers in steel wire drawing, lubricants for steel wire drawing, drawing aluminum wire, drawing machines and lubricants in aluminum wire drawing, wire drawing for stainless steel, nickel and tungsten, profile drawing,

pretreatment and the use of lubricant when profile drawing steel, tube drawing, tube drawing methods, lubricants and surface pretreatment for tube drawing, drawing of steel tube, titanium tube, aluminum tube, and copper tube [122, 155, 156, 158].

7.11.2.4 Hydroforming

Process principle, process configuration, tribological aspects of hydroforming, lubricants for hydroforming [123, 159, 162].

7.11.2.5 Lubricants for Rolling

Rolling speed, surface and material quality, friction and lubrication when rolling, rolling steel sheets, hot rolling of steel sheets, sheet cold rolling, rolling emulsions, circulation systems for emulsions, strip cleanliness and annealing, re-rolling, finest sheet cold rolling, cold rolling of high-alloy steel sheets, aluminum hot rolling, aluminum cold rolling, rolling other materials [124, 160].

7.11.2.6 Solid Metal-Forming Lubricants (Solid-Forming, Forging, and Extrusion)

Extrusion, impression die forging, forming temperatures, friction and lubrication in cold extrusion and cold forging, friction and lubricant testing methods, selection criteria for lubricant and lubrication technology, lubricating oils for cold extrusion of steel, phosphate coatings and soap lubricants for cold extrusion of steel, demands put on zinc phosphate coatings, reactive soap lubricants, solid lubricants for cold extrusion of steel, warm extrusion and forging, lubrication in four different temperature areas, lubrication when hot forging, demands on hot forging lubricants, hot forging of steel, aluminum forging, isothermal and hot die forging, application and selection of lubricants for die forging [115, 157, 161].

7.12

Lubricating Greases

Lubricating greases belong to a very special family of lubricants with regards to their composition, manufacture, and application. A number of important books detailing greases and their uses have been published during the past 30 years, including C. J. Boner [213] (in 1976), J. L. Ischuk [214] (in 1996), A. T. Polishuk [215] (in 1998), and W. J. Bartz [216] (in 2000). In 2007, W. Dresel and R.-P. Heckler produced a comprehensive chapter in *Lubricants and Lubrication*, which included details of compositions with formulas, manufacturing methods, and applications; an updated version of this text the basis of the following subsections.

7.12.1

Definition

With regards to lubricating greases, Dresel has provided the following definition: “Lubricating greases can be defined as solid to semi-fluid products of the dispersion

of a thickening agent in a liquid lubricant” [217, 218]. They usually contain additional compounds to impart special properties, and usually the thickening agent is a metal soap. It is not easy to classify greases as either liquids or solids – the transitions are fluid. On the liquid side, oils containing $\ll 5\%$ w/w thickening agents – in general polymers – already have structural viscosity, but not yet a yield point, and therefore have been named non-fluid oils. On the solid side, suspensions of $>40\%$ (w/w) solid lubricants in oils are usually called *pastes*. When they also contain thickening agents typical of greases, they are also called *grease pastes*. It can, nevertheless, be said that greases in general contain from 65 to 95% (w/w) base oils, from 5 to 35% (w/w) thickeners, and from 0 to 10% (w/w) additives.

Whilst, in 1954, Boner listed thirteen advantages of greases over oils, in 1996 Lansdown [218] referred to only six: (i) greases have no stop–start problems; (ii) greases perform better under squeeze film conditions; (iii) greases solve sealing problems; (iv) greases supply surplus lubricant without special design; (v) greases help to avoid the contamination of clean products; and (vi) greases enable the use of solid additives [219].

Compared to lubricating oils, greases have only two disadvantages: first, they are not the correct choice when heat transfer is a problem; and second, they have a lower speed limit because of their higher effective viscosity.

7.12.2

Classification

In the past, greases have been named – and, indeed, and are still being named – after the industry in which they are used (e.g., steel mill greases), after the type of application (e.g., wheel-bearing greases), after their prevalent application temperature (e.g., low-temperature greases), or after their range of application (e.g., multi-purpose greases). The meaning of the latter term has changed over the years, such that some names say very little regarding the quality of the performance of the greases in question. Although, the consistency of a solid to semi-fluid body is a very complex subject, the penetration of one body into another one can be measured easily, using simple devices. Consequently, even today greases are named according to the consistency classes as defined by the US National Lubricating Grease Institute (NLGI) in 1938, and in accordance with the cone-penetration method developed in 1925 (Table 7.23).

Nowadays, the performance of lubricating greases is described by norms such as ISO 6743-9 or DIN 51 825 which define mainly the consistency, upper and lower operating temperature, water resistance, and load-carrying capacity; and for automotive greases by ASTM D 4950, which has been followed by the consideration of reference greases and the introduction of the NLGI Certification Mark. Yet, to some extent greases are best judged simply by the chemical and physical properties of their base oils and the agents thickening them; naturally, the consistency of greases will be increased with their increasing thickener content, causing subsequent changes in their properties. At the same time, these properties may best reflect the reasonable limits of practical applications.

Table 7.23 Classification of greases by NLGI numbers.

NLGI number	Appearance	ASTM worked penetration (1/10 mm)	Application
000		445–475	Gear greases
00	Semi-fluid	400–430	
0		355–385	Greases for bearings
1	Soft	310–340	
2	Creamy	265–295	
3		220–250	
4		175–205	
5		130–160	Block greases
6	Soap-like	85–115	

7.12.3

Thickeners

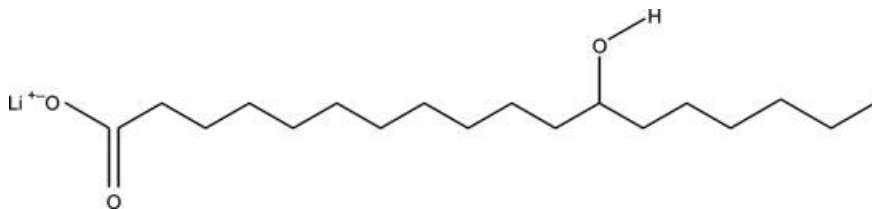
Thickeners not only transform liquid lubricants into consistent lubricants, but rather also change their properties.

7.12.3.1 Soaps

In general, a maximum thickening effect is achieved with carboxylic acids having 18 carbon atoms; these are usually prepared from vegetable-derived 12-hydroxystearic acid or from animal- or vegetable-derived stearic acid, or from their esters, usually their glycerides, and from the hydroxides of elements of the alkali and alkaline earth metals. By causing the base oils of greases to gel, soaps provide greases with most of their unique properties. They are not present only as crystallites and dissolved molecules, but mostly in a separate phase represented by agglomerates termed *fibrils* or *fibers*. All such components are present, and have the properties of grease, even in the smallest lubrication gap. This means that the still popular picture of a thickener as a sponge which releases and soaks up its base oil—which serves as the “real” lubricant—is, at the least, misleading

- **Soap anions:** The carbon chain length of a carboxylic acid affects the solubility and surface properties of a soap. Longer and shorter carbon chains reduce its thickening capacity. Increasing the chain length increases solubility in the base oil, while shortening the chain length reduces solubility. A branched alkyl chain lowers the melting point of a soap, and reduces its thickening effect
- **Soap cations:** The soap cations also are responsible for the essential properties of soap greases. The cations govern the thickener yield, the dropping point (according to DIN ISO 2176), the temperature at which a grease becomes liquid under normal conditions, the water resistance and, to some extent, the load-carrying capacity of a grease. Lithium soaps were the most prominent, at ca. 50%, followed by calcium, sodium, and aluminum soaps. The importance of the latter has steadily decreased during recent decades, however.

- Lithium soaps:** The dropping point of mineral oil-based NLGI 2 grease is usually between 185 °C and 195 °C. For such a multipurpose grease, ca. 6% (w/w) of soap is required with a naphthenic oil, ca. 9% (w/w) with a paraffinic oil, and ca. 12% (w/w) with a PAO. The fiber size in lithium 12-hydroxystearate (5) greases is usually between 0.2×2 and $0.2 \times 20 \mu\text{m}$. Good multipurpose properties, for example, a high dropping point, good water resistance, good shear stability (which has been related to hydrogen-bonding of the hydroxyl groups), and a good response to additives are the reasons why lithium 12-hydroxystearate-based greases have now been the most popular for more than 50 years. They have found a wide range of applications from EP greases based on oils with kinematic viscosities of ca. $200\text{--}1000 \text{ mm}^2 \text{ s}^{-1}$ at 40 °C for heavy loads, through multipurpose greases based on mineral oils with kinematic viscosities from $60\text{--}120 \text{ mm}^2 \text{ s}^{-1}$ at 40 °C for all types of bearings, greases made with diesters or PAO oils and kinematic viscosities of $15\text{--}30 \text{ mm}^2 \text{ s}^{-1}$ for high-speeds, to those with oil-insoluble polyalkyleneglycols for gears.



(5)

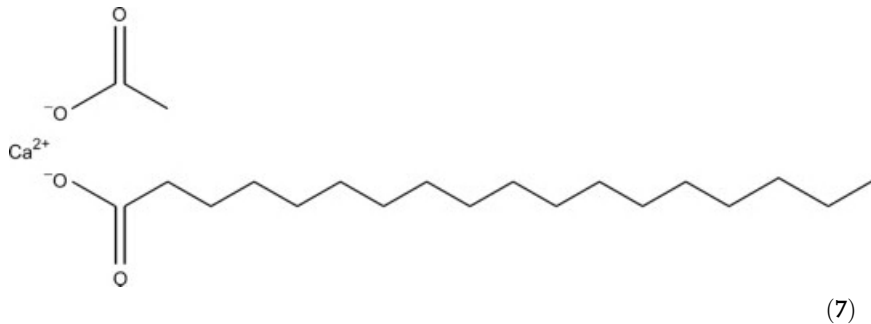
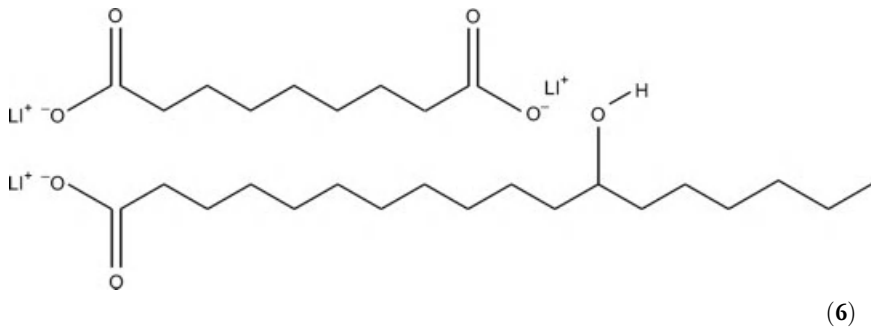
- Calcium soaps:** Calcium soaps prepared from 12-hydroxystearic acid are still referred to as anhydrous calcium soaps. Similar to the corresponding lithium soaps, they indeed contain up to 0.1% (w/w) soap. Calcium soaps mainly based on stearic, palmitic, or oleic acid are still termed hydrated calcium soaps. For these greases, both the cost of raw materials and the performance levels are low.
- Sodium soaps:** Compared to lithium and calcium 12-hydroxystearate greases, the importance of greases based on sodium soaps is nowadays low, although in the form of semi-fluid products they still are of some interest for the lubrication of gears.
- Other soaps:** Aluminum soap-based greases are usually produced with pre-manufactured aluminum soaps, usually aluminum stearate. They have dropping points of up to 120 °C, and their upper temperature limit is 80–90 °C. They have good water resistance and adhesive properties, but have been largely replaced by lithium greases. Mixtures of soap greases are termed “mixed-soap greases,” the properties of which largely depend on the relative proportions of the two or more soaps.

7.12.3.2 Complex Soaps

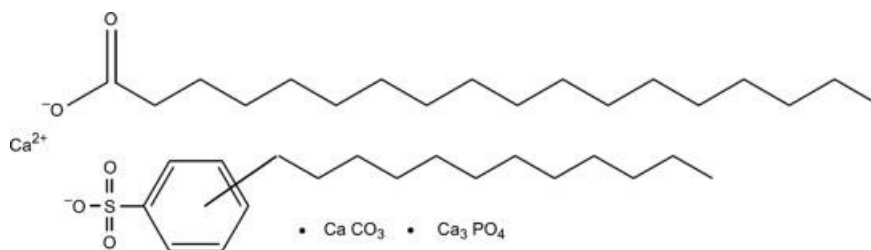
With complementary salts of inorganic acids (e.g., boric and phosphoric acid), with short-chain carboxylic acids (e.g., acetic acid), or with dicarboxylic acids (e.g., azelaic [220] and sebacic [221] acids), or with more complex acids, such as the

dimeric variety – all of which are derived from vegetable oils – simple soaps can form certain types of complex soap.

- **Lithium complex soaps:** Apart from their higher upper-temperature limit (between 160–180 °C), some lithium complex soap-based greases perform similarly to the corresponding simple soap-based products; however, because of the many possible complementary salts, not all of their properties can be generalized. Of the many known formulations, the most widespread is based on 12-hydroxystearic acid and azelaic acid (6). Lithium complex soap systems can consist, for example, of lithium 12-hydroxystearate plus lithium adipate or lithium azelate, lithium dimerate, lithium sebacate, lithium terephthalate, lithium borate, or lithium phosphite.
- **Calcium complex soaps:** All commercial calcium complex greases contain acetic acid as a complementary acid (7). Complex calcium complex greases have good shear stability and water resistance, a low oil separation, and good load carrying capacity. Their upper temperature limit is 160 °C.



- **Calcium sulfonate complex soaps:** Competitive greases based on this complex were first offered in 1985. Initially, they comprised *in situ*-produced overbased calcium sulfonates and the calcium salts of other sulfonates, of 12-hydroxystearic acid, and of boric acid. The complex could be improved by replacing calcium borate by phosphate 8. The greases are extraordinarily corrosion-protective and resistant to shear, and have load-carrying capacities that can be matched only by greases of other soaps that contain large amounts of additives.



(8)

- **Aluminum complex soaps:** Today, only one of the possible aluminum complexes is still widely used. This comprises aluminum stearate and benzoate aluminum complex greases of the type that have good water resistance and good low temperature properties.

7.12.3.3 Other Thickeners

The reaction products of one molecule of MDI (di-4,4'-isocyanatophenylmethane) or other diisocyanates with two molecules of monoamines are termed *diureas*. *Tetraureas* are the reaction products of two molecules of diisocyanate with one molecule of diamine and two molecules of monoamine. The upper temperature limit of oligourease greases is not determined so much by the stability of the thickener, the decomposition of which usually starts slightly below 250 °C, but rather by the stability of the base oil. These greases are, therefore, superior to soap-based greases when the application temperatures exceed 180 °C.

- **Polymerized perfluorinated hydrocarbons:** These thickener, usually micronized polytetrafluoroethylene (PTFE) powders, are the choice for greases that must function at temperatures above 220 °C, albeit with an upper temperature limit of about 270 °C.
- **Clays:** Clays or, to be more precise, bentonite-type aluminosilicates (mainly the smectites montmorillonite and hectorite) are the most important inorganic thickeners. They are usually treated with quaternary ammonium compounds, for example, trimethyl stearyl ammonium chloride, and the activators mentioned above.

7.12.4

Base Oils

Whilst, in principle, all of the lubricating oils described in Sections 7.2 and (7.3) can be used as base oils for greases, in general only those oils with kinematic viscosities ranging from 15 to 1500 $\text{m}^2 \text{s}^{-1}$ at 40 °C are used [234]. In addition to these base oil families, certain specialties should be mentioned: for example, high-molecular-weight esters prepared from diols or polyols and dicarboxylic acids with viscosities $>2000 \text{mm}^2 \text{s}^{-1}$ at 40 °C are used as base oils in greases that must be solvent-resistant. Silicone oils can be regarded as polyethers of alkylated silicic acids and, in contrast to other greases, silicone greases are better distinguished according to the

properties of their base oils. The kinematic viscosities of silicone oils for greases range from ca. 75 to ca. 10 000 mm²s⁻¹ at 40 °C. Partially phenylated dimethylsilicone oils have very good low-temperature properties, and are used with all types of thickener, depending on their (often military) application. Apart from being suitable for temperatures up to 270 °C, perfluorinated ethers thickened with PTFE powders are the only greases that can function in the presence of aggressive chemicals, such as oxygen or chlorine. This is also their major advantage over the corresponding greases that are based on partially fluorinated silicone oils.

7.12.5

Additives

Most of the additives used in liquid lubricants (see Section 7.5) can also be used in greases, and in similar fashion, though in general at substantially higher concentrations. Interactions between the thickeners and additives must therefore always be considered. A typical lithium 12-hydroxystearate-based multipurpose grease contains at least 0.2% (w/w) of an antioxidant or a mixture of antioxidants, between 0.5–1.0% (w/w) of one or several corrosion inhibitors, ca. 0.05% (w/w) of a metal deactivator and, in its EP-version, up to 2.5% (w/w) EP/AW additives, depending on the type chosen. The antioxidant level can reach 3% (w/w) more in high-performance greases, while high-molecular-weight products are preferred as antioxidants. Very few of the additives are only applicable in, and are favorable for, greases [217].

7.12.6

Manufacture of Greases

The properties of greases, and especially of metal soap-based greases, depend not only on their composition but also (and to almost the same extent) on the way in which the thickeners are prepared and dispersed.

7.12.6.1 Metal Soap-Based Greases

It is possible, as one stage of grease manufacture, for a metal soap which has been prepared in an independent first step, or a commercially available soap, to be dissolved or dispersed and then heated and re-cooled under defined conditions in a suitable base oil. A few years ago, this technology became known as “dry technology,” but because of the higher costs of the thickener it was recommended only for highly sophisticated synthetic greases with a precise chemistry, or for functional base fluids that would react with the water or, even worse, with the steam generated during the neutralization process. In general, fatty acids or their glycerides (and/or even their methyl esters) will react with aqueous solutions or suspensions of the described metal hydroxides in part of the base oil, with each batch of grease being produced via the following schedule:

- 1) Dissolution or dispersion of the fatty acids in one-third to two-thirds of the base oil at temperatures up to 90 °C.

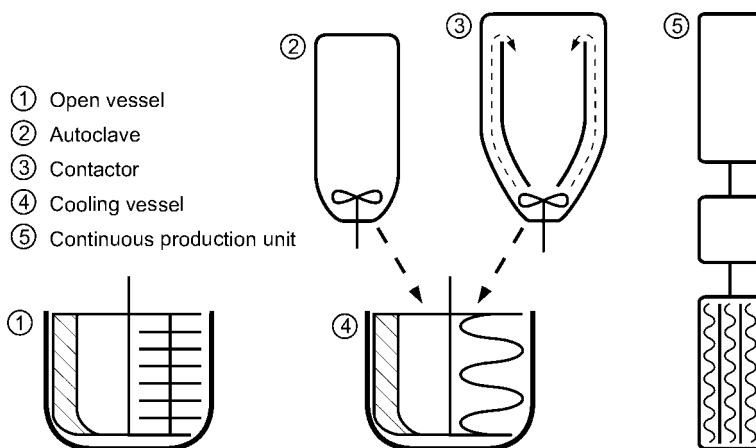


Figure 7.38 Reactors for the manufacture of greases.

- 2) The addition of the metal hydroxides as a solution or suspension in water.
- 3) Heating to temperatures between 115 to 150 °C or, under pressure, at 180–250 °C, depending on the type of reactor.
- 4) Dehydration of the soap by heating at 180–200 °C, or by pressure release.
- 5) Crystallization during cooling to 150–130 °C, combined with the addition of further base oil.
- 6) The addition of additives at temperatures below 80 °C.
- 7) (Pre)filtration and homogenization with one of several possible devices.
- 8) Adjustment of the specified consistency or flow pressure.
- 9) (End)filtration, deaeration, and packing into containers.

For this process, different types of reactor or reactor combinations are used (Figure 7.38). Typically, single reactors are usually open vessels heated by gas, steam, or heating oil, with mixing achieved using single-action, double-action, or counter-rotating stirrers. These are usually designed as planetary stirrers, although turbines or dispenser disks can also be used.

7.12.7

Applications of Greases

The selection of a grease is always a compromise between the demands of a customer and the circumstances that the grease must face during its operational life. When selecting a grease, the following points must be taken into account: temperature, speed, load including centrifugal forces and vibrations, re-lubrication intervals based on a knowledge of the lubrication points, for applications which can be roller bearings, plain bearings, chassis, joints, door locks, switches and seals of different design. It should also be mentioned that the desired characteristics may occasionally contradict each other.

7.12.7.1 Rolling Bearings

The rolling bearing industry, which represents a key area of use for greases, supports many types of manufacturer not only with bearings (which may be either standard or tailor-made products), but also with consulting and services concerning the design of new equipment and the maintenance of that already in existence. The lifetime of rolling bearings is connected with that of the grease used, especially under extreme conditions. In this regard, sophisticated test equipment has been developed over the years, mainly to ensure a better lifetime predictability for the selected bearing, together with the selected grease. The test rigs FAG FE 8 and SKF R2F, and later also FAG FE 9, are widely accepted in Germany (see Chapter 8). Today, cleanly produced and low-noise greases are meeting demands of reliability and also of lifetime requirements for rolling bearings. The stringent requirements of high-precision bearings, for small bearings in video and audio applications, and bearings for military use have been established for years. On the basis that approximately 80% of all bearings are grease-lubricated, engineers have published a series of guidelines to define the life factors of rolling bearings. The German Society for Tribology published such a handbook in 1994 [222], which focuses on the so-called α_{23} -value, which describes the influence of a grease taking into account the bearing size, speed, viscosity, and temperature. Current knowledge of the factors that affect calculating the lifetime of these bearings has been released in the new handbook of the German Society for Tribology, the second edition of which was published in September 2006. Conventional lithium greases in NLGI class 2 are recommended for most types of bearing at working temperatures up to 120 °C, whereas greases of NLGI class 1 are preferred for needle bearings. For bearings exposed to temperatures above 120 °C, complex soap- or polyurea-thickened greases are preferable, while for bearings that must operate under high load and/or low speed, the base oil viscosity must be, at minimum, $200 \text{ mm}^2 \text{ s}^{-1}$ at 40 °C. Greases for use in cold climates, or for aerospace or military use, must ensure an effective performance down to below -70 °C. The low-temperature performance can be checked by using tests of low-temperature torque (ASTM D 1263), low-temperature penetration (AFNOR NF T 60-171), and flow pressure (DIN 51 805). Greases of these type require base oils with a sufficiently low pour point. In many military applications, long-life properties are also required, but these can be fulfilled only by the use of synthetic base oils. Because plain bearings are often exposed to moisture or water, calcium soap-thickened greases are recommended in this case. When open housings are used in a dusty atmosphere, frequent re-lubrication makes it possible to wash out the contaminated grease. The $n \cdot d_m$ -value (the speed multiplied by the average of inner and outer diameters of a bearing), as a means of selecting the correct base oil viscosity for a grease, can be accepted only as a rule of thumb, as its dependence on base oil viscosity has not yet been established, and there is no commonly accepted test method yet available.

7.12.7.2 Cars, Trucks, and Construction Vehicles

Among the approximately 30 hidden greases (Figure 7.39) in a modern car, only the constant-velocity (CV) joint greases are required in substantial quantities. Although improved conventional lithium greases containing molybdenum disulfide are still

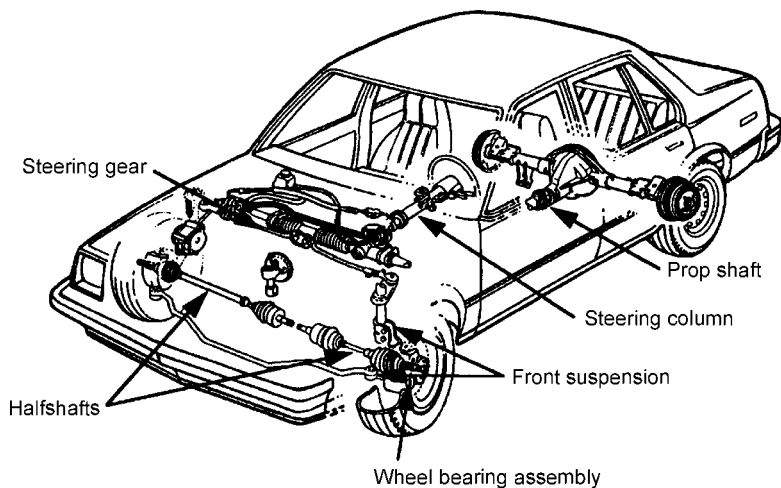


Figure 7.39 The greases that are “hidden” in a modern motor car.

in use, lithium complex or polyurea greases are already preferred in some modern cars, and this usage will increase in the future. Most of the greases used in cars, for example in CV joints, hub units, starters, alternators, seat adjustments, clutches release bearings, belt–pulley bearings, window levers and windshield wiper gears, are specified and approved by the large motor companies, and have been developed in close cooperation with the grease manufacturers. For the same application, however, different motor companies have different grease specifications and approvals; for example, most European and US motor companies prefer lithium complex greases in the front wheel bearings, whereas Japanese manufacturers prefer polyurea greases. ASTM D 4950 describes the minimum requirements of current greases in automotive service–fill applications for passenger cars, trucks, and other vehicles operating under various service conditions. Grease packs fulfilling these minimum requirements may have the NLGI certification marks.

- LA Classification

Chassis components and universal joints under mild duty

- Frequent re-lubrication
- Non-critical application

- LB Classification

Chassis components and universal joints under mild to severe duty

- Prolonged re-lubrication intervals
- High loads
- Severe vibration
- Exposure to water or other contaminants

- CA Classification

Service typical of wheel bearings operating under mild duty

- Frequent re-lubrication
 - Non-critical applications
 - GB Classification
- Service typical of wheel bearings operating under mild duty/moderate duty
- Normal urban, highway and off-highway service
- GC Classification
- Service typical of wheel bearings operating under mild duty/severe duty
- High bearing temperatures
 - Frequent stop-and-go service (buses, taxis, police vehicles)
 - Severe braking service (trailer, towing, heavy towing, mountain driving)

In recent years, lithium-based multipurpose greases have replaced several other greases for the re-lubrication of trucks and construction equipment. Conventional lithium soap based greases that require frequent re-lubrication are still in use for the wheel bearings of trucks and trailers. Modern trucks and trailers with prolonged oil-drain intervals require lithium complex greases with semi-synthetic or fully synthetic base oils. Lithium greases containing black solid lubricants are recommended for chassis points, and for plain bearings of construction equipment. Many trucks and buses, and also much construction equipment, uses centralized lubricating systems, designed for semi-fluid greases of NLGI class 00 or 000, for onboard re-lubrication. Other systems require greases of NLGI class 2. Lithium greases optimized for low-temperature applications, good pumpability, and low oil separation are recommended in this case.

7.12.7.3 Steel Mills

In Europe, calcium complex and sometimes polyurea greases based on mineral oil are used for lubricating continuous-casting equipment, whereas the US market prefers aluminum complex and polyurea greases, and Japanese equipment manufacturers mainly recommend polyurea greases. Currently, calcium sulfonate complex greases are achieving increasing commercial acceptance in Europe and the USA, because of their high EP values and excellent corrosion-protection properties. Some rolling bearing manufacturers equip continuous castings with double- or triple-sealed bearings that are greased for life, preferably with synthetic polyurea greases. When sealing of the bearings is not perfect, then re-lubrication has a cleaning function, whereby the contaminated grease that might result in a limited lifetime could be squeezed out. Conventional EP lithium greases, calcium complex greases, calcium sulfonate complex greases, lithium complex greases, and aluminum complex greases, all of which are based on mineral oils, are used in hot-rolling equipment. Most customers require a minimum base oil viscosity of $200 \text{ mm}^2 \text{ s}^{-1}$ at 40°C , with the rotating shift system being used typically for hot-rolling lubrication. In general, the bearings are not re-greased during operation, but only during maintenance. Many different greases, for example, conventional EP lithium greases, lithium complex greases, calcium complex greases, and calcium sulfonate complex greases—all of which are based on mineral oil—are used in cold-rolling equipment. Modern greases use a lithium-calcium mixed soap for improved water resistance, while the use of

some calcium complex greases has led to a significant prolongation of bearing lifetime in the pickling section of the mill.

7.12.7.4 Mining

Open-pit mines which use hydraulic excavators and dumper trucks and/or wheel bucket excavators and belt systems to ship the spoil and coal are especially large consumers of grease. Lithium, lithium–calcium mixed-soap-based or lithium complex greases with base oil viscosities $>350 \text{ mm}^2 \text{ s}^{-1}$ at 40°C and an effective EP and AW additive package are used in this case. Black solid lubricants are also recommended. Because the equipment is exposed to dust or water and mud, the sealing efficiency of the bearings determines their lifetime, and must be supported by grease. In the case of excavators or drag lines, and in the underground mines, many kilometers of wire rope are used, during the production of which lubricants are applied not only to ensure corrosion protection but also to minimize the friction of the single wires when the rope is stretched under load. The amount of lubricant in the core should be approximately 25% (w/w) of the core. Lay-up lubricants based on wax-resins are applied during manufacture to ensure lubrication of the individual wires and stands. However, following their production, the wires must have corrosion protection, which can be achieved by painting or by applying a bitumen-based lubricant with a solvent.

7.12.7.5 Railroads and Railways

Depending on the design of the driving system of the locomotive, a gear oil or a gear grease is required. The poor sealing properties of these types of gears lead to leakage, but this is usually minimized by the use of bitumen-based products. Modern greases are thickened with lithium or sodium soap, and based on mineral oils of up to $2000 \text{ mm}^2 \text{ s}^{-1}$ at 40°C . Traction motor gear greases are not described in terms of consistency; rather, the apparent viscosity is usually checked with a Brookfield viscometer, for example with a number 3 spindle at 93°C and at 4 rpm and giving results of 5000 to 10 000 cP. The axle bearings are greased with conventional lithium EP greases. The development of ready-to-build-in axle boxes, coupled to the increasing speed of modern trains, have led to improvements in the high-temperature performance and lifetime of greases. Switch lubrication, wheel flange lubrication (mainly used in Europe), and rail track-side lubrication in curves, as used mainly in the USA and Canada, cause environmental problems. Biodegradable greases based on esters have better wear-protection and consumption performance [223, 224], but must be sprayable because of the means of application.

7.12.7.6 Gears

For gears, fibrous sodium soap greases of NLGI-class 0, 00, or even 000, consistency are used. Although the load-carrying capacity, AW properties and adhesion of these greases is especially good, lithium-based greases and greases based on synthetic hydrocarbons or polyglycols are currently gaining in importance. The greases used in the gears of do-it-yourself tools are rather sophisticated, as in modern drilling machines the greases must fulfill several tasks, namely to lubricate the gears,

bearings and the piston responsible for the hammer-drilling operation. Power tools for professional use have even more stringent requirements with regards to low-temperature torque, high-temperature performance, and lifetime. The so-called “girth” open gear drives which are widely used for many large systems in the primary industries [225] require an adhesive grease which is based on high-viscosity oils and usually sprayed onto the gear teeth by means of a centralized lubricating system. In this case, a precise adjustment is required, because the girth gear drives invariably occupy key positions in manufacturing processes. Consequently, most manufacturers of adhesive greases have developed a maintenance scheme with a tribological emphasis, and offer this as a service to their clients.

7.12.7.7 Other Applications

Greases for lubricating the machines used in food processing must fulfill specific requirements relating to food legislation, human health protection, taste, and odor. These properties must be approved by internationally accepted tests and organizations [226]. In the USA, the FDA lists those ingredients permitted for use in food-grade grease formulations (21 CFR 178.3570). Because greases applied in textile machines might contaminate the textiles produced, they are formulated with white oils and thickened with water-soluble sodium soaps, and thus are removable by washing.

7.12.7.8 Application Techniques

Greases are applied by hand and brush, with gloves, grease dispensers, grease guns, and pumps from all types of container (e.g., tins, pails, drums, or even bulk). The pumps can be driven manually, by the use of a power supply, or by compressed air. Most pump systems use a follower plate which is fitted into the container and follows the grease level. The rubber lip must follow the inner surface of the grease container, so as to avoid any air being sucked in. Trucks, buses, construction and forestry equipment, continuous casting and cold-rolling equipment, paper mills, printing machines, presses, excavators for open-pit mines, and many more machines that are used industrially have centralized lubricating systems. These systems can be designed for greases in NLGI-class 2 as a parallel type for single- or dual-line systems, normally using valves or manifolds, or as series type which usually employs progressive piston-type metering manifolds. For NLGI-classes 00 and 000, single-line systems with valves that are of a similar design to oil-centralized lubrication systems are used.

7.13

Solid Lubrication

Detailed information regarding solid lubricant substances and their application, for example in dry-film lubricants, has been provided by C. Busch [227], and much of the following information is related to Busch’s basic results. The application of solid lubricants in metal-forming processes has been described by T. Mang [228] and

T. Mang and W. Buss [229]. Details of surface engineering with hard antiwear layers, including physical vapor deposition (PVD) and chemical vapor deposition (CVD), are presented in Chapter 6.

7.13.1

Classification of Solid Lubricants

A solid lubricant is often defined as any solid material which reduces friction and/or wear of contacting surfaces in relative motion. A vast range of materials and coatings could be judged to behave as solid lubricants on the basis of this definition. Whilst various systems have been used to classify the different types of solid lubricants, an arbitrary—but useful—approach is to classify them as structural lubricants, mechanical lubricants, soaps, and chemically active lubricants (including chemically active additives; see Section 7.5). The main purpose of all these substances is to build up a continuous adherent hard or soft film on the rubbing surfaces. Such films can be applied by a variety of mechanical, chemical, electrochemical or physical processes that include dipping, lapping, painting, immersion, electrolysis, electrophoresis, spraying, plating, welding, baking, cupping, sintering, or ionic plating in vacuum.

7.13.1.1 Structural Lubricants

Currently, the most widely used solid lubricants are graphite and molybdenum disulfide, the highly satisfactory lubricating properties of which are assumed to result from their layered lattice structures. In addition to these two substances can be included other solids such as metal halides and sulfides that have, in the main, inherent lubricant properties, a lamellar hexagonal crystal structure, and which are usually anisotropic. Structural lubricants other than graphite and molybdenum disulfide which are not yet used extensively in industry, include graphite fluoride, molybdenum diselenide, tungsten disulfide, tungsten diselenide, niobium disulfide, tantalum disulfide, titan disulfide, barium hydroxide, cobalt chloride, boron nitride, and borax.

7.13.1.2 Mechanical Lubricants

There are different types of substances within this class, the lubricating effect of which is based on different physical and mechanical properties or special conditions. A common classification divides these lubricants into self-lubricating substances, substances that require a supporting medium to create lubricating properties, and those with indirect lubricating properties based on their hardness.

Self-Lubricating Substances These can be classified as organic compounds, metal films, chemical surface layers, and glasses. Organic compounds can be linear polymers [thermoplastic types such as polytetrafluoroethylene (PTFE), fluoroethylenepropylene (FEP), perfluoroalkoxy (PFA), polyethylene (PE), polypropylene (PP), polyurethane (PU), polyamide, polyacetals, polyterephthalate, polysiloxanes, Nylon], or crosslinked polymers (thermosetting types such as phenol–formaldehyde, epoxy resin, unsaturated polyester resin, and polyimides). The sliding characteristics of

polymers depend on their chemical nature and the mating partner. The permissible load is a function of the heat dissipation. Whilst temperature changes have very little influence on the friction characteristics of polymers, the addition of MoS₂, graphite, and metal powder improves the frictional characteristics of the polymers and increases their hardness. Graphite also increases the elasticity module of PTFE.

- **Self-lubricating metal films:** Friction can be reduced by coating the body material surfaces with a thin film of a soft metal, because the friction depends on the shear strength of the soft metal film. The durability depends on the film hardness, homogeneity, and adhesion. The lubricating effect of soft metal layers is limited by their melting point (e.g., lead, tin, copper or copper alloys).
- **Chemical surface layers (conversion films):** In addition to the naturally occurring oxide films present on the surface of most base materials exposed to air, other solid lubricant films can be formed by chemical or electrochemical action on the metal surface. Chemical surface coatings such as zinc, iron, or manganese phosphates behave similarly to soft metal coatings, but consist not of a metal but rather of metal salts. *Bonderization* (phosphate treatment) creates a thin, microcrystalline, strongly adhering phosphate layer on the metal surface; this reduces the coefficient of friction and the danger of seizure during the running-in period. The lubricating efficiency of the layer, which is normally 2–5 μm thick, is based on its lower shear strength in comparison with the metal.
- **Glasses:** The structure of glasses consists of random three-dimensional (3-D) networks in which the formation of chains or sheets is possible. The constituents of glass are divided into network formers (SiO₂, B₂O₃, Al₂O₃, Na₂O, etc.) and network modifiers (K₂O, MgO, CaO, PbO, etc.). The strongest bonds in these glasses are the Si–O bonds, with an average bond distance of 1.62 Å. There is no absolute Si–O bond distance in a glass because of the absence of symmetry, which means that glass softens and has no fixed melting point. The lubrication properties of glass depend on the composition. The coefficient of friction at a given temperature is a function of the viscosity, the thermal conductivity, the rate of shear, the area of shear, the capacity to dissolve different amounts of oxide from the surface of the material to be lubricated, and the contact angle between the glass and the material, because this determines the capacity of the glass to wet the material. The importance of glasses used as lubricants is specially to be seen in metal-forming operations with operating temperatures up to approximately 1500 °C.

Substances That Need a Supporting Medium These can be classified as inorganic compounds and metal powders. Inorganic compounds are metal fluorides, metal phosphates, metal hydroxides Ca(OH)₂, Mg(OH)₂, Zn(OH)₂, metal oxides PbO, ZnO, FeO, and Fe₂O₃. Natural oxide films on metals, which are usually approximately 100 Å thick, have been investigated by Whitehead with regards to their influence on the coefficient of friction. Their action was found to depend primarily on the relative mechanical properties of metal and oxide. It is generally accepted that the oxide film reduces surface damage, makes sliding smooth, and often reduces

friction. Sulfides, fluorides, phosphates, and hydroxides are each claimed to act as a supporting agent or a catalyst by producing friction- and wear-reducing layers. Calcium hydroxide, for example, supports the production of a layer of Fe_3O_4 on the rubbing surface of steel. This oxide has better tribological properties than the more common $\alpha\text{-Fe}_2\text{O}_3$, possibly because of its more favorable close-packed cubic lattice structure compared to the corundum-like lattice structure of Fe_3O_4 . The process of formation of these layers depends on the chemical composition of steel and, in particular, on its surface chemistry. Phosphate layers can also be applied by galvanic techniques. Such procedures are mainly used to create phosphate layers as precoatings for dry-film application, and as lubricant carriers in cold metal-forming processes. In addition to acting as a lubricant carrier, the phosphate coating can be plastically deformed with the steel slug and, therefore, in conjunction with the lubricant, prevents metal-to-metal contact so as to reduce surface friction and wear. The three main types of phosphating solutions contain zinc, iron, and manganese phosphates, of which zinc phosphate is probably the most widely used. In contrast to structural lubricants and self-lubricating mechanical lubricants, the lubricating properties of the other mechanical lubricants are mainly based on the supporting effect of a carrier substance or a binder. The main purpose of these substances, which include Pb, Sn, Zn, Cu, Ag, and In, is to improve the adhesion and cohesion properties of the non-self-lubricating mechanical lubricants.

Other Coatings Coatings applied by PVD, CVD and other processes are described in Chapter 8.

- **Soaps:** Soaps are the metal salts of the higher saturated and unsaturated fatty acids and of resin acids, and they are sometimes understood to include salts of naphthenic acids and synthetic fatty acids. The most effective of these are polar compounds with active groups in a long-chain molecule, presumably because the reactive group attaches itself to the surface being lubricated and resists removal. They often give the lowest coefficients of friction obtainable with solid lubricants, but in general cannot be used above their melting points, or at high loads. The main function of soaps in lubrication technology is in the preparation of greases (this subject is discussed in more detail in Section 7.12). The main use of soaps as lubricants in their own right depends on their formation *in situ* on a metal surface, by the chemical attack of a fatty acid on the metal.

7.13.2

Products Containing Solid Lubricants

7.13.2.1 Powders

In order to ensure that solid lubricants in the form of powder provide sufficient coverage in a tribological system, these lubricants must have the appropriate properties to enable them to create a film (cohesive properties) and also to adhere (adhesive properties). Three requirements result from this:

- The level of adhesion between the lubricant film and the surface of the material must be great enough to ensure that this lubricant film adheres to this surface when it is subjected to friction.
- The internal cohesion of the film must be sufficiently large that the film does not split when subjected to friction.
- The adhesion between the particles and layers in the shearing direction should be as small as possible to keep the resistance to friction low.

These main requirements can be met only by self-lubricating dry lubricants. MoS₂, because of its crystalline structure (layer grid) and bonding type (covalent bonding of a metal (Mo) and strong polarizing effect of a non-metal (S) with a high degree of polarization), meets these requirements as well as can be achieved; it is, as a result, the most commonly used. Other solid lubricants which are applied in powder form are organic compounds such as PTFE and graphite, although these fulfill the requirements listed above to a limited extent only. Before the solid lubricant powder can be applied, the surface of the material must be thoroughly cleaned. Roughing the surface mechanically or with phosphates improves adhesion, and therefore also the lifetime. The lubricant can be effectively applied by simple rubbing with cloths, sponges, brushes, or polishing pads or polishing buffs, by applying it using suitable carriers, and coating by cathode evaporation in an ultra-high vacuum.

7.13.2.2 Solid Lubricants in Carrying Media

As mentioned above, very few solid lubricants have the appropriate adhesive and cohesive properties which enable them to create an effective lubricating layer with low friction coefficients while providing a sufficient lifetime. Most substances used as solid lubricants require a carrying medium, a bonding agent, and/or pre-treatment of the material surface, to help create—or improve—their adhesive and film-creating properties. The substances commonly used as bonding agents include: organic binding agents, such as resins; inorganic binding agents, such as silicates; and oils, greases, and water. It is also advantageous to pretreat the surfaces by degreasing, sandblasting, corroding, etching, phosphating, anodizing, and also by activation, for example with a low-pressure plasma.

7.13.2.3 Dispersions and Suspensions

Dispersions and suspensions in carrying liquids with low volatility are mainly used in areas where, for tribological reasons, a dry lubricating film should be created, but where the effective application of a powder is not possible for technical reasons. The same types of solid lubricant are used here in the same way as for powders.

Dispersions and suspensions of solid lubricants in water are usually used to coat mass elements for cold and hot forming. The most commonly used substances here are salts, special white solid lubricants, and graphite. Dispersions and suspensions in oils also act as aids in forming techniques, and they are also used as additions in gear- and oil-lubricating systems. The solid lubricants used here in forming techniques are the same types as those used as dispersions and suspensions in water.

MoS₂ plays a dominant role as an additive to lubricating gears and for general use in oil lubricating systems.

7.13.2.4 Greases and Grease Pastes

The addition of solid lubricants to greases is primarily intended to have a positive effect on their capacity to absorb pressure, and their ability to withstand wear and tear, and friction. The specific advantages of solid lubricants in comparison with oil-soluble, chemically reactive additives is that they react neutrally to many types of plastic and elastomer, they perform well at high temperatures, and they have good safety reserves with regards to emergency running properties, which come into action when the layer of grease collapses. The use of black solid lubricants such as graphite and MoS₂ also has a beneficial effect on running-in processes, and the capacity to withstand wear and tear in boundary and mixed-friction areas. Where oscillating movements or vibration is involved, white solid lubricants have the advantage. The exceptional aging stability shown by solid lubricants is particularly important in terms of the lubricant's lifetime, and can be used to advantage in the appropriate systems and structures. Generally speaking, solid lubricants in greases are used at concentrations of 1–3%; when this proportion rises to over 10%, they are known as “grease pastes,” because the solid lubricant at this concentration has a noticeable thickening effect. High-performance lubricating greases do not usually contain a single lubricating element, but instead are made up of combinations of two or more substances, which have a synergistic effect. This applies both to the combination of graphite and MoS₂ and to mixtures of different inorganic solid lubricating substances, for example calcium hydroxide, zinc phosphate, or iron sulfide.

7.13.2.5 Pastes

Pastes are solid lubricants suspended in a carrying oil, and in order to achieve the correct paste consistency, the proportion of the solid lubricant must be at least 40%. To reduce any undesirable “bleeding” effects (i.e., separation from the soap), modern formulations often include a small amount of soap, although tribologically this plays only a minor role. Black pastes usually contain graphite or MoS₂, and/or combinations of both these types of solid lubricant. Because of their high load-bearing capacity, black pastes are particularly useful when movement with very slow relative speeds is involved; examples include assembly processes and running-in processes. Pastes prepared from combinations of white solid lubricants are especially suitable for use where oscillating movements or vibration is involved. White pastes are particularly good at preventing the wear and tear that results from vibration, and have been proven to afford excellent protection against fretting corrosion. These special white solid lubricants create thin adhesive layers on the surfaces which are subject to friction. The layers principally adhere to the surfaces because of tribochemical (e.g., zinc diphosphate) and/or physical adhesive forces (e.g., calcium hydroxide). Another special feature of these layers is that they regenerate themselves; this, combined with the layers' innate high degree of resistance to wear and tear, means that longer operating periods can be achieved than when normal greases are used, without any

need for additional re-lubrication. Another area where pastes are traditionally used is for the lubrication of screw connections. Often, special screws made from steels that are resistant to high temperatures and based on chrome/nickel alloys, are prone to seizure because an oxide layer is not created. The pastes used in this particular application area usually contain combinations of solid lubricants and special metal powders. More recent developments have shown that the use of formulations which do not contain metal, but rather are based on white solid lubricants, perform well when used at high temperatures.

7.13.2.6 Dry-Film Lubricants

Lubricating varnishes or dry-film lubricants are suspensions of solid lubricants and other additives in a solution of inorganic or organic binding agents. The most commonly used solid lubricants are MoS₂, graphite, and PTFE. Each of these solid lubricants has characteristic properties, which determine where it can be used. The most important of the additives are pigments which protect against corrosion. The main types of binding agent used are organic resins (acrylic, phenolic, epoxy, silicone, urethane, imide), cellulose, and inorganic silicates and phosphates. Hydrocarbons or water are used as solvents. Dry-film lubricants can be used in a variety of ways, depending primarily on the number, shape, and/or particular requirements with regard to partial coating. They are applied by using dipping centrifuges and drums, and by various types of spraying procedure. The hardening process depends on the type of binding system, and occurs at ambient temperature or in an enameling stove. When they have hardened, the lubricating varnishes form a highly adhesive, dry film of lubricant, with the proportion of solid lubricant in the layer created in this way being as high as 70%. Solid lubricants with a layer structure (MoS₂) have a floating effect in the wet film, whereby the die layers arrange themselves horizontally as the film dries and settle on top of each other in individual layers. In this way, a separating layer is created between the base unit and the opposing unit of the tribological system which, in an ideal situation, is between 10 and 15 μm thick. When placed under pressure, the texture of the layer becomes compressed, such that an extremely smooth, shiny film surface is created (Figure 7.40). PTFE lubricating varnishes are usually applied in much thinner layers, typically 3–5 μm thick, although special PTFE coatings that provide lifetime lubrication may be applied in layers of up to 15–30 μm thickness. The effectiveness of the lubrication, the lifetime, and the reduction in wear and tear of dry-film lubricants is not constant, but rather is influenced by a variety of different factors, including: (i) their composition, and in particular the type of binding agent, the ratio of solid lubricants to the binding agent, the types of solid lubricants, and the film thickness; (ii) the properties of the substrate to which the lubricating varnish is applied, in particular the cleanliness, roughness, and hardness of the surface; and (iii) the surface and the way in which the crystallites are arranged will have a considerable impact on their lifetime. Various pretreatment procedures can be used to achieve the best possible surface, with sandblasting, phosphating, anodizing, etching, or corroding being the most suitable for metallic substrates. Plastic and elastomer surfaces can be pretreated by chemical and mechanical processes, and by

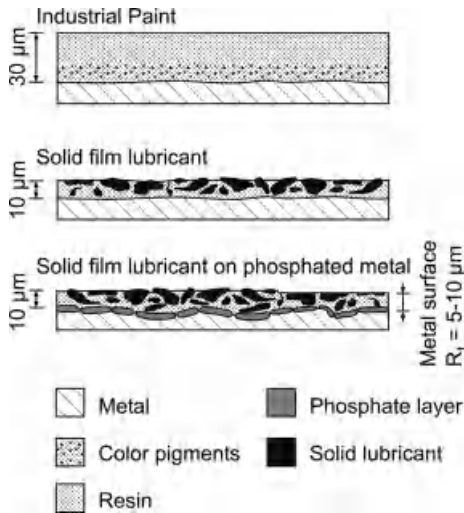


Figure 7.40 The composition of solid-film lubricants.

energetic activation procedures. Dry-film lubricants can be used in a multiplicity of ways [230–232].

7.13.3

Industrial Uses of Products Containing Solid Lubricants

Significant fields of application include the lubrication of machine elements and use in process auxiliaries for various production technologies, such as the production of glass or metal-working.

The main field of activities of the “classic” solid lubricants, such as graphite, MoS_2 , waxes, soaps, salts, or even soft metals, lies more in the area of non-chip-forming and, especially cold- and hot-forging, pressure die-casting and drawing, and cold-extrusion operations. In the 1990s, internal high-pressure forming was added as a new area of application for solid lubricants. Applications in metal-forming processes have been described by T. Mang [228] and by T. Mang and W. Buss [229]. Solid lubricants are available generally as a powder, as a pigment embedded in a resin or wax film, or as a dispersion in oil or water. The variety of industrial uses of solid lubricants can be made clearer by studying the lubrication of different machine elements.

7.13.3.1 Screw Lubrication

Special high-temperature pastes are used for the lubrication of screw connections at high working temperatures. These pastes comprise a basic oil which is mixed with different solid lubricants, and may contain additional additives. Both, in formulation and in selection, care must be taken to ensure that the components do not contain sulfur, zinc, lead, or aluminum, as this may lead to damaging changes in the screw material, an example being stress crack corrosion at high temperatures. The

components should also be free from nickel, which is hazardous to health. Screws for high-temperature applications are created from high heat-resistant, generally austenitic, materials with alloy components such as nickel, chromium, or molybdenum, as this enables only very thin oxide layers to develop on the surface of the thread flanks.

Apart from other properties, which must also be fulfilled by some lubricants at lower application temperatures, there are special formulations for avoiding tribo-corrosion and fit rust (Passungsrost). Particularly effective here are greases and pastes, if combined with white solid lubricants prepared from metal hydroxides, phosphates, and sulfides. For many screw lubricating applications, special dry-film lubricants are also available as an alternative to greases and pastes. The advantage of a lubricating varnish is its simple application in an immersion centrifuge or spray drum, both of which are time-tested procedures for the coating of mass-produced parts. Notably, the handling of coated screws is clean and suitable for robotic systems. Special areas of application for lubricating varnishes and slide films include metric screws, thread-cutting screws, thread-shaping screws, thread-grooving screws, all types of wood screws, screws made from plastic, and screws made from aluminum alloys, magnesium alloys, and titanium alloys, for example [233].

7.13.3.2 Roller-Bearing Lubrication, and Slide Guideways

Greases or pastes containing solid lubricants must always be used when reliable separation of the roller body and bearing ring at low speeds and high loads cannot be ensured by grease alone. Over and above this, greases or pastes containing solid lubricants have good emergency running properties, and also afford high safety under shock and impact stress. Greases or pastes with white solid lubricants are preferable for use in roller bearings employed in oscillating operations, whereas lubricating varnishes are the best solution for applications in a vacuum, for example, in air and space travel, nuclear engineering, extreme temperatures, or for micro-setting movements. Special constructions also enable solid lubricants to be incorporated in the bearing material; this enables the production of maintenance-free bearings.

Slide guideways and other slide surfaces (e.g., infeed wedges) are mainly in the boundary or mixed lubrication regime. The best solution for these operational requirements is lubrication with PTFE belts and slide liners based on epoxy resin, with the incorporation of solid lubricants such as MoS₂, graphite, or polyurethane. Pastes or lubricating varnishes containing solid lubricants are likewise suitable and offer themselves for the running-in phase and the warm-up and cool-down phases in normal operation. In this way, the boundary and mixed-friction zone can be safely worked through without wear occurring, even with pure oil lubrication, and emergency running properties can be achieved.

7.13.3.3 Chain Lubrication

The development of a hydrodynamic lubricating film is not possible because of the high surface pressure and low sliding speed between the different elements of a chain link. With the given mixed friction, it is only possible to limit wear and achieve an

acceptable service life for the machine elements by using solid lubricants. When selecting a suitable lubricant, special consideration must be given not only to the different chain-drive construction types, but also to the material pairs, the operating parameters, and the ambient conditions. For solid, highly viscous lubrication, care must be taken to ensure adequate creep or penetration into the narrow gaps, for example, between the bolt and bush. The lubricant must also have an appropriate adhesion capacity so that it is not spun off at high chain speeds or high centrifugal forces at the turning point (pinion and wheel).

7.13.3.4 Plastic and Elastomer Lubrication

In plastic and elastomer lubrication, the material compatibility plays a particularly important role. Swelling, shrinking, or embrittlement are the most serious changes which elastomers can experience when they come into contact with lubricants. Solid lubricants have limited influences on elasticity module, tensile strength, and hardness. In addition to reducing friction and protecting against wear during the assembly process, the separating effect of the lubricant is also important. Examples in elastomer lubrication are O-rings and seals in automotive applications. Most requirement profiles can be covered adequately by lubricating varnishes and films containing solid lubricants.

In plastic lubrication, the special features of substances—that is, the interaction between the plastic and lubricant—must also be taken into consideration. Particular attention must be paid to the tendency to develop stress cracking. Because of the multitude of different types of plastic available, direct compatibility tests are recommended on the plastics to be employed. As with elastomer lubrication, the influence of solid lubricants in compatibility testing is of limited significance. Oils, greases and pastes containing solid lubricants, and also lubricating varnishes and slide films, can be used successfully for lubricating plastic and steel, and plastic–plastic pairs. The running-in process must also be given enough attention in the use of plastic materials and, as a general rule, can be positively influenced by solid lubricants.

7.14

Laboratory Methods for Testing Lubricants

Testing lubricants in laboratories and test fields is an indispensable part of the research and development of lubricants. In most industrial applications, moreover, it is necessary to monitor the actual condition of a lubricant in use, with the objective of sustaining the proper functionality of machines and lubricating systems and prolonging the lifetime of the lubricant. Lubricants must be monitored carefully and, often, be maintained by treatment with appropriate chemical substances.

The properties of lubricants are usually determined by use of standardized laboratory test methods. Some important users, notably car manufacturers or steel mills, employ specific methods that are considered here.

Table 7.24 Common laboratory test methods for lubricants according to international standards [266].

	AFNOR	ASTM	DIN	IP	ISO	Test method
Aging/oxidation stability			51352 T1	48		Determination of oxidation characteristics of lubricating oil
			51554	280		Determination of oxidation characteristics of lubricating oil acc. to Baader
Air release	T60-150	D 943	51587		4263	Determination of oxidation stability of inhibited mineral turbine oils
		D 2893	51586			Determination of oxidation characteristics of extreme-pressure lubricating oils
		D 4742				Oxidation stability of gasoline engine oils by thin-film oxygen uptake (TFOUT)
		D 2272		229		Determination of the relative oxidation stability by rotating bomb of mineral turbine oil
		D942	51808	142		Determination of oxidation stability of lubricating grease-oxygen bomb method
		D 3427	51381	313	DIS 9120	Determination of air-release value of hydraulic, turbine and lubricating oils
		D 611	51775	2	2977	Determination of aniline and mixed aniline point
		D 482	EN 7	4	6245	Determination of ash
		D 874	51575	163	3987	Determination of sulfated ash of lubricating oils and additives
		D 128	51803			Determination of ash of lubricating greases
Atomic spectroscopy		D 4628			Emission spectroscopy	

(Continued)

Table 7.24 (Continued)

	AFNOR	ASTM	DIN	IP	ISO	Test method
Boiling range/ distillation		D 2887	51581 T2			Boiling range distribution of petroleum fractions by gas chromatography Determination of evaporation loss—gas chromatographic method
Carbon distribution	M07-002	D 86 D 2140 D 3238	51751 51378	123	3405	Determination of distillation characteristics Determination of carbon-type composition Calculation of carbon distribution and structural group analysis of petroleum oils by the n-d-M method
Carbon residue	T60-117	D 524		14	4262	Ramsbottom carbon residue of petroleum products
Cloud point	T60-116	D 189	51551/T1	13	6615	Carbon residue of petroleum products—Conradson method
Corrosion tests	T60-105	D 2500		219	3015	Determination of cloud point
	M07-015	D 130	51759 T1	154	2160	Copper corrosion of liquid mineral oil hydrocarbon
	T60-151	D 665	51585	135	7120	Rust-prevention characteristics of steam turbine oils and hydraulic oils
		D 1748	51359	366		Rust-prevention characteristics of corrosion preventing oils in humidity cabinet
		B 117	50 021			Corrosion tests: spray tests with different sodium chloride solutions
			50 017			Climates and their application; condensed water-containing climates
	T60-135		51802	220	CD 6294	Rust-prevention characteristics of lubricating greases—SKF-Encor method
		D 130	51811	154	2160	Copper corrosion or lubricating greases
		D 4627	51360/T2	287		Rust-prevention characteristics of water mix metal working fluids—Chip/filter
			51360/1	125		Rust-prevention characteristics of water mix metal working fluids—Herbert corrosion test

Demulsibility	T60-125	D 1401	ISO 6614	6614	Demulsibility characteristics of lubricating oils
Demulsibility	T60-101	D-2711	51757	3675	Determination of density, and API gravity of crude oils and petroleum products—hydrometer method
Density	T60-121	D 1298	133	6244	Determination of drop melting point of wax and petrolatum
Dropping point/ melting point	T60-102	D 127	132	2176	Determination of dropping point of lubricating greases
Elastomer		D 566			Compatibility of lubricating grease with elastomers
		D 4289			Testing of rubber and elastomers
			53 521	37	Determination of tensile strength at break, tensile stress at yield, elongation at break and stress values
			53 504		Shore A and Shore D hardness test
Evaporation	T60-161	D 5800	53 505		Determination of evaporation loss of lubricating oil – Noack method
			51581 T1		
Filterability	NF E 48-690			13357-2	Measurement of the filterability of mineral oils
Flash point	T60-118	D 92	ISO 2592	2592	Determination of open flash and fire point—Cleveland method
	M07-036				Determination of closed flash point – Abel Pensky method
	EN57		51755		
	M07-019	D 93	51758	2719	Determination of closed flash point – Pensky–Martens method
Flow pressure			51805		Determination of flow pressure of lubricating greases – Kesternich method
Foam	T60-129	D 892	146	6247	Determination of foaming characteristics of lubricating oils
Infrared spectrometry	T60-185		51451		Aqueous machining fluid foaming tendency Analysis by infrared spectrometry

(Continued)

Table 7.24 (Continued)

	AFNOR	ASTM	DIN	IP	ISO	Test method	
Hydrolytic stability		D 2619				Hydrolytic stability of hydraulic fluids (beverage bottle method)	
Neutralization number	T60-112	D 974	51558/T1	139		Neutralization number – Color-indicator titration method	
Oil separation	T60-133	D 128	51809/T1	37		Determination of acidity and alkalinity of lubricating grease	
	T60-191		51817	121		Determination of separation from lubricating grease – pressure filtration method	
Penetration		D 1742				Oil separation from greases during storage	
	T60-132	D 217		50	2137	Determination of cone penetration of lubricating grease	
	T60-119	D 937	51580	179	3986	Determination of cone penetration of petrolatum	
	T60-123	D 1321	51579	376	3992	Determination of needle penetration of petroleum wax	
pH value					51369	Determination of pH value of water-mixed-metal working fluids	
Polyaromatic hydrocarbons						346	Determination of polycyclic aromatics – dimethyl sulfoxide extraction method
Pour point	T60-105	D 97		15	3016	Determination of pour point	
Roll stability		D 1831				Roll stability of greases/Shell roller	
Saponification number	T60-110	D 94	51559/1	136	6293	Method of saponification number – titration method	
Shear stability		D 3945	51382	294		Determination of shear stability of polymer-containing oils – diesel injector rig method	
Sulfur	M-07-052	D 3120	51400 T7	373		Determination of sulfur content–microcoulometry (oxidative) method	
Total acid number/ Total base number		D 2896		276	3771	Determination of base number perchloric acid–potentiometric titration method	

	D 664		177		Determination of neutralization number–potentiometric titration method
Viscosity	T60-112	D 974	139	51558	Neutralization number–color-indicator titration method
	T60-100	D 446	71	51366	Cannon-Fenske viscosimeter method
	T60-100	D 445	71	51562	Kinematic viscosity of transparent and opaque liquid–s-Ubbelohde viscosimeter method
	T60-152	D 2983	267	51398	Determination of low-temperature viscosity of automotive fluids – Brookfield viscosimeter method
		D 2602	383	51377	Determination of apparent viscosity of engine oils between –30 °C and –5 °C – cold-cranking simulator method
	D 4741	370		Determination of dynamic viscosity–high-shear Ravenfield viscosimeter method	
	D 2270	T60-136	226	ISO 2909	Calculating viscosity index from the kinematic viscosity at 40 and 100 °C
	D 4684				Determination of yield stress and apparent viscosity of engine oils at low temperature
	D 3829				Predicting the borderline pumping temperature of engine oil
	D 1092			53 015	Falling ball viscosimeter according to Höppler
				51810	Measuring apparent viscosity of lubricating greases
					Apparent viscosity of lubricating greases by rotary viscosimeter
Water	D 6304	T60-154	438	51777/T1/T2	Determination of water content of petroleum products by use of the Karl Fischer reagent
	D 95	T60-113	74		Determination of water content of petroleum products–distillation method
Water resistance	D 1264		215		Water resistance of greases under dynamic conditions/water washout test
				51807/1	Behavior of lubricating greases in the presence of water

(Continued)

Table 7.24 (Continued)

	AFNOR	ASTM	DIN	IP	ISO	Test method
Wear		D 1947	51354/1	334/166		FZG gear test rig/load-carrying capacity
		D 2266	51350/1			Shell four-ball test for greases/mean wear scar diameters determination
		D 2596	51350/4	239		Shell four-ball test for greases EP properties
		D 4172				Shell four-ball test for oils/wear test
		D 2783	51350/1	239		Shell four-ball test for oils/weld test
		D 2509		326		Timken test for lubricating greases
		D 2782	51434/T3	240		Timken test for lubricating fluids

This table is not named table in: Lubricants, pp. 729–735.

The most common laboratory test methods according to international standards are provided by Roman Müller [266] (see Table 7.24), which relates to:

- **AFNOR:** Association Francaise de Normation (French Association for Normalization)
- **ASTM:** American Society of Testing Materials (USA)
- **DIN:** Deutsches Institut für Normung (German Institute for Normalization)
- **IP:** Institute of Petroleum (UK)
- **ISO:** International Standard Organization

7.15

Lubricants in the Environment

A large proportion of the lubricants pollute the environment, either during or after use. This may be technically desired (i.e., total-loss lubrication) or occur as a result of mishaps such as leaks, emissions, spillages, or other problems. Lubricants and functional fluids are omnipresent due to their widespread use, and they thus pollute the environment in small, widespread amounts and rarely in large, localized quantities. The following information is based essentially on studies conducted by R. Luther 2007 [236] (updated in 2009), and earlier publications of T. Mang, R. Luther, and H. Ihrig [237–244].

A major research project is of special importance for the development of environmentally friendly lubricants, lubricant systems, and the awareness of environmental and safety at work aspects. Between 1997 and 2009, The Deutsche Forschungsgesellschaft (DFG) sponsored the Collaborative Research Center SFB 442: Environmentally Friendly Tribosystems at the University of Aachen, (RWTH Aachen, coordinated by H. Murrenhoff) [240]. In this case, the machine tool served as an application model for many lubricant families as metal-cutting fluids, forming lubricants, hydraulic fluids, or gear oils. Although the final report is due to be published in 2010, many interesting results have been published in the meantime (e.g., Refs [246–248]).

7.15.1

Terminology and Focus of Development

The terminology used in connection with “environmental compatibility” has to be split between the subjective and the objective.

Subjective criteria (non-measurable) include:

- Environmentally friendly
- Environmentally compatible

Objective criteria (measurable or provable) include:

- Biodegradability

- Water solubility, water pollution
- Ecological toxicity and physiological safety
- Performance, approvals, oil-change intervals
- Efficiency improvements, lower energy consumption
- Emissions reduction in use
- Compatibility with conventional lubricants and materials
- The use of renewable raw materials
- Environmental awards.

Normally, a biodegradability of at least 60% (according to OECD 301) or 80% (according to CEC L-33-A-93) is considered as a main objective criterion for “Bio-Lubricants,” although the other criteria will acquire greater importance in the near future. Developments during the past 25 years to formulate biodegradable lubricants based on natural oils have followed tradition, even though the market share today amounts only to few percent. The statistical data and the main legislation described in this chapter apply to experiences in Germany, which has – besides some countries in Western Europe (e.g., Holland, Austria, Switzerland) and Scandinavia – the highest amount of biodegradable lubricants worldwide. Every year, about 40–50% of the approximately 5 million tonnes of used lubricants in Europe ultimately will pollute the environment. This interface with the environment, and the resultant pollution of the atmosphere, ground or water, is either technically desired (total-loss lubrication) or is the result of leaks or other problems (CONCAWE Report no. 5/96; see also Section 7.16 and Figure 7.41). (*Note:* CONCAWE is the oil companies’ European organization for environment, health and safety.)

Even though mineral oil products can be relatively rapidly biodegraded by naturally occurring microorganisms, these natural degrading systems are overwhelmed by the volume of the losses. In recent years, rapidly biodegradable total-loss lubricants based on esters, polyglycols and natural oils have significantly eased lubricant-based pollution. In the past, when mineral oil-based products were used almost exclusively, leakages and other causes allowed a part of these lubricants to pollute the environment and indeed today, the soil and ground water is severely contaminated by these materials and, in particular, some of their ingredients. Fortunately, this problem has spurred both society and politics into action, as reflected by the diverse legislations and recommendations, and the issuing of environmental awards to products which cause less damage. The overall aim here is to avoid—or, at least, reduce—environmental pollution, and the use of environmentally friendly materials and substances will play increasingly important roles in the scope and procedures of the EU Eco Audit. Nonetheless, the most effective measure for preventing environmental pollution is—and will continue to be—the avoidance of physical containment by lubricants. But, most importantly, the technical prerequisites for this approach are already in existence, and should be fully utilized.

From a technical standpoint, and disregarding development and overall costs, it is accepted that more than 90% of all lubricants could be made rapidly biodegradable. However, this change will only take place if the ecological benefits of using harvestable raw materials is made clear and, best of all, quantified in monetary terms.

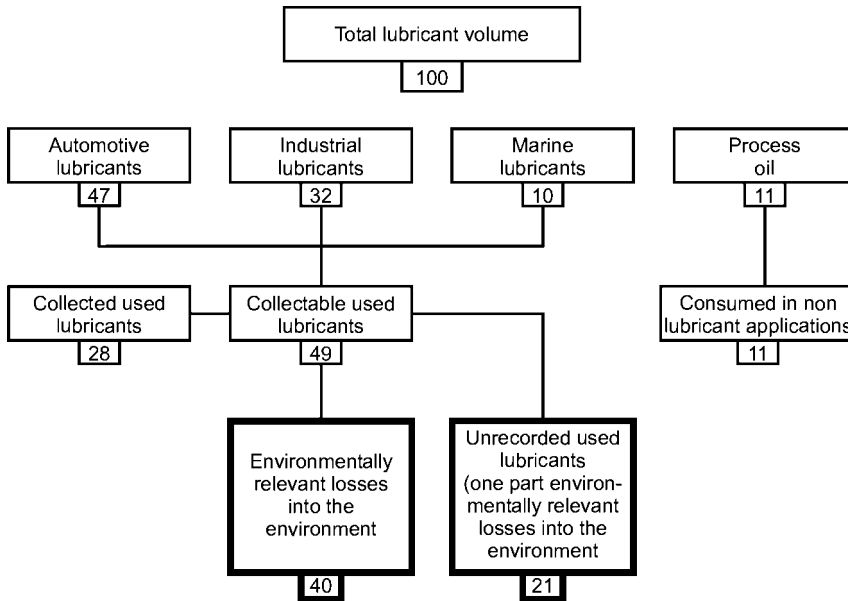


Figure 7.41 Lubricating oil supply, use, and disposal in Western Europe (CONCAWE 1996) [249].

Now that corresponding laws and guidelines are in place, environmental legislation will have economic repercussions. In addition to national laws, European guidelines are gaining relevance in the different European countries such that all new production facilities must comply with the EU machinery guidelines that came into force on 1 January 1995. These superseded previously applicable German Legislation concerning safety and the protection of human health and, along with thorough documentation, include mandatory measures to reduce operator stress and fatigue. Compared to older plant, this provides the operators of new machinery with greater safety. In practice, the implementation of these regulations requires the use of environmentally harmless lubricants. In Germany, the selection of rapidly biodegradable lubricants, especially those classified as “not water pollutant,” not only reduce the expense of oil spillages or disposal but also keep the costs of complying with health and safety regulations to a minimum. Compared to mineral oil-based products, the selection of low-evaporation ester and vegetable oil-based lubricants allows lower-viscosity materials to be used. This enables faster machining and reduces drag-out losses that, in turn, leads to increases in economy and productivity, and generates product optimization.

Today, active environmental protection is steadily gaining importance, the trend being towards clean and environmentally friendly factories in which people like to work, and which combine the requirements of advanced industrial technologies with environmental protection considerations. This is a major objective for a number of companies in a variety of industries. In the field of metal-working (see Section 7.11),

for example, ecologically friendly cutting fluids can significantly reduce the operating costs related to disposal, complying with water laws, maintenance, downtime, washing operations between machining steps, or water-reconditioning and splitting plants. Furthermore, environmentally harmless products are generally nontoxic, and their skin compatibility is much better than that of mineral oil products. Taken together, this creates ecological and economic points of view which promote the use of environmentally friendly lubricants. The vast majority of rapidly biodegradable lubricants currently on the market are based on saturated or unsaturated ester oils, with the acids required for esterification mostly obtained from vegetable oils. Unfortunately, compared to the equivalent mineral oils, ester oils are significantly more expensive, and this is a major barrier to their wider acceptance. However, the overall cost of a lubricant results from the interaction between aging and temperature stability, disposal costs, machine compatibility (multifunctional oil) machine investments, maintenance measures, oil-change intervals, operating costs, reconditioning possibilities, reductions in storage costs, reductions in emissions, reductions in the cost of preventive health and safety measures, risk minimization and lower clean-up costs after spillages, or simpler plant license procurement.

In particular, the use of fully saturated synthetic esters offers a number of opportunities. Today, pure vegetable oil formulations are used only for lower-demand processes, such as total-loss chain saw oils or mold-release oils, and some types of greases. Today's users are very interested in the potential life of the new generation of environmentally friendly lubricants. Rapeseed oil-based hydraulic fluids are normally used in lightly stressed systems, and can be changed at the same intervals as mineral oils. An increasing use is also being made of ecologically friendly fluids based on saturated and unsaturated synthetic esters, which satisfy the technical demands that are defined by higher performance, longer life, low oil volume and more rapid oil circulation times. An additional benefit is that the disposal of ester-based lubricants is generally nonproblematic.

An analysis of the economics of renewable raw materials often includes high EU agricultural subsidies (e.g., of rapeseed oil) as a critical factor, though this is relatively insignificant for the manufacture of biolubricants. Typically, EU vegetable oil prices depend on world market prices that, in turn, are largely affected by the price of soybeans, which account for a large fraction of the world's total vegetable oil production. As almost half of the world's soybean production is in the USA, vegetable oil prices—and therefore also oil acid or oil ester prices—are heavily dependent on the size of the US soya harvest.

An increasing correlation of the prices of vegetable oils with the price of crude oil must be recognized in some respects, because the use of vegetable oils in combustion engines, both for energy production and by traffic, is increasing. One driving force here is the European Directive 2003/30/EG of 8 May 2003, to promote the use of biofuels or other renewable fuels for transport.

Technically, rapidly biodegradable alternatives based on harvestable raw materials are available as replacements for most mineral oil-based lubricants. Biobased lubricants are also available for particularly demanding applications, such as engine lubrication. Yet, biobased lubricants have failed to achieve an important market

penetration that reflects their excellent technical performance and ecological potential, mainly because of their high price. In an effort to improve this situation, a Market Introduction Program for biobased lubricants was started in Germany, to promote the change from mineral oil-based lubricants to rapidly biodegradable lubricants produced from renewable raw materials. The principal conditions of application here were in the ecologically sensitive areas of agriculture, forestry, and water supply, the message being to exploit the risk reduction potential of biobased lubricants without any need for special environmental legislation. At six years after its introduction, the Market Introduction Program was considered to have been successful, albeit under difficult conditions. Nonetheless, the program is ongoing, with research and development on ecologically harmless lubricants being sponsored by European and national projects. Currently, governments are offering research sponsorship for projects aimed at improving and demonstrating the performance of biodegradable lubricants, and in particular of lubricants which are thermally and hydrolytically stable, and also stable to oxidation, without their biodegradability being significantly altered. At a European level, the "European Renewable Resources and Materials Association" (ERRMA), a representative body promoting the use of renewable new materials in technical applications, continues to focus its efforts on biolubricants and bioplastics, based on the forecasts for these product groups.

7.15.2

Tests to Evaluate Biotic Potential

The possibility of measuring the environmental impact of lubricants has often been discussed. This issue here is to monitor not only the biodegradability of materials in the natural environment (water, soil), but also their ecotoxicological potential in animals and humankind.

7.15.2.1 Biodegradation

Although the limit for rapid biodegradation has not been exactly defined, most legislation and recommendations employ the following criteria for non-water-soluble lubricants: Degradation >80% according to CEC L-33-A-93, or degradation >60% according to OECD 301B. The details of the most important tests are shown in Table 7.25, although many ISO, ASTM and national procedures are also available with more-or-less similar methods and restrictions. Notably, many important regulations no longer refers to the CEC L-33-A-93 test, as it is now essentially obsolete, having been mainly substituted by an OECD 301 procedure.

7.15.2.2 Ecotoxicity

When developing environmentally acceptable lubricants, it is vital to consider certain toxicological criteria, the aim being to protect life in various areas, especially in aquatic regions (i.e., water areas) and in non-aquatic regions (i.e., terrestrial areas). The following test procedures are of particular importance (especially with regards to ecolabeling):

Table 7.25 Important methods for testing the biodegradation of lubricants.

Test	Short description; relation to other tests	Limit for “rapid degradation”
OECD 301B	“Modified Sturm test”, aerobic degradation, ultimate biodegradation	≥60 % in 28 days
OECD 301C	“Modified MITI Test”, aerobic degradation, measurement of O ₂ consumption, for volatile components	≥60% in 28 days
OECD 301D	“Closed Bottle Test”, aerobic degradation, preferred for water-soluble products, but possible for non-water-soluble substances	≥60% in 28 days
OECD 301F	“Manometric Respirometry Test”; for water-soluble and non-water-soluble substances	≥60% in 28 days
OECD 302B	“Zahn-Wellens/EMPA Test”, assesses inherent biodegradability for water-soluble substances	
CEC L-33-A-93	“Inherent degradation”, aerobic degradation, water-soluble part of degradation not considered, only for poorly water-soluble substances. Because of primarily degradation, the values are higher than OECD 301 results, by up to 20%.	≥80% in 21 days
BODIS test, ISO 10708	Two phases “Closed Bottle” test, similar OECD 301D	

- Bacterial toxicity, according to DIN 38 412-8; this determines cell multiplication-inhibiting values (EC₁₀ and EC₅₀). The *Pseudomonas* type used for this test is found in waste water and soil.
- The bacterial test, according to OECD 209 or ISO 8192, determines acute toxicity through the inhibition of oxygen consumption; the results of this test are EC₅₀ values.
- The algae toxicity test according to OECD 201 or DIN 38 412-9 is yet another test for aquatic systems (measurement of chlorophyll fluorescence and determination of EC₁₀ and EC₅₀ values).
- One of the most important test procedures in German legislation concerning the aquatic area is a test on small living organisms, the “Daphnia test” (using *Daphnia magna* Straus, a water flea) according to DIN 38 412-11 or OECD guideline 202.
- In the aquatic area, fish toxicity, according to OECD 203 or DIN 38 412-15, performed on the golden orfe (*Leuciscus idus*), is important. The test results provide the LG₀, LG₅₀ and LG₁₀₀ values.
- Fish toxicity, according to OECD guideline 204, is incorporated in the German eco label “Blue Angel.” Any possible pollution of the nonaquatic terrestrial area (i.e., soil and plants) is evaluated with the plant growth test according to OECD guideline 208 (i.e., wheat, cress, and rape seeds). Naturally, toxicity testing for environmental protection purposes must also include mammal and human toxicity, and also more occupational safety aspects.

7.15.3

Environmental Legislation

Various criteria of the environmental legislation restrict the application of conventional lubricants and also influences the character of environmentally friendly lubricants, for example, emission thresholds (evaporating lubricants), the water pollution legislation in Germany with the definition of “Water Hazardous Classes” and “Water Pollution Categories.” Water hazard classes have a major influence on the storage and handling of these substances. The German regulation for using water-endangering lubricants (VAwS) will take greater care with highly water-polluting substances than for non-water-hazardous substances.

Other German and European laws are important for the application and development of lubricants, in particular: The Dangerous Preparations Directive (DPD, 1999/45/EC); the Environmental Liability Law; the Chemical Law (Hazardous Substances Law); Transport Regulations; waste and recycling laws; air pollution regulations; water pollution regulations; German Law for Soil Protection; German Water Law; waste water charges; German Emission Law; and Drinking Water Directive (for detailed information, see Ref. [236]).

7.15.3.1 RECh (Registration, Evaluation and Authorization of Chemicals)

On 13 February 2001, the European Commission adopted the White Paper “Strategy for a Future Chemicals Policy.” This proposed a wide-ranging fundamental overhaul of EU chemical control legislation—that is, the Dangerous Substances Directive (DSD), including the notification scheme for new substances, the DPD, the Existing Substances Regulation, and the Marketing and Use Directive. In essence, legislation for new and existing substances would be merged. The previous EU chemical control measures resulted in a too-great disparity between new and existing substances, with the high cost of notification of new substance stifling innovation. Furthermore, existing substances accounted for >99% by volume of chemicals in commerce, but were poorly assessed and controlled in comparison. The aim of REACH was to place a duty on companies that produced, imported and used chemicals, so as to assess the risks arising from their use, and to take the necessary measures to manage any risks identified. Hence, the burden of proof that commercial chemicals were safe was transferred from the regulators to industry. The consequence was that testing results would have to be shared, in order to reduce animal testing, and registration of information on the properties, uses, and safe use of chemical substances would be an integral part of the new system. These registration requirements would vary, depending on the volume of a substance produced, and on the likelihood of exposure of humans or the environment. This European directive came into force on 1 June 2007, and the preregistration of some products started on 1 June 2008.

7.15.3.2 The GHS (Globally Harmonized System) of Classification and Labeling

The use of chemical products to enhance and improve life is a widespread practice worldwide. Alongside the benefits of these products, however, there is also the potential for adverse effects on people or on the environment. As a result, several

countries and organizations have developed laws or regulations over the years that require information to be prepared and transmitted to those using chemicals via labels or a safety data sheet (SDS). Given the large number of chemical products available, their individual regulation is simply not possible for any entity. The provision of information supplies those using chemicals with the identities and hazards of the chemicals, and enables any appropriate protective measures to be implemented locally. Although these laws or regulations are similar in many respects, the differences are sufficiently significant to result in different labels or SDS for the same product in different countries. As a result of variations in definitions of hazards, a chemical may be regarded as flammable in one country, but not in another; or, it may be believed to cause cancer in one country, but not in another. Decisions on when or how to communicate hazards on a label or SDS thus vary around the world, and companies wishing to be involved in international trade must employ experts who can follow the changes in these laws and regulations and prepare different labels and SDS. In addition, given the complexity of developing and maintaining a comprehensive system for classifying and labeling chemicals, many countries have no system.

The EU decided to integrate such global harmonization in the REACH directive; this integration is planned for single chemicals in 2010, and for mixtures in 2015.

7.15.4

Environmentally Friendly Lubricants - Driving Forces

All industrialized countries have laws which are designed to protect waters, the ground, working places and the air from pollution. Yet, the only ban on the use of mineral oil-based lubricants exists in Austria, and this only for chain-saw oil. In fact, Austria banned mineral oil-based chain-saw oils, with effect from 1 May 1992, following a resolution (No. 647) passed on 16 October 1990. Germany and a number of other countries have implemented provisions or quasi-legal procedures which are designed to promote the use of this new generation of products (e.g., the Environmental Seal in Germany). There is also political pressure to channel considerable funds into environmental protection. The following summarizes the laws and legislative initiatives in Germany which have an effect on the development and use of lubricants. Even if European legislation increasingly dominates national legislation, many individual laws and directives have still to be considered. The fundamental point is that "...if lubricants are released into the environment during or after use, water, the ground and air are endangered." The relevant ecological laws and regulations, especially in Germany are: The German Water Law; The Drinking Water Directive; The German Ground Law; The Federal Emissions Law; The Recycling and Waste Law; The Chemicals Law; The Environmental Liability Law; German Parliament initiatives; and the "Blue Angel" environmental seal.

A recent addition to the German Chemical law also defines hazardous substances and mixtures according to hazardous parameters. New to the list is the parameter "Environmentally dangerous," which means that those products (or their decomposition products) can alter the nature of water, the ground, the air, animals, plants,

and microorganisms. Additives which display these features are thus also unsuitable for the development of ecologically friendly lubricants. The effects on the use of lubricants are, for example: “A reduction in the substances which pollute workplaces,” or “The use of fewer ‘risky’ substances (e.g., oil changing, maintenance and production materials, the use of lubricants as production materials, contact with lubricants, during the servicing of machinery, etc.)” This limitation in the Chemicals Law, and those in the Water Law, severely restricts the number of additives which are suitable for environmentally friendly, rapidly biodegradable lubricants. A further Chemicals Law restriction on additives for rapidly biodegradable lubricants results from the complicated approval procedures which are necessary for new substances.

The German Federal law to protect the ground came into force in 1999. This law is a framework law, similar to the Water Law and the Federal Emissions Law, and implementation will be the responsibility of the Federal States. While the Water Law only has an indirect effect on the ground (in the sense that clean water does not pollute), the Ground Law should avoid the build-up of ecologically harmful substances in the ground. The law was aimed at private and industrial landowners, along with the operators of factories (avoidance and preventative, clean-up and re-cultivating measures). The aim of the law was to provide a greater precision regarding environmental damage, and a further restriction on the use of ecologically harmful substances. Effects on the use of lubricants included: As a significant proportion of lubricants pollute the ground, the Soil Law will have profound effects on lubricant applications, for example, the clean-up measures for mineral oil-polluted ground. Because threshold values are not part of national laws designed to protect the ground, most European countries use the “Holland List,” which stipulates when mineral oil contamination requires cleaning-up. According to this list, the thresholds which then require clean-up measures are:

- 1) $>500 \text{ mg kg}^{-1}$ in residential areas and in Protected Water Zones
- 2) $>1000 \text{ mg kg}^{-1}$ for general cleaning-up
- 3) In individual cases, and when confirmed by an independent expert, up to 5000 mg kg^{-1} can be tolerated (such as in industrial areas with no ground water relevance).

It is assumed that the necessary disposal and cleaning of 1 m^3 of earth costs approximately €1000. This fact also promotes the development of environmentally friendly products, which may in turn generate far lower clean-up costs. The German Water Law offers direct protection for waters, and only indirect protection for the ground. The important articles of the German Water Law defined for Plant and Equipment for handling water-polluting substances (mineral oils and their derivatives): “Plants and equipment designed to store, fill, manufacture or treat water-polluting substances as well as plant and machinery using water-polluting substances in trading companies and the public sector must be designed, constructed, installed, maintained and operated in such a way that no contamination of waters or any other disadvantageous changes in the characteristics of the water can occur. The same applies to pipe work within the boundaries of a company.” The application of these guidelines to the storage and use of lubricants could lead to restrictions if larger

Table 7.26 German regulations for the use of water-endangering lubricants.

Volume of the stock plant (m ³)	Non-water hazardous	WHC 1	WHC 2	WHC 3
≤ 1	Non-water hazardous materials and preparations are not subject to the VAWS	F0 + R0 + I0	F0 + R0 + + I0	F1 + R2 + I0
> 1 to ≤ 10		F1 + R0 + I1	F1+ R1 + I1	F2 + R2 + I0/ F1 + + R3 + I0
> 10 to ≤ 100		F1 + R1 + I1	F1 + R1 + I2/ F2 + R1 + I1	F2 + R2 + I0/ F1 + R3 + I0
> 100		F1 + R1 + I2/ F2 + R1 + I1	F2 + R2 + I0/ F1 + R3 + I0	F2 + R2 + I0/ F1 + R3 + I0
Ground areas:		F0 – no special requirements, internal company requirements are valid F1 – impervious areas F2 – like F1, but with proof		
Storage capability:	R0 – no special requirements, internal company requirements are valid R1 – storage capability is sufficient up to taking effect of the security precautions R2 – storage capability equals the volume of the liquid R3 – double wall with leak detector			
Infra structure:	I0 – no special requirements, internal company requirements are valid I1 – independent signaling unit in connection with permanent occupied production sites I2 – Alarm and measurement plan			

quantities of oil were to be involved (central warehouses, large mobile plant, etc.). According to the Environmental Agency's "Guideline on Handling Water-Polluting Substances," the potential hazard depends on the volume of the plant and the Water Pollution Category of the substances used therein (see German regulations in Table 7.26). The aim is then to reduce this potential and thus avoid the massive cost of renewing plant and equipment by setting up a plant and equipment register, securing and sealing the flooring, and setting up containment capacity and infrastructure measures. However, this is possible only with biodegradable lubricants.

The charges for directly routing wastes into public sewers depend on the degree of contamination. The corresponding law of waste water charges defines: "The definition of hazardous substances, for example, heavy metals such as zinc and barium in lubricant additives, organic halogen compounds, and so on, and the charges for hazardous substances." During use, such as in machine tools, lubricants come into contact with metal-working fluids, slideway oils, and hydraulic oils. When water-miscible cutting fluids are split, some part of the hydraulic oil's additives may remain in the aqueous phase and, under unfavorable circumstances, this may lead to increased waste water charges. This problem has led to the development of zinc- and ash-free hydraulic oils. The use of ecologically friendly lubricants can also make a positive contribution to reducing pollution, as well as lowering waste water charges. The cleanliness of drinking water is already an objective of the Water Law, particularly with regards to the restrictions applicable in protected Water Zones.

7.15.5

Standardization of Environmentally Compatible Hydraulic Fluids

The best-known standardization of environmentally compatible lubricants concern hydraulic fluids, because until now this has been the application with the greatest amount of biodegradable alternatives. The most important regulations for environmental compatible hydraulic fluids are listed in Table 7.27.

7.15.5.1 The German Regulation VDMA 24 568

The well-known minimum requirements of mineral oil-based hydraulic fluids of DIN 51 524 do not satisfy the specifications of rapidly biodegradable hydraulic fluids. In order to do justice to the technical performance of different fluids, the VDMA (Association of German Machinery and Plant Manufacturers) created the specifications 24 568 (Minimum Technical Requirements) and 24 569 (Change-Over Guidelines). These specifications detail the minimum technical requirements of the ecologically safe product families (see Section 7.8); HETG (environment-compatible hydraulic fluids based on triglycerides, i.e., vegetable oils); HEES (based on synthetic esters); and HEPG (based on polyglycols).

7.15.5.2 ISO Regulation 15 380

The increasing importance of environmentally friendly fluids is reflected at an international level by the ISO (International Standards Organization): ISO 15 380 “Lubricants, industrial oils and related products class L) – Family H (hydraulic systems) – Specification for categories HETG, HEES, HEPG, HEPR” (see Section 7.8). The European activities of The European Committee for Oil Hydraulics and Pneumatics (CETOP) also reflect this activity. The ISO standard 15 380 deals with ecologically harmless fluids (ref. VDMA 24 568 and 24 569, enlarged to 1-IEPR) and includes, in addition to technical requirements (see Table 7.27), specific demands regarding the environmental impact of the hydraulic fluid. ISO 15 380 is the “technical standard” of European Eco-Labeling of Lubricants and for the German “Blue Angel.”

7.15.6

Environmental Seal

In an effort to combine the environmental behavior and technical properties of lubricants, many countries have introduced so called eco-labels or “eco-logos.” These labels should provide a sense of security to the users of environment-compatible products. Currently, among many household appliances, most countries include lubricants in their system of eco-labeling.

7.15.6.1 Global Eco-Labeling Network

The Global Eco-Labeling Network (GEN) is a new international initiative of the national environmental labeling organizations, with the purpose of creating a forum for information exchange and the promotion of eco-labeling. The GEN is a non-profit-making association of organizations from around the world.

Table 7.27 Regulations for environmentally compatible hydraulic fluids: minimum requirements HEES 46.

	ISO 15380	EU Margerite 2005/ 360/EC	Blue Angel RAL-UZ 79	White Swan Version 4.2	Swedish Standard 15 54 34 ed. 4
Technical requirements	The technical criteria of EC Directive 2005/360/EC ("EC Ecolabel for Lubricants"), RAL-UZ 79 ("Blue Angel") and Nordic Ecolabelling for Lubricants (Version 4.2, "White Swan") for hydraulic fluids refer to ISO 15380; the German VDMA Guideline 24568 is obsolete.				
Foam	ISO 6247 (24/93/24)	ISO 6247 (24/93/24)	ISO 6247 (24/93/24)	ISO 6247 (24/93/24)	ISO 6247 (24/93/24)
Requirement	150/0, 75/0, 150/0	150/0, 75/0, 150/0	150/0, 75/0, 150/0	150/0, 75/0, 150/0	150/0, 75/0, 150/0
Air-release	ISO 9120	ISO 9120	ISO 9120	ISO 9120	ISO 9120
Requirement	max 10	max 10	max 10	max 10	max 10
Seal swell	ISO 1817	ISO 1817	ISO 1817	ISO 1817	ISO 1817
Requirement	Volume -3% to +10%	Volume-3% to +10%	Volume -3% to +10%	Volume -3% to +10%	Volume -3% to +10%
Hydrolytic stability	Elongation -30%	Elongation -30%	Elongation -30%	Elongation -30%	Elongation -50%
Requirement	Tensile strength -30%	Tensile strength -30%	Tensile strength -30%	Tensile strength -30%	Tensile strength -50%
Cu corrosion	Hardness \pm 10%	Hardness \pm 10%	Hardness \pm 10%	Hardness \pm 10%	Hardness \pm 10%
Requirement	Not specified	Not specified	Not specified	Not specified	Not specified
Rust prevention	None	None	None	None	None
Requirement	ISO 2160 (100 °C, 3 h)	ISO 2160 (100 °C, 3 h)	ISO 2160 (100 °C, 3 h)	ISO 2160 (100 °C, 3 h)	ISO 2160 (100 °C, 3 h)
Demulsification	Rating max 2	Rating max 2	Rating max 2	Rating max 2	Rating max 1b
Requirement	ISO 7120, procedure A	ISO 7120, procedure A	ISO 7120, procedure A	ISO 7120, procedure A	Rating max 1b
Oxidation stability I	Pass	Pass	Pass	Pass	ISO 6614
Requirement	ISO 6614	ISO 6614	ISO 6614	ISO 6614	max 30 min
Requirement	None	None	None	None	ASTM D 943 - dry
Requirement	ASTM D 943 - dry	ASTM D 943 - dry	ASTM D 943 - dry	ASTM D 943 - dry	min 1000h
Requirement	Report	Report	Report	Report	

Oxidation stability II	DIN 51554-3 (95 °C/72 h)	DIN 51554-3 (95 °C/72 h)	DIN 51554-3 (95 °C/72 h)	DIN 51554-3 (95 °C/72 h)	ASTM D 943 DIN 51554-3
Requirement	Visc. max + 20%	Visc. max + 20%	Visc. max + 20%	Visc. max + 20%	Visc. max + 20%
Low-temperature properties	ISO 3104 (-20 °C/7 days)	ISO 3104 (-20 °C/7 days)	ISO 3104 (-20 °C/7 days)	ISO 3104 (-20 °C/7 days)	ISO 3104 (-20 °C/3 days) max. 2400 mm ² s ⁻¹
Requirement	No precipitates/no particles	No precipitates/no particles	No precipitates/no particles	No precipitates/no particles	
Filterability	Not specified	Not specified	Not specified	Not specified	ISO 13357-2
Requirement	None	None	None	None	None
FZG gear test	DIN 51354	DIN 51354	DIN 51354	DIN 51354	DIN 51354
Requirement	min 10	min 10	min 10	min 10	min 10
Vane pump	ASTM D2882/IP 281	ASTM D2882/IP 281	ASTM D2882/IP 281	ASTM D2882/IP 281	DIN 51389 (=ASTM)
Requirement	120/30	120/30	120/30	120/30	120/30
Shear stability	Not specified	Not specified	Not specified	Not specified	DIN 51350-6/ASTM D445
Requirement	None	None	None	None	>6.5 mm ² s ⁻¹ @100 °C
Occupational safety aspects					
Requirements concerning single substances	Not permitted if appearing in OSPAR list, organic halogen + nitrite compounds, metals or metallic compounds with the exception of sodium, potassium, calcium and magnesium	Not permitted if classified as • T+, T, R-45, R-46, R-48 or R-68 or • accord, to MAK 905, TRGS or EC cat. 1,2,3 – carcinogenic or – mutagenic or – toxic to reproduction	Not permitted if classified as • T+, T, R-45, R-46, R-48 or R-68 or • accord, to MAK 905, TRGS or EC cat. 1,2,3 – carcinogenic or – mutagenic or – toxic to reproduction	• Base fluids should not be carcinogenic	• R-42 or R-43 are only permitted up to 1%

(Continued)

Table 7.27 (Continued)

	ISO 15380	EU Margerite 2005/ 360/EC	Blue Angel RAL-UZ 79	White Swan Version 4.2	Swedish Standard 15 54 34 ed. 4
Requirements concerning the final formulated product		Product shall not have been assigned any R-phase indicating environmental and human health hazards according to EC Directive 99/45/EC	<ul style="list-style-type: none"> • Not classified as Xi or N, according to EC Directive 99/45/EC • max 50% concentration leading to classification of the formulation as Xn accord, to 99/45/EC 	Formulated hydraulic oil should not <ul style="list-style-type: none"> • be classified as N • no health hazard • no explosion hazard 	Formulated hydraulic oil should not <ul style="list-style-type: none"> • be harmful
Environmental aspects					
Base fluids		Base fluids (>5%) each <ul style="list-style-type: none"> • aquatic toxicity in OECD 201 and 202 $\geq 100 \text{ mg l}^{-1}$ 	Base fluids (>5%) each <ul style="list-style-type: none"> • >70% BOD/ThOD resp. CO₂ within 28 days • >80% in BODIS test • LC/EC₅₀ not <100 mg l⁻¹ 	Base fluids each <ul style="list-style-type: none"> • readily degradable and not R-50/53, not R-51/53, not R-50, not R-52/53, not R-53 	Base fluids (>5%) each <ul style="list-style-type: none"> • >60% BOD/ThOD resp. CO₂ within 28 days (if solubility <100 mg l⁻¹) • >70% COD in 28 days (if solubility >100 mg l⁻¹) • LC/EC₅₀ >100 mg l⁻¹ • No limitation on individual substances (see below)
Additives		<ul style="list-style-type: none"> • Cumulative mass concentration of substances must be: <ul style="list-style-type: none"> - $\geq 90\%$ ultimately biodegradable (f.e. $\geq 60\%$ in OECD 301) 	<ul style="list-style-type: none"> • Max 5% inherently or not biodegradable substances, max. 2% nonbiodegradable • not R-51/53 and bioaccumulative 	<ul style="list-style-type: none"> • No limitation on individual substances (see below) 	

<p>Polymers</p>	<p>– ≤5% inherently bio-degradable (f.e. >70% in OECD302C) – ≤5% non-biodegradable • substances that are non-biodegradable and bioaccumulative are not permitted Substance does not bioaccumulate if its MM > 800 or has a molecular diameter >1.5 nm</p>	<p>• not R-52/53 and bioaccumulative • not EC₅₀ < 100 mg/l in OECD 208 • not LC₅₀ < 100 mg/l in OECD 209</p> <p>• Not mobile • LC/EC₅₀ > 100 mg l⁻¹ in OECD 201, 202 or 203 • EC₅₀ > 100 mg l⁻¹ in OECD 208</p>
<p>Formulated product</p>	<p>• Biodegradability accord. to ISO 14593 or ISO 9439: >60% • Fish ISO 7346-2: LC₅₀ > 100 mg l⁻¹ • <i>Daphnia</i> ISO 6341: EC₅₀ > 100 mg l⁻¹ • Inhibition ISO 8192: EC₅₀ > 100 mg l⁻¹</p>	<p>• max 2% nondegradable • no AOX, NO₂ salts, metals, except 0.1% Ca</p> <p>• max 3% R-53 or R-52/53 • max 2% R-50 or R-50/53 • max 1% R-51/53</p>
		<p>• max 1% of components with LC₅₀ < 1 mg l⁻¹ • max 5% of components with LC₅₀ = 1–100 mg l⁻¹</p> <p>(Continued)</p>

Table 7.27 (Continued)

	ISO 15380	EU Margerite 2005/ 360/EC	Blue Angel RAL-UZ 79	White Swan Version 4.2	Swedish Standard 15 54 34 ed. 4
Renewable material	No requirements	>50% in hydraulic fluids	No requirements, but the German Market Introduction Program requires 50% renewable components	min 65% renewable substances in the product required	No requirements, but the environmental criteria laid down in SS 155434 correspond to the B level of the "Clean lubrication" definition of the City of Göteborg. The A level of the "Clean lubrication" definition of the City of Göteborg requires that only material from renewable resources are used

7.15.6.2 European Eco-Label

The current EU Eco-Label (“EU Marguerite”) award scheme has been in operation since 1993, when the first product groups were established. For all product groups, the relevant ecological issues and the corresponding criteria have been identified on the basis of comprehensive studies of environmental aspects related to the entire life-cycle of these products.

With publication in the *Official Journal of the European Community* on 5 May 2005, the directive 2005/360/EG came into force, establishing ecological criteria and related assessment and verification requirements for the award of the Community Eco Label to Lubricants. The “Competent Body” for the eco-labeling process was the Netherlands “Stichting Milieukeur.” Final selection of the first version of the EU Eco-Label for Lubricants was driven by the environmental relevance of the products, which included hydraulic fluids, chain-saw oils, concrete-release agents, other total-loss lubricants, two-stroke engine oils, and lubricating greases. Automotive lubricants were not included, because the most relevant environmental issues for these types of lubricant differ from those selected. According to some Life Cycle Assessments, fuel efficiency improvements by using advanced engine and gear oils is of greater importance to the environment than biodegradability. However, this does not exclude the possibility of developing criteria for automotive lubricants in the future. The European Commission decided on a prolongation of the criteria from 18 November 2008. The criteria for the European eco-labeling of lubricants are:

- The product shall not have been assigned any R-phrase, and any aquatic toxicity and requirements with regard to biodegradability must be measured for each component (for this criterion, determination for the fully formulated product is not of interest).
- Specific substances are to be excluded as intentionally added ingredients from lubricants applying for the EU Eco-label.
- The demand for a minimum content of renewable raw material within the finished product (45–70% w/w carbon content derived from renewable raw materials).
- Minimum technical requirements, special appearance of the Eco-label with the text “Reduced harm for water and soil during use; reduced CO₂ emissions.”

7.15.6.3 The German “Blue Angel”

The world’s first eco-labeling program, the German “Blue Angel,” was created in 1977 to promote environmentally sound products, relative to others in the same group categories. The authorities hoped that it would be seen as a positive step, not only for individual consumers but also for the retailers and manufacturers. The institution responsible for assessing such proposals is the Umweltbundesamt (German Environmental Protection Agency, UBA) guided by an eco label jury which considers these proposals. The jury is composed of representatives from industry, environmental organizations, consumer associations, trade unions, the Churches, and public authorities, in order to ensure that the interests of various groups in society are taken into consideration. The label is composed of a blue figure with

outstretched arms surrounded by a blue ring with a laurel wreath. A standard inscription, "Umweltzeichen" (environmental label) is at the top of the logo, and a second inscription for the individual product group is found at the bottom, for lubricants it is "... because rapid biodegradable." This eco-label relies on information and voluntary cooperation, as well as on the motivation and the willingness of each individual to make a contribution towards environmental protection. The Blue Angel is addressed at all market players, enabling retailers and consumers to make deliberate choices in favor of environmentally sound alternatives. Once approved, eco-labeled products are reviewed every two or three years to reflect state-of-the-art developments in ecological technology and product design. The Eco-Label Jury scrutinizes product groups twice yearly. The criteria for awarding the Blue Angel includes: the efficient use of fossil fuels; alternative products with less of an impact on the climate; reduction of greenhouse gas emission; and conservation of resources. The German environmental award should highlight products which are more environmentally compatible than others. The following environmental awards have been issued for lubricants: RAL UZ 48 for Chainsaw oil (1988); RAL UZ 64 for rapidly biodegradable lubricants (1991); and RAL UZ 79 for rapidly biodegradable hydraulic oils (1996). Together with the German Ministry for the Environment, Nature Protection and Nuclear Safety, the awarding committee has decided that the conditions for issuing this award will consider results obtained by the RAL organization consisting of a commission of consumer experts, manufacturers, and the Federal Environment Agency. The actual issuing of the award is performed by the RAL organization. The third issuing guideline represents a tightening-up of the first two guidelines, in that it covers the use of hazardous substances (additives). The guideline combines demands originating in chemical law, the law on water, biodegradability and eco-toxicological evaluations. The "Blue Angel" combines the performance level of the requirements of ISO 15 380 with environmental relevant criteria, which are not compatible with the requirements of the European Eco-label.

7.15.6.4 **Nordic Countries (Norway, Sweden, Finland, Iceland): The White Swan**

The Nordic White Swan label claims to be neutral, independent, and the world's first multinational eco-labeling scheme. Only products that satisfy strict environmental requirements on the basis of objective assessments are allowed to display the environmental product label. The criteria for the eco-labeling of lubricating oils (Nordic Eco labeling 05.09.1997) encompass lubricating oils with a lubricating and pressure-transmitting effect. The product group encompasses engine oil, transmission oil, hydraulic oil, lubricating grease, two-stroke oil, metal-cutting fluid, chain-saw oils, and mold oils.

7.15.6.5 **The Canadian "Environmental Choice" (Maple Leaf)**

The "Environmental Choice Program" (ECP), which is Environment Canada's eco-labeling program, provides a market incentive to manufacturers and suppliers of environmentally preferable products and services, and thereby helps consumers to identify products and services that are less harmful to the environment.

Established in 1988, the ECP was the second national eco-labeling initiative undertaken. Canada's "Environmental Choice" Eco-Logo symbol of certification features three stylized doves intertwined to form a maple leaf, representing the consumers, industry, and government working together to improve Canada's environment. A product or service may be certified because it is made or offered in a way that improves energy efficiency, reduces hazardous byproducts, uses recycled materials, or because the product itself can be reused. Product manufacturers, importers or purveyors of services may apply for a license to use the Eco-Logo once a guideline containing criteria relevant to the product or service type has been approved. Environmental Choice guidelines are based on the best information available at the time, and are upgraded as new information and technology make higher standards possible. Guidelines are developed in consultation with industry, environmental groups, universities and independent technical and scientific advisors.

Currently, Environmental Choice has more than 1400 approved products, with 119 licensees and 29 guidelines under which companies may be licensed and their products certified. In the area of lubricants, there are listed anticorrosion products, automotive engine oil, synthetic industrial lubricants, and vegetable-based industrial lubricants.

7.15.6.6 Other Eco-Labels

- **Austria:** The Austrian eco-label includes only one relevant lubricant guideline (published under no. UZ 14, January 1997): Chain-saw oils based on vegetable oil.' This guideline is usable for chain-saw oils with an amount of vegetable oil of at least 95%; it is permissible to add 5% additives.
- **France:** The "NF Environment mark" is the Eco-Logo for France; this was created in 1992 and features a single leaf covering a globe. Certification is based on a multi-criteria approach, combining technical and environmental requirements. For chain-saw oils, a French Eco-label has been available since 2003: "Lubrifiants pour Chaines de Tronconneuse."
- **Japan:** Since 1989, the Japanese Environmental Association (JEA) has administered the Eco Mark Program with the goal of disseminating environmental information on products, and encouraging consumers to choose environmentally sound materials. The scheme also is applicable to lubricants. The Eco Mark Program is intended as a means of offering a choice of products with a lower environmental impact.
- **USA:** The Green Seal is an American non-profit environmental labeling organization that awards a Green Seal of Approval to products found to cause significantly less harm to the environment than other similar products. The Green Seal certification mark identifies those products which are environmentally preferable, and empowers consumers to choose products based on their environmental impacts. Green Seal develops environmental standards for consumer products through a public review process that involves manufacturers, environmental organizations, consumer groups, and government agencies.

Products are certified only after rigorous testing and evaluation. Underwriters Laboratories Inc. (UL) is the primary testing contractor for Green Seal. Green Seal certifies products in over 50 categories that include, apart from major household appliances, also re-refined engine oil.

- **Netherlands:** The Netherlands has a special system to give support to environmental compatible products– the accelerated depreciation of environmental investments, the so-called VAMIL regulation.

7.15.7

Biodegradable Base Oils for Lubricants

The main “chemistry” concerning biodegradable lubricants relates to the different types of ester oil; these include: vegetable oil from harvestable raw materials (e.g., rapeseed or sunflower oil); semi-saturated, transesterified ester oils with natural fatty acids (e.g., trimethylopropanetrioleate); and fully saturated, synthetic esters based on chemical modified vegetable oils or mineral oil (e.g., diisotridecyladipate). Other (in principle) biodegradable base oils are mostly not present in the market of “environmentally compatible lubricants,” for a variety of technical or environmental reasons, including PAG, low-viscosity PAOs (PAO2), and some special types of synthetic hydrocarbon with viscosity up to of $6 \text{ mm}^2 \text{ s}^{-1}$ at 100°C . Natural fatty oils such as castor oil, palm oil, rapeseed oil, soybean oil, sunflower oil, lard, tallow and sperm oil have all been used in lubricants for many years. In these so-called “triglycerides” of more or less unsaturated fatty esters, the type of base is biodegradable and, compared to mineral oils, will show excellent tribological qualities (low friction coefficient, good wear protection). Unfortunately, their range of use is limited by a lower stability against thermal oxidative and hydrolytic stress, and partly inferior cold flow properties. Nonetheless, these limits can be improved gradually either with the use of additives, or via the selection, cultivation, or genetic modification of new types of plant. As an example, new types of high-oleic sunflower oils (HOSO) have been developed with an oleic acid content in excess of 90%, from which it appears possible to formulate oils for higher performance levels.

Besides the values of ecotoxicity and biodegradability, the evaporation loss of esters and vegetable oils is also excellent (as can be seen in Figure 7.13). The lower evaporation loss of ester oils has major advantages with regards to emissions from machine tools in metal-working, and also for the emissions (notably particle emissions) of internal combustion engines. Typically, the use of an ester oil rather than a mineral oil will improve the viscosity–temperature behavior of a lubricant.

Most vegetable oils, synthetic esters, and glycols display excellent friction and wear behavior under boundary lubrication conditions. The high degree of polarity of these lubricants results in their superiority compared to mineral oil-based lubricants, and this has been proven by a series of tests. For example, experimental investigations on twin-disk test rigs have shown that the friction coefficient of vegetable oils, synthetic esters and glycols is approximately half that of mineral oils.

7.15.8

Additives

The most important additive families for biodegradable lubricants are EP/AW additives, corrosion-protection additives, and antioxidants (for detailed information, see Section 7.5). Sulfurized fatty materials serve as environmentally friendly EP additives, while the use of sulfur as an additive in esters provides an AW effect. Sulfur carriers with 15% total sulfur and 5% active sulfur have also proven to be effective in rapidly biodegradable esters and vegetable oils. Both, vegetable oils and synthetic esters show a high polarity, and this applies also to corrosion inhibitors, such that a competitive reaction will occur on the metal surface. Special calcium sulfonates, succinic acid derivatives or ash-less sulfonates can each be used to provide corrosion prevention. Special phenolic and aminic materials are suitable antioxidants for the formulation of biodegradable lubricants.

7.16

Disposal of Used Lubricants

The fate of the lubricants sold every year in Western Europe is shown schematically in Figure 7.41, with only 49% being collectible and only 28% actually collected [249]. (*Note:* This chart also includes process oils, which are not lubricants.) From these data it is possible to identify not only the intensive gathering of collectible oils, but also any improvements in the environmental compatibility of lubricants, of which more than 50% pollute the environment by way of total-loss applications, leaks, evaporation, and other routes.

Currently, used lubricating oils represent the largest amount of liquid non-aqueous hazardous waste worldwide [250].

7.16.1

Possible Uses of Waste Oil

Today, as used lubricants represent a major problem for the environment, their ecologically compatible use is an important environmental protection measure.

Used lubricants are created when all mechanical possibilities in a machine, or at the user's premises, no longer suffice to maintain the performance of the lubricant; this occurs especially when the chemical additives have been used-up and aging byproducts are present in the oil. The demand that some new lubricants should be created from used products is based on the erroneous notion that re-refining can restore the original condition of a lubricant. In fact, lubricants lose value during their use and re-refining and, at best, only the value of the base oil can be restored. In the case of conventional mineral oils, this value is only slightly higher than for fuels or heating oils, and this is also the reason why re-refining is barely economical without legislative provisions or subsidies. From a global competition point of view, other disposal options include the direct incineration of untreated waste oils, the simple

pre-treatment (cleaning) and alternative uses such as flux oils for bitumen, or the manufacture of secondary feeds in sec-feed plants for catalytic crackers and as a blending stock for high-sulfur fuels.

The different possibilities for regeneration, recycling, and waste-to-energy applications of used lubricants has been illustrated by Krishna (2006) for an integrated steel plant as an important consumer of lubricants [251].

There have, in the past, been serious discussions to compare the environmental impact of re-refined oils by using advanced re-refining techniques with primary products (especially virgin base oils) and combustion; indeed, such discussions are on-going today. The results of a study conducted in 2005 [252] led to the conclusion that:

“In summary, re-refining of used oils leads to significant resource preservation and relief from environmental burdens when compared to the production of base oils in large-scale crude oil refineries.”

Another study conducted to investigate the environmental impact of re-refining motor oils [253] in the USA maintained that:

“The preservation of energy as an environmental consideration favors re-refining or combustion in larger industrial applications. The energy balance favors re-refining because the energy consumption that occurs during the distillation and hydrotreating is less than that consumed in burning the used oils as fuel in space heaters. The environmental impact of re-refining is a substantial improvement over burning with respect to human toxicity potential, heavy metals, eutrophication, aquatic ecotoxicity, carcinogenic substances, photochemical oxidant potential and acidification potential. Even though re-refining consumes energy during the refining process the level of Energy consumption required is greatly outweighed by the amount of energy saved by reusing the oil. The estimated amount of energy savings due to the current re-refining of used oils in the United States is 63 million gallons annually.”

On the other hand, the cement industry— as an important user of used oils [254]— has declared that, from a life cycle point of view, there is no evidence that the regeneration of waste oils is the optimum waste treatment option. Rather, the industry recommends not to privilege regeneration over recovery of waste oil in IPPC installations.

7.16.2

Legislative Influences on Waste Oil Collection and Reconditioning

The EC Directive 87/101 contains a recommendation to all member countries concerning the regeneration of used oils, insofar as economic, technical, and organizational conditions allow. The emission thresholds for incineration plants

(<3 MW) make the burning of untreated used oils difficult, although in some European countries incineration in smaller plants is still possible. Legislation permits incineration in high-temperature furnaces, and by the cement-manufacturing industry. In some countries, fuels and heating oils reclaimed from used lubricants are not taxed, and are thus subsidized.

The problem of polychlorinated biphenyls (PCBs) which surfaced in Europe in 1983, has had a significant influence on European legislation on wastes. The presence of PCBs, which entered the re-refined oil chain via fire-resistant hydraulic oils or condenser oils, led to changes in German waste oil legislation. Although, today, the PCB problem has almost disappeared, the division of waste oils into two groups has led to considerable consequences, as used oils containing more than 0.2% chlorine cannot be re-refined and are subject to expensive disposal procedures. This has, in turn, promoted the development of chlorine-free lubricants.

Re-refined used oils are subsidized in Italy, while in Germany both the manufacturers and distributors of lubricants have transferred their legal requirement to properly dispose of waste oils to collection organizations.

In the USA, state laws on this subject differ; since 1986, used oils have been classified as hazardous wastes in California, and other states have since followed. In some states, the collector is paid up to 20 cents per gallon by the oil user, whereas in other states the collector has to pay. Only 17% of all used oil in the United States is actually re-refined [253].

Viewed globally, some extremely differing situations exist. While some countries do not regulate the collection and disposal of used oil, and it is generally not collected, other countries can point to high collection and disposal rates.

7.16.3

Re-Refining

Despite the re-refining of used oils to lube base oils dating back to 1935 [255], re-refining was unable to find acceptance for a number of reasons: (i) there were high processing costs, and therefore high selling prices, compared to relatively low virgin oil prices; (ii) there was an inadequate removal of carcinogenic polycyclic aromatics; (iii) in most markets, re-refined oils had a negative image; and (iv) there was an increasing complexity of base oil blends in engine and other lubricants. In fact, in 1998, only 7% of Western Europe's base oil demand was satisfied by re-refined products.

Although numerous re-refining technologies have been developed over the past 25 years, and many were patented, very few proved to be suitable for large-scale application [256–261]. In general, the following process stages are common to all re-refining methods:

- 1) Separation of larger solid impurities, along with most of the water; this is normally achieved by sedimentation.
- 2) Separation of the volatile parts (fuel residues in engine oils, solvents and low-boiling-point lubricant components). This is normally achieved by atmospheric

distillation. The separated light hydrocarbons can normally be used in-house for energy creation.

- 3) Separation of the additives and aging byproducts. This can be achieved by acid refining, solvent (propane) extraction, vacuum distillation, or partly also by hydrogenation.
- 4) Finishing process to separate any remaining additives, aging byproducts and refining reaction products. This normally requires hydrofinishing with absorbents such as bleaching clay or mild, or selective solvent extraction (e.g., Furfural).

The re-refinement of used engine oils leads only to an acceptably low content of carcinogenic PACs, by using solvent extraction or by hydrotreating.

7.16.3.1 Sulfuric Acid Refining

The sulfuric acid refining process was mostly developed by Meinken (see Figure 7.42 for details of the flow plan). Compared to older acid-based methods, various process stages reduce the amount of acidic sludge and bleaching clay that is generated, as well as increasing the lube oil yield. Today, because of the acidic sludge problem, acid refining has largely been replaced by other methods, although some such plants are still in operation.

7.16.3.2 Propane Extraction Process (IFP, Snamprogetti)

Of the principal extractive refining processes used, the technology of the IFP (Institut Francais de Petrole) system is worthy of mention. The system initially used propane extraction together with acid refining, but later combined this with hydrofinishing. Propane extraction is also used by Snamprogetti (Italy) as the main refining step

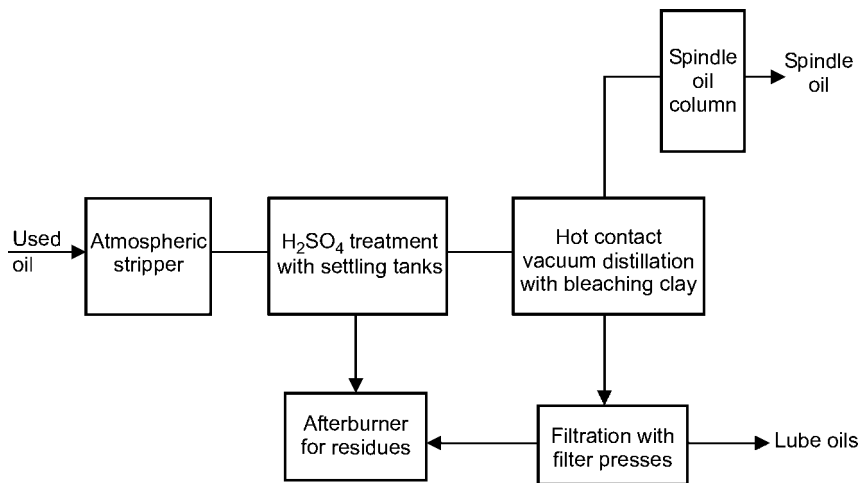


Figure 7.42 Sulfuric acid re-refining. The flow chart of the Meinken process.

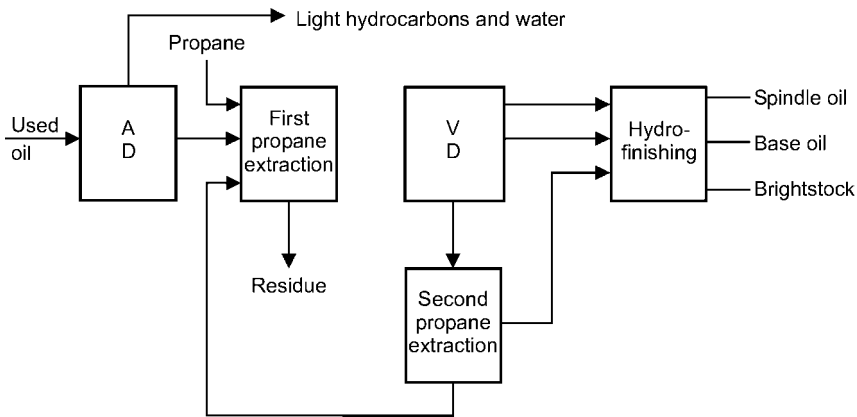


Figure 7.43 Re-refining by propane extraction (IFP, Snamprogetti). AD, atmospheric distillation; VD, vacuum distillation.

before and after vacuum distillation. The process, with propane extraction, is shown schematically in Figure 7.43 [262–264].

7.16.3.3 Mohawk Technology (CEP-Mohawk)

The Mohawk Process (subsequently CEP-Mohawk), which uses high-pressure hydrogenation, was introduced in the USA during the late 1980s. The process begins with thin-film vacuum distillation (after flashing the light hydrocarbons and water), and this is followed by hydrogenation of the distillate at 1000 psi over a standard catalyst. The special steps realized a catalyst life of 8–12 months, which was essential for the economy of the process.

Two further advantages of the Mohawk process are the much smaller amount of effluent water which requires treatment, and the cheaper materials for site construction (due to an absence of corrosion). The Mohawk process, which is based on the KTI process, has been licensed by Evergreen Oil (USA and Canada).

7.16.3.4 The KTI Process

The KTI (Kinetics Technology International) process combines vacuum distillation and hydrofinishing to remove most of the contamination and additives. The key to the process is the thin-film vacuum distillation, which minimizes thermal stress through the use of mild temperatures (<250 °C). The hydrofinisher removes sulfur, nitrogen, and oxygen, such that the yield of finished base oils is high (82% on a dry waste oil basis).

7.16.3.5 PROP Process

In PROP technology, which was developed by Phillips Petroleum Company, the key elements of the process are the chemical demetalization (mixing an aqueous solution of diammonium phosphate with heated base oils) and a hydrogenation process. A bed of clay is used to adsorb the remaining traces of contaminants in order to avoid poisoning of the Ni/Mo catalyst.

7.16.3.6 Safety Kleen Process

This process uses atmospheric flash for removing water and solvents, a vacuum fuel stripper, vacuum distillation with two thin-film evaporators, and a hydrotreater with fixed-bed Ni/Mo catalysts. When using high severity, the hydrotreater is in a position to reduce the level of polynuclear aromatics; it also removes higher-boiling chlorinated paraffins.

7.16.3.7 DEA Technology

The best results with regards to the technical and environmental quality of the re-refined oil and the elimination of PAHs are provided by a combination of thin-film distillation, followed by selective solvent extraction. In this process, the distillates from the vacuum thin-film distillation towers at the re-refinery are finally treated in a lube refinery solvent extraction plant, followed by hydrofinishing. Following this extraction process, the PAH content is lower than that of virgin solvent neutrals.

7.16.3.8 Other Re-Refining Technologies

Vaxon (Enpotec fabrication facilities in Denmark) uses three or four vacuum cyclone evaporators and a finishing treatment with chemicals. The key step in the ENTRA Technology is the special vacuum evaporation in a vacuum linear tubular reactor (single tube). After continuous evaporation by means of rapidly increasing temperature, vapor condensation is performed by fractional condensation. Complete dechlorination can be achieved with metallic sodium, and clay polishing is used as a finishing process.

The TDA (Thermal De-Asphalting) process has been developed by Agip Petroli/Viscolube, based on the technology of PIQSA Ulibarri in Spain. The process employs a chemical treatment to facilitate subsequent de-asphalting. The de-asphalting process is combined with high fractionating efficiency (so-called TDA unit), and finishing is achieved by clay treatment or hydrofinishing.

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8

Mechanical–Dynamic Tribology and Testing Methods

8.1

Introduction

The word “tribology” originates from the Greek “tribos,” which means rubbing. The tribology of mechanical–dynamic contacts is defined as the science of interacting surfaces in relative motion. In any machine, there are many component parts that operate by rubbing together; some examples of this are hydrodynamic journal bearings (Figure 8.1a), cylindrical roller bearings (Figure 8.1b), tooth contact in gears (Figure 8.1c), cams and tappets, piston rings, seals, or wet brakes. By focusing on sliding/rolling contacts, it becomes apparent that there are significant differences between the tribology of journal and roller bearings, as the lubrication conditions that characterize the sliding/rolling contacts differ from each other as well as, for example, from those in toothed wheels. As shown in Figure 8.1, the lubrication conditions in the tooth contacts are the most difficult, consequently, very often the most difficult lubrication conditions will challenge the requirements for such a tribological contact.

A friction force is the resistance encountered when model bodies move relative to another with a sliding/rolling contact speed (Figure 8.2). The static friction force relates to how hard it is necessary to push an object to make it move, while the dynamic friction force relates to how hard the object must be pushed to keep it moving. The ratio of the frictional force to the normal force is called the coefficient of friction (commonly known as μ). All of these components have two surfaces which come into contact, support a load, and move with respect to each other. Although surfaces may appear smooth, on the microscopic scale they are rough, and when two surfaces are pressed together contact is made at the peaks of the roughness or asperities. Consequently, the “real” area of contact can be much less than the “apparent” or “nominal” area. At the points of intimate contact, it is possible that adhesion, or even local welding, might take place. In order to slide one surface over the other, it is necessary to overcome friction, wear, and contact mechanics. In addition, a force must be applied to break the lubricated or nonlubricated junctions.

In grinding and polishing processes, whilst the generation of high wear rates is desirable, wear is usually unwelcome as it will lead to increased clearances between the moving components, to increased mechanical loading, and maybe even to

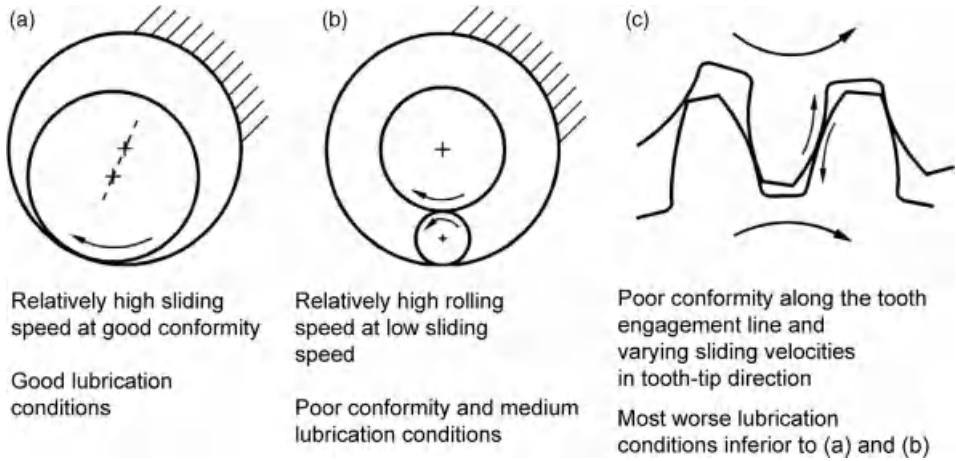


Figure 8.1 (a) Hydrodynamic journal bearing; (b) Cylindrical roller bearing; (c) Tooth contact lubrication.

fatigue. When a sufficient film forming by a lubricant (Figure 8.3a) is missing, and the asperities of one surface over another come into contact, there is a possibility that wear forms can occur:

- The subsequent breaking of all the very small junctions can cause material removal, and result in the phenomenon of adhesive wear (Figure 8.3b).

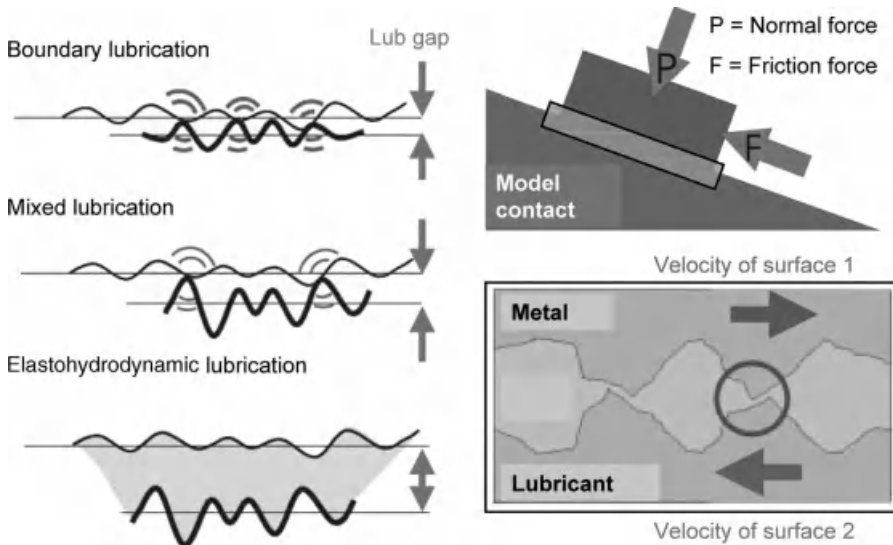


Figure 8.2 Two interacting surfaces in relative motion are pressed together; the lubricant fills out the gap in between surface roughnesses (asperities).

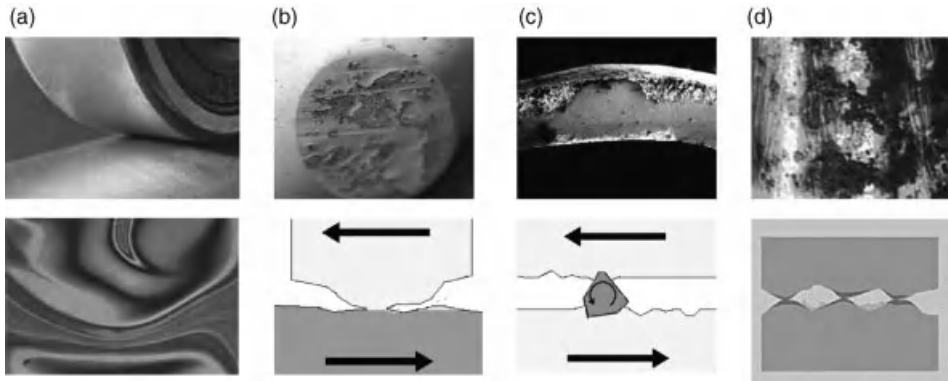


Figure 8.3 Different basic wear types of mechanical–dynamic contacts on a metal surface. (a) Two surfaces in motion held apart by a film-forming lubricant; (b) Adhesive wear on a metal surface; (c) Abrasive wear on a metal surface; (d) Tribo-oxidation on a metal surface.

- Alternatively, the asperities of a hard surface can plow grooves in a soft surface, a situation referred to as abrasive wear (Figure 8.3c).
- One of the main reasons for frequently changing the engine oil of a car is that it becomes contaminated with hard debris particles that can wear out the engine components' surface, causing disruptive wear.
- Corrosion or corrosive wear occurs when surfaces are oxidized or rust, principally in the presence of humidity or water (this is termed tribo-oxidation) (Figure 8.3d).
- Erosive wear occurs when particles or even water droplet strike a surface and break off a bit of the material.

The design of mechanical components is such that the load is supported on a small area. This leads to high stresses, which in turn can cause high friction, wear, and contact fatigue; hence, contact mechanics represents an important part of tribology. To summarize, the study of friction, wear, lubrication and contact mechanics are all important parts of tribology. Related aspects include surface engineering, which means the modification of a component's surface to improve its function, for example by applying a surface coating, surface roughness, and rolling contact fatigue, where repeated contacts causes fatigue to occur.

8.2

Tribological System Categories within Mechanical–Dynamic Tests

Mechanical–dynamic testing has become an essential element in the development of modern tribology, to appoint where standardized tribological, mechanical–dynamic test rigs and test methods play decisive roles in the development of machine elements, and especially for coatings, lubricants, and additives. Standardized test methods represent the basic means of achieving the required performance of original equipment manufacturer (OEM) specifications for lubricants. A variety of so-called


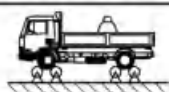
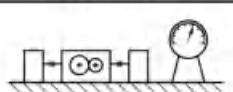
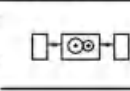
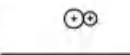
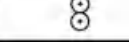
Category	Type of test Test conditions	Test system	
I	Field trial - Normal operating conditions - Extended operating conditions		Poor repeatability but close to real requirements
II	Test laboratory with complete vehicle (equipment) or plant - Close to normal operating conditions - Extended operating conditions		Medium repeatability and less environmental impact
III	Test laboratory with plant or construction elements - Normal operating conditions - Extended operating conditions		Testing of components and medium repeatability
IV	Experiment with standard construction element or scaled down plant		Testing of serial standard components with good repeatability
V	Experiment with test equipment operating close to normal conditions		Testing of specimen with excellent repeatability
VI	Experiment with simple laboratory test equipment (bench test)		

Figure 8.4 Tribological system categories within mechanical–dynamic testing.

“house-internal” methods complete the range of today’s tribological, mechanical–dynamic testing.

Currently, the wide range of tribological, mechanical–dynamic test machines and test methods that are available includes simple laboratory instruments and field tests conducted under “real” conditions. The different types of tribological test are classified, among others, by the German DIN 50 322 (see Figure 8.4) [1]. However, the continuing, gradual reduction of the test-sequence plan from a field test to a simple friction contact may lead to substantial improvements in the repeatability and reproducibility of a test method, and the validity of results from a simple screening test will decrease proportionally. One major problem of the classification according to DIN 50 322 is the allocation of certain test devices and methods to their corresponding categories. The transitions between such categories must be considered as fluent, and enable an overlapping or a combination of two categories in a single test method.

8.3

Simple Tribological Mechanical–Dynamic Test Machines and Test Methods

8.3.1

Four-Ball Apparatus

The four-ball apparatus is one of the oldest and best-known simple test benches for liquid and solid lubricants. The four-ball geometry is a popular test method, because

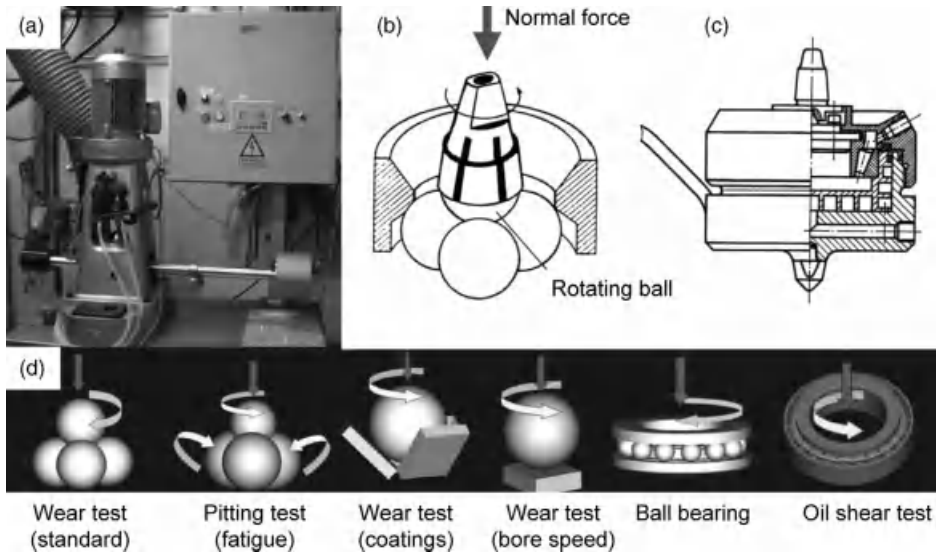


Figure 8.5 (a) The four-ball apparatus; (b) Test principle of the four-ball apparatus; (c) Test adapter for determination of shear stability of lubricants containing polymers; (d) Examples of the variety of four-ball test adaptations.

the specimen is inexpensive and wear measurement is simple. This machine enables the precise determination of antiwear (AW) properties and the coefficient of friction (μ). As shown in Figure 8.5, this simple geometry also enables the determination of the extreme pressure (EP) characteristics of greases and lubricating oils, based on welding tests that are standardized worldwide (see Table 8.1). In the four-ball test, a roller bearing ball is allowed to rotate under pressure and at a constant speed on three fixed steel balls, with the contact lubricated using an oil or a solid lubricant. The gradual increase of the normal force (contact pressure) then enables an accurate determination of the weld load, the AW protection, and the friction coefficient of the lubricant. During these tests, the driving or rotating ball wears down the load dependently, seizes, and then welds to the three stationary balls. This indicates that the wear marks or the EP level of the lubricant have been exceeded on the three stationary balls, and leads to the effects of different oils and additives.

During recent years, several adaptations of the four-ball apparatus have been developed to acquire additional information on the pitting load capacity and the shear stability of polymer-containing lubricants. In this case, surface-modified steel balls (see VW-PV-1444) and a variety of tapered roller bearings (VW-PV-1417, DIN 51 350 part 6 or CEC L-45-T-98) are used (see Figure 8.5d). In addition, further modifications of the test adapters enable the determination of μ -values and the temperature behavior of a lubricant within the roller bearing. In accordance with test procedure VW-PV-1454, the test adapter used determines the steady-state operating temperature, temperature increase, and the friction of the test bearing in relation to the respective lubricant, using an axial thrust ball bearing. More recent results obtained

Table 8.1 Four-ball apparatus test standards.

Application	Test method
Standard test method for wear-preventive characteristics of lubricating fluids	ASTM D 4172
Wear-preventive characteristics of lubricating grease (four-ball method)	ASTM D 2266
Standard test method for the determination of the friction coefficient of lubricants using the four-ball apparatus	ASTM D 5183
Measurement of EP properties of lubricating fluids (four-ball method)	ASTM D 2783
Measurement of EP properties of lubricating grease (four-ball method)	ASTM D 2596
Standard test method for determination of load-carrying capacity and mean Hertz load	FTMS No, 791 b Method 6503.2
Determination of EP and AW properties of lubricants – four-ball apparatus	IP 239/85
Standard test method for lubricants using the Shell four-ball apparatus	DIN 51 350
General working principles	DIN 51 350, Part 1
Weld load of liquid lubricants	DIN 51 350, Part 2
Wear load of liquid lubricants	DIN 51 350, Part 3
Weld load of solid lubricants	DIN 51 350, Part 4
Wear load of solid lubricants	DIN 51 350, Part 5
Shear stability of polymer-containing lubricants	DIN 51 350, Part 6
Viscosity shear stability of transmission lubricants – tapered roller bearing	CEC L-45-T-98
Testing of lubricants – Determination of shear stability of lubricating oils containing polymers– Testing in the four ball tester	ISO/WD 998 877
Mechanical shear stability of engine oils	VW-PV-1450
Pitting load capacity of solid lubricants	VW-PV-1417
Pitting load capacity of liquid lubricants	VW-PV-1444
Standard test method for temperature increase in the axial thrust ball bearing adapter (ARKL)	VW-PV-1454

using this test adapter have shown that the steady-state oil sump temperatures measured can be transferred to transmissions and industrial gears, depending on the lubricant, after being adjusted to the realistic load and speed ratio referring to the application. As ever, today's numerous specifications for gear and hydraulic lubrication oils and for all types of grease and paste require four-ball data for most lubricants. The most common test standards used for the four-ball apparatus are listed in Table 8.1.

8.3.2

Brugger Apparatus and Reichert's Friction–Wear Balance

The Brugger apparatus (according to DIN 50 347) and Reichert's friction–wear balance are both important tools for determining the wear characteristics of water-containing and non-water-containing metal-working fluids, hydraulic fluids, and

Table 8.2 Reichert's friction–wear balance and Brugger apparatus test standards.

Test machine	Application	Test method
Reichert's friction–wear balance	Standard test method for determining the pressure compensation capacity using the frictional wear–balance according to Reichert	VKIS worksheet No. 6
Brugger	Testing under boundary lubricating conditions using the Brugger apparatus	DIN 51 347
Apparatus	General working principles Procedures for greases	DIN 51 347, Part 1 DIN 51 347, Part 2

greases. Today, most manufacturers in the metal-working industry specify wear-data according to Reichert or Brugger, so as to ensure an adequate quality standard and quality control for their metal-working and hydraulic fluids. The most common test standards are listed in Table 8.2, and these wear tests will be included in the development of virtually every new formulation. For this test, a cylindrical roller is firmly clamped using a lever-handle system, and then pressed crossed-axially against a slip ring, by applying a normal force (see Figure 8.6a). The slip ring is then allowed to rotate cross-directionally to the roller. In accordance with Reichert, the lower third (approximately) of the test ring is first dipped into the test fluid. After a propagation of 100 m at a constant speed of the rotating slip ring, the elliptical wear mark produced on the roller's surface is measured. For the Brugger test, the slip ring is rotated for

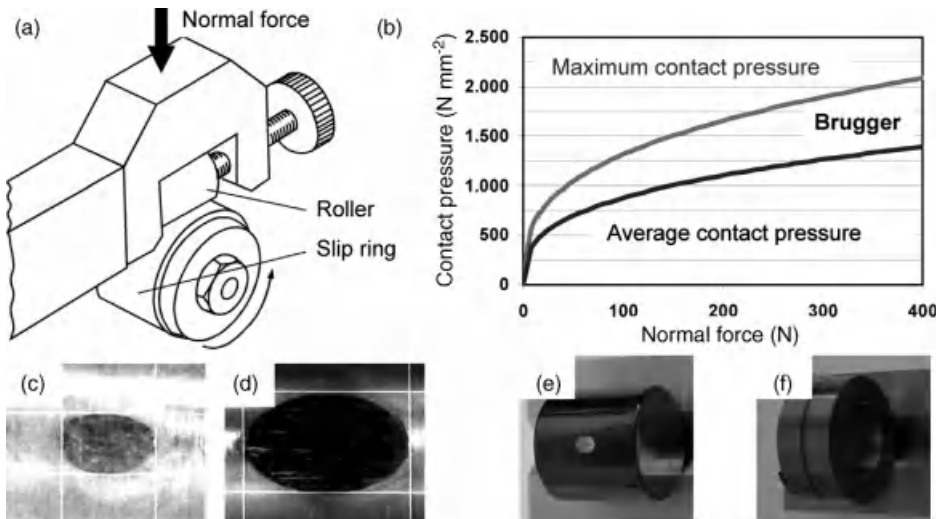


Figure 8.6 (a) Schematic representation of Brugger and Reichert's friction–wear balance; (b) The Brugger rig applied normal force and contact pressure graph; (c–f) Examples of wear marks: (c) canned milk; (d) cola; (e) DLC coating; (f) an example of a race track wear mark on the slip ring.

30 s with 5 ml of the test fluid lubricating the friction contact; notably, it is essential that the fluid remains on the surface throughout the test period. Based on the wear marks created and measured, the average specific contact pressure can be recalculated from the applied constant normal force, with the degree of wear being related to the wear rate. Both, the Reichert friction–wear balance and the Brugger apparatus equalize the contact pressure by producing smaller or larger wear marks. Graphs of the maximum and average contact pressure occurring in the test arrangement are shown in Figure 8.5b, while examples of wear marks measured on the Brugger apparatus are shown in Figure 8.5c–f.

8.3.3

Falex Test Machines

Falex test machines are mostly standardized by the American Society for Testing and Materials (ASTM), and used for the testing of lubrication oils, greases, solids, and surface materials. Worldwide, these test machines are widely used to measure and evaluate the properties of tribological contacts.

8.3.3.1 Falex Block-on-Ring Test Machine

The Falex block-on-ring test machine is used as a developmental and quality-control instrument to simulate the sliding and oscillating wear between lubricated and dry conditions (see Figure 8.7a). The pressure chamber and heater cover enable testing at elevated temperatures and in noncorrosive gases. The test geometry consists of a rectangular test block that is loaded on a rotating or oscillating ring, such that a

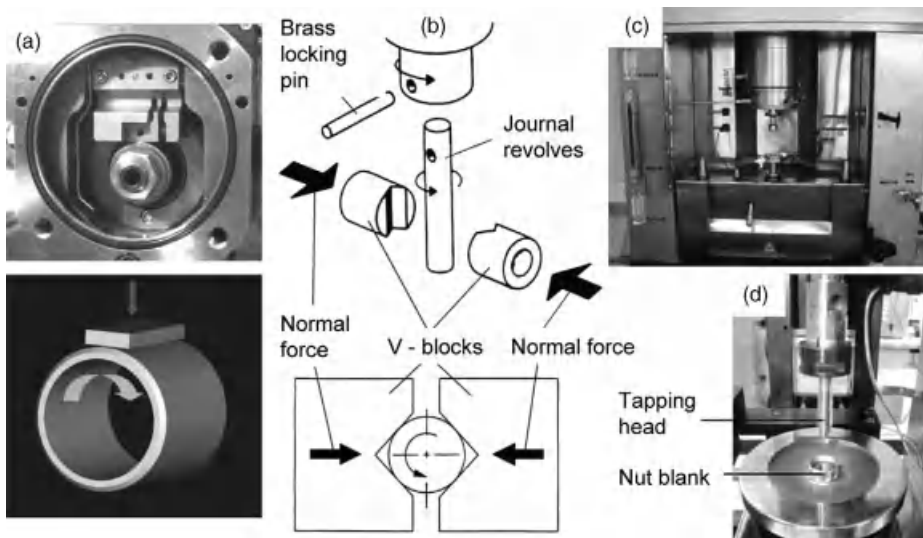


Figure 8.7 The Falex test machines. (a) Block-on-ring test machine; (b) Schematic of the pin and vee block test machine; (c) High-performance multispecimen test machine; (d) Tapping torque test machine.

uniform contact velocity profile is created. The block can then be replaced by a ball (to increase the contact pressure) or a conforming block (to reduce the contact pressure). The test blocks can be machined to test a wide variety of products. The test machine has a variable test load (<4000 N) and speed (<3000 rpm), and employs a heated test chamber (150 °C or 302 °F; higher temperatures can be used if special seals are available), and a high-pressure test chamber (<10 bar or <145 psi) for using noncorrosive gases or in the regulation of humidity, while the on-line measurements of friction, temperatures, and total wear are additional features. Details of the test standards are listed in Table 8.3.

8.3.3.2 Falex Pin and Vee Block Test Machine

The Falex pin and vee block test machine is the oldest industrially standardized friction and wear test machine. In this case, a rotating journal pin is first pressed between two blocks with V-notches, after which the normal force is increased gradually at a constant rotational speed. The scuffing load is determined at the point when the pin, having a softer neck, breaks at the designated breaking point; hence, if a lubricant withstands the applied force then the wear-loss of the softer pin is measured. The Falex test, a schematic of which is shown in Figure 8.7b, is conducted at ambient temperature; the test standards acquired are listed in Table 8.3. The tests are run at fixed speeds, enabling loads of up to 13 350 N (3000 lb; 1350 kg) for different test materials, while controlling on-line wear, friction, load, and temperatures via the monitoring system.

8.3.3.3 Falex High-Performance Multispecimen Test Machine

The Falex high-performance multispecimen test machine represents an extremely flexible test instrument for conducting industrial simulations (see Figure 8.7c). The multispecimen machine can be used for almost any tribological investigation that involves sliding or rolling contacts. Currently, over 60 standard adapters are available for performing a variety of simulation tests, including sliding wear, abrasion, erosion, forming, impact, and different rolling/sliding ratios. This test machine enables any combinations of high load (<10 000 N; 2250 lb; 1000 kg), high speed (<10 000 rpm), and high-temperature testing (up to 800 °C; 1470 °F). The PC-controlled monitoring system enables the programming of both the acceleration (<1000 rpm s⁻¹) and loading profiles (<1000 N s⁻¹). Today, the automatic simulation of dynamic conditions and start–stop cycles, variable flexibility enabling the simulation of the effects of low-component stiffness, and on-line measurement of friction, speed, load, and temperature are typical standards. Details of the present-day test standards used worldwide are listed in Table 8.3.

8.3.3.4 Falex Tapping Torque Test Machine

The Falex tapping torque test machine was developed to enable the repeatable and precise characterization of cutting lubricants (see Figure 8.7d). In this test, a Procunier tapping head performs tapping operations, while the torque produced on a nut blank is monitored using a load cell. In this way, the efficiency of a cutting fluid can be determined in accordance with ASTM D 5619 (see Table 8.3). Tapping

Table 8.3 ASTM test standards for Falex test machines.

Test machine	Application	Test method	
Falex block-on-ring	Calibration and operation of the Falex block-on-ring friction and wear-testing machine	ASTM D 2714	
	Wear life of solid-film lubricants in oscillating motion	ASTM D 2981	
	Test method for wear-preventive properties of lubricating greases using the (Falex) block-on-ring machine in oscillating motion	ASTM D 3704	
	Ranking resistance of materials to sliding wear using block-on-ring wear test	ASTM G 77	
	EP properties of lubricating greases	ASTM D 2529	
	EP properties of lubricating fluids	ASTM 2729	
	Ranking resistance of polymeric materials to sliding wear using block-on-ring wear test	Proposed STM	
	Measuring wear properties of dry-film solid lubricants using a block-on-ring machine in unidirectional motion	Proposed STM	
	Falex pin-and-vee block ^{a)}	Endurance (wear) life and load-carrying capacity of solid-film lubricants	ASTM D 2625
		Method for measuring wear properties of fluid lubricants (Falex method)	ASTM D 2670
Measurement of EP properties of fluid lubricants (Falex pin-and-vee block methods)		ASTM D 3233	
Evaluating thin-film lubricants in a drain and dry mode using a pin-and-vee block machine		ASTM D 5620	
Properties, antiwear, friction and corrosion protection of fluid lubricants – Falex machine		IP 241	
Falex high-performance multispecimen test machine		Test method for wear rate and coefficient of friction of materials in self-lubricated rubbing contact using a thrust washer testing machine	ASTM D 3702
	Test method for wear-preventive characteristics of lubricating fluids (four-ball method)	ASTM D 4172	
	Coefficient of friction using a four-ball wear test machine	ASTM D 5183	
	Wear-preventive characteristics of lubricating grease (four-ball method)	ASTM D 2266	
	Wear testing with a pin-on-disk apparatus	ASTM G 99	
Falex tapping torque	Test method for comparing metal-removal fluids using the tapping torque test machine	ASTM D 5619	

a) Included in Federal Test Methods (FTM) and OEM specifications.

- FTM-791-3807.1, FTM-791-3812.1.
- Chrysler Corporation 461-C-84-01, 461-C-84-02, 461-C-84-03.
- Ford Motor Company FMC-BJ1-1.

simulation via tapping operations in standardized nut blanks (e.g., aluminum, steel, stainless steel), drilling, reaming, and anti-forming simulations are possible using this test machine. A roll-forming adapter which is used to characterize rolling fluids has a dual speed range (10–450/20–900 rpm) and a data-acquisition system that enables the torque trace and torque averages to be stored. Subsequently, average torque values can be plotted and compared with a reference in order to determine the efficiency of the lubricant or coating under test.

8.3.4

Timken Test Machine

The Timken test machine (see Figure 8.8a) is licensed by the Timken company, which manufactures steel and bearings. The machine is essentially used to determine the anti-scoring protection afforded by greases and lubricating oils, in accordance with ASTM D 2509 and D 2782. However, it may also be used to determine wear resistance or adhesion strength of coatings supporting variable speed and pneumatic loading. Typically, gear oils and EP greases applied to the roller bearings used in industrial plants must meet Timken specifications. The lubricant test is conducted in a friction arrangement which comprises a cuboid-arranged block and a rotating test cup (see Figure 8.8b). The test is run with a lubrication oil circulation system, which can be adjusted variably, and with a grease feeder with a feed volume of 45 g min^{-1} . The normal force (load stage), which is increased gradually, is first brought into friction contact via the test block, after which weighing the test block and test cup enables any

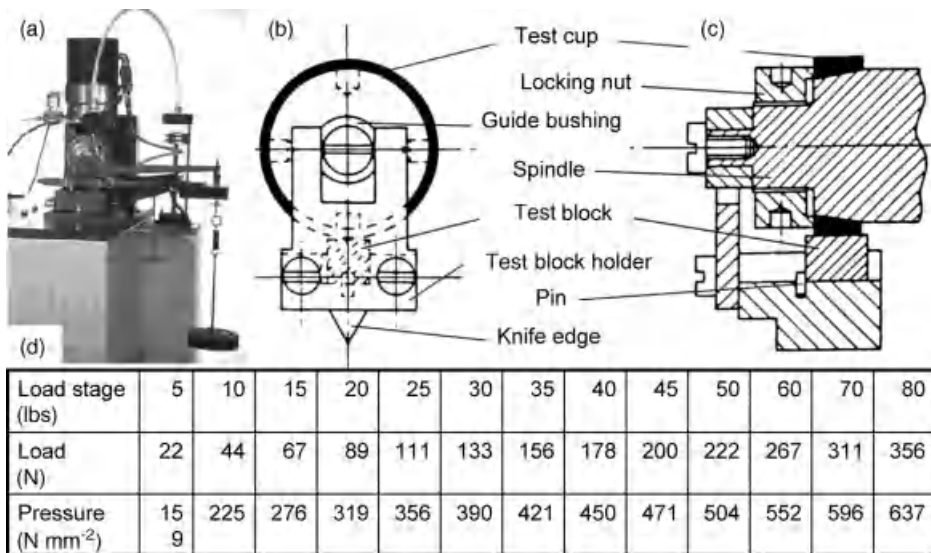


Figure 8.8 The Timken test machine. (a) Timken test rig; (b) Schematic of the test set-up; (c) Cross-sectional view of the test set-up; (d) Timken load stages and contact pressures.

Table 8.4 Test standards for Timken test machines.

Application	Test method
Measurement of load-carrying capacity of lubricating grease (Timken)	ASTM D 2509 IP 326/83
Measurement of EP properties of lubricating fluids (Timken)	ASTM D 2782 IP 240/92
Standard test method in the mixed-lubrication regime using the Timken test machine	E-DIN 51 434
General working principles	E-DIN 51 434, Part 1
Procedures for lubricating oils	E-DIN 51 434, Part 2
Procedures for lubricating greases	E-DIN 51 434, Part 3
Standard test method for liquid and plastic lubricants using the Timken test machine	VDEh, SEB 181 302

wear-loss to be determined. Normally, the duration of the test at each load stage is 10 min at a speed of 800 rpm. Any scuffing that occurs between the test cup and the test block will depend on the applied normal force and will, initially, lead to score marks on the surfaces of the test pieces. Scuffing is connected with a sudden drop in the rotational speed and/or with an increased noise level. If scuffing occurs during a load stage, a non-scuffing test run in the previous load stage must be proven and documented as the determined so-called “good-load-stage,” together with the total wear of the test block and test cup (test ring). With the Timken system, greases are tested at ambient temperature, and lubricating oils at 40 °C (104 °F). Today, the Timken rig, a schematic representation of which is shown in Figure 8.8c, remains a very important test tool in the steel industry.

Among the test standards listed in Table 8.4, Timken specifies a lubricant for bearing applications as having a good-load of 45 lb (20 kg; 200 N). In order to meet the requirements of antiwear, the steel industry normally defines a maximum weight loss of 5 mg and 6 mg at a good-load-stage of 40 lb (18 kg; 178 N), though higher good-loads will very often lead to an increased degree of wear (cf. Figure 8.8d).

8.3.5

High-Frequency Reciprocating Test Machines

8.3.5.1 High-Frequency Reciprocating Rig (HFRR)

The HFRR is a microprocessor-controlled reciprocating friction and wear-test system which enables the rapid, repeatable assessment of the performance of fuels and lubricants. It is particularly suitable for wear-testing relatively poor lubricants (e.g., diesel fuels), and for boundary friction measurements of engine oils, greases, and other compounds. The HFRR test for diesel fuel lubricity gained CEC “A” (approval) status in September 1996 following an extensive round-robin program. Other test standards based on the HFRR system are listed in Table 8.5.

Table 8.5 Test standards for high-frequency reciprocating test machines.

Test machine	Application	Test method
HFRR	Measurement of diesel fuel lubricity	CEC F-06-A-96
	Standard test method for evaluating the lubricity of diesel fuels by use of the high-frequency reciprocating rig (HFRR)	ASTM D 6079
SRV	Assessment of lubricity by use of the high-frequency reciprocating rig (HFRR)	IP 450/2000
	Part 1 test method	BS ISO 12 156-1
	Automotive fuels – diesel – requirements and test methods	EN 590
	Gas oil – testing method for lubricity	JPI 5S-50-98
	Standard method for measuring the friction and wear properties of EP lubricating oils by use of the SRV test machine	ASTM D 6425
	Standard test method for determining the EP properties of lubricating greases by use of a high-frequency linear oscillation (SRV) test machine	ASTM D 5706
	Standard test method for measuring the friction and wear properties of lubricating grease using a high-frequency, linear-oscillation (SRV) test machine	ASTM D 5707
	Tribological test method using a high-frequency, linear-oscillation test machine (SRV);	DIN 51 834
	General working principles	DIN 51 834, Part 1
	Determination of measured friction and wear quantities for lubricating oils	DIN 51 834, Part 2
	Determination of the tribological behavior of materials in reaction with lubricants	DIN 51 834, Part 3
	Definition of data formats for test results	DIN 51 834, Part 5
	Tribological test method for solids using a high-frequency, linear-oscillation test machine (SRV)	DIN 51 834, Part 6
Textile machinery and accessories – needle and sinker lubricating oils for weft knitting independent needle machines – part 2 Minimum requirements synthetic oil-based	DIN 62 136, Part 2	

8.3.5.2 High-Frequency, Linear-Oscillation Test Machine (SRV)

The high-frequency, linear-oscillation test machine (Schwing-Reib-Verschleißprüfgerät; SRV) is designed to simulate very small displacements under very well-known conditions of load, speed, and environmental control. It is used to investigate the typical scuffing phenomena that occur in automotive components, and also in aircraft and machines that vibrate. The effects of humidity and operating conditions on the surface degradation of coatings and materials can be tested using such a machine.

The test methods cover procedures for determining the EP properties of lubricating fluid and greases in high-frequency, linear-oscillation motion. Further test methods cover procedures for determining the μ -values of a lubricating oil or grease, and its ability to protect against wear when subjected to high-frequency, linear-

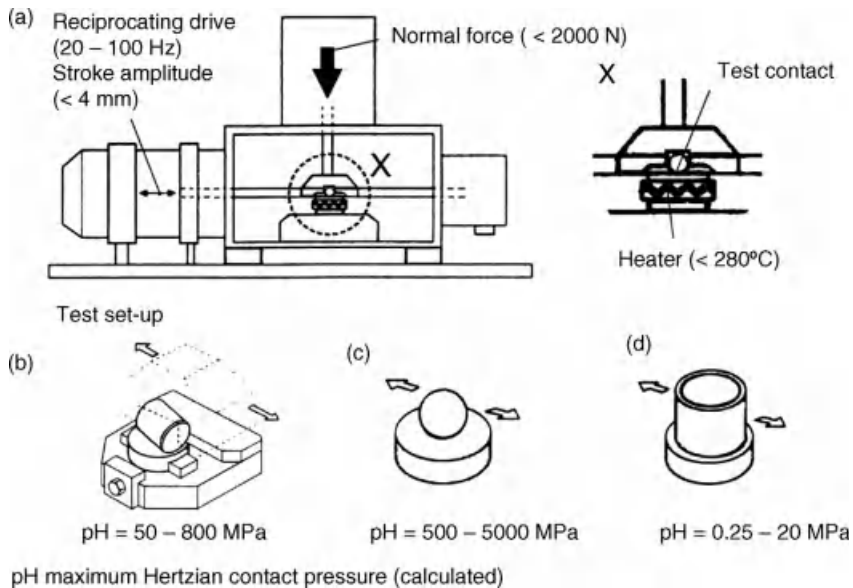


Figure 8.9 High-frequency, linear-oscillation test machine (SRV). (a) Specimen set-up; (b) Cylinder/disk contact; (c) Ball/disk contact; (d) Ring/disk contact.

oscillation motion at a test load of 200 N, a frequency of 50 Hz, a stroke amplitude of 1.0 mm, duration of 2 h, and temperature within the range of the test machine, specifically, ambient to 280 °C (536 °F). Other test loads (e.g., 10–1200 N for model SRV-I, 10–1400 N for model SRV-II, and 10–2000 N for model SRV-III and SRV-IV), frequencies of 5–500 Hz and stroke amplitudes of 0.1–4.0 mm can be varied, if specified. The precision of this test method depends on the conditions stated, and on test temperature of 50 or 80 °C (122 or 176 °F). Average wear scar diameters on balls and μ -values are determined and reported. Further test modes include the linear reciprocation testing of scuffing under variable humidity, using electrical contact measurements by normal load variations, or surface fatigue evaluation. A schematic of the test arrangement is shown in Figure 8.9, and some important test standards are listed in Table 8.5. One major advantage of using the SRV machine is the capability of performing systematic property studies, both simply and quickly, using only small amounts of lubricant. The determination of properties which differ from those of the test standards does, however, require sufficient experience with this test machine, as does the interpretation of any test results obtained.

8.3.6

Mini Traction Machine (MTM)

The MTM is a computer-controlled, precision traction-measurement instrument which enables the fully automated traction mapping of tribological contacts, lubri-

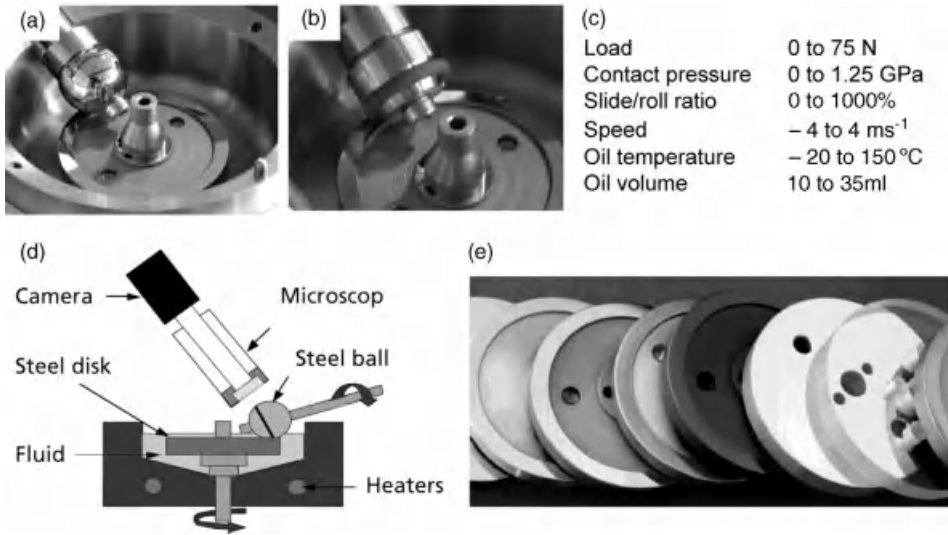


Figure 8.10 Mini-traction machine (MTM). (a) Standard test specimens configuration; (b) Soft compliant contact; (c) Test parameters; (d) Schematic of the test set-up; (e) Nonferrous metals and others materials.

cants, and other fluids. The machine simulates the lubrication regime found in nonconforming components such as cams, valve trains, gears, and rolling element bearings. The test contact is formed between a polished three-quarter-inch (19 mm) ball and a 46 mm-diameter disk, each independently driven to produce a sliding/rolling contact (see Figure 8.10a). In order to conduct a test, a small sample of fluid is placed in the test reservoir, after which the system is phased through a series of loads, speeds, slide/roll ratios and temperatures, following any one of several standard test programs, or using a custom program defined by the operator. Typically, a complete series of traction and “Stribeck” graphs at five different temperatures up to 150 °C (302 °F) can be generated, guaranteeing repeatable test results. The MTM system provides a rapid means of evaluating the performance of new formulations of traction fluids at the development stage. The instrument has been designed so that high contact pressures, temperatures, and speeds can be achieved by means of a safe, compact, bench-mountable system. Whilst the MTM is recognized as being an important development tool for lubricants, no standardized test methods are yet available.

The characteristics of soft contacts differ from the more usual steel-on-steel contact. In particular, the lack of stiffness of a soft material means that there will be considerable elastic deformation of the specimen under load. Furthermore, elastic hysteresis of the materials means that there significant rolling friction will be present, in addition to the usual sliding friction. The MTM has been designed with the study of soft contacts in mind, through the addition of load feedback and a capability to calculate both the sliding and rolling friction. To produce a soft compliant contact in

the MTM, the upper specimen may be a soft ball or a readily available standard sized O-ring, supported by the O-ring holder (see Figure 8.10b).

The range of test parameters is listed in Figure 8.10c. When performing the standard test, the steel ball is loaded against the steel disk and run under mixed sliding/rolling conditions for a fixed duration. Periodically throughout the test, the ball is stopped, loaded in reverse against the glass disk, and a film thickness map recorded of the complete contact area. This allows film-thickness measurements to be taken of any reaction films as they form (as shown schematically in Figure 8.10d).

While the surface finish influences the lubrication regime, the material components affect the surface chemistry in the contact (additives reaction). By studying specific applications, the MTM specimens can be manufactured from a broad range of materials (see Figure 8.10e); the typical nonferrous metals available include bronze, copper, brass, or aluminum alloys, while other available materials are tungsten carbide, glass, elastomer disks, and elastomer O-rings. Coated specimens such as diamond-like carbon (DLC) can also be tested. For example, electroless nickel plating can lead to the deposition of a layer of nickel–phosphorus alloy (containing various proportions of phosphorus) on specimens. A wide range of tests using the MTM system have been reported [2–6].

8.3.7

Low-Velocity Friction Apparatus (LVFA): The Tribometer

The General Motors low-velocity friction apparatus (LVFA) was designed during the 1960s, and has since proved capable of enabling the highly repeatable evaluation of friction–velocity characteristics at low sliding speeds [7, 8]. The LVFA uses a small-scale annular part that has been manufactured from the original friction material, in a wet clutch, wet brake, or torque-converter application, running against a steel counterpart. The LVFA uses a flywheel coast-down to evaluate a full range of sliding speeds, whereby the normal load is applied by deadweights through a lever at the bottom of the apparatus. The variable-speed friction tester (VSFT) [9] and the Tribometer [10–12] are modified versions of the LVFA. Notably, the Tribometer tests employed in Europe are also very similar to the LVFA [13, 14].

8.3.8

Diesel Injector Apparatus

The diesel injector apparatus enables an evaluation of the shear stability of polymer-containing fluids. The test methods measure the viscosity loss (%) of polymer-containing fluids, as evaluated by a diesel injector apparatus procedure using European diesel injector test equipment. The viscosity loss reflects the polymer degradation that occurs by shear at the nozzle. The test apparatus is defined by a CEC L-14-A-93 procedure, while the ASTM test methods differ from CEC L-14-A-93 in terms of the time required for calibration. When testing, a sample of 170 ml of lubricant is subjected, for a specified number of cycles, to a shear stability test in the apparatus. The kinematic viscosity is determined (at 40 °C for hydraulic fluids and at

Table 8.6 Test standards for the diesel injector apparatus.

Application	Test method
Evaluation of the mechanical shear stability of lubricating oils containing polymers (fuel injection pump)	CEC L-14-A-93
Test method for fuel-injector shear stability test (FISST) for polymer-containing fluids	ASTM D 5275
Standard test method for shear stability of polymer-containing fluids using a European diesel injector apparatus	ASTM D 6278
Standard test method for shear stability of polymer-containing fluids using a European diesel injector apparatus at 30 and 90 cycles	ASTM D 7109
Determination of the shear stability of polymer-containing oils – diesel injector rig method	IP 294/83
Determination of the shear stability of polymer-containing oils	DIN 51 382

100 °C for crankcase oils) before and after application of the shear stress, with shear stability being defined by the relative viscosity loss. According to DIN 51 382, the number of cycles should be 30 for crankcase oils, and 250 for hydraulic fluids; in contrast, the ASTM scheme proposes that the viscosity loss should be evaluated after both 30 and 90 cycles of shearing. The ASTM D 2603 sonic shear test has also been used for a similar evaluation of shear stability, though the limitations are as indicated in the transfer to applications. To date, no detailed attempt has been undertaken to correlate the test results of the diesel injector apparatus with those of the sonic shear test method. Notably, although the ASTM D 5275 test method may also be applied to shear oils in a diesel injector apparatus, it tends to produce different results (as detailed in Table 8.6).

8.3.9

Further Standardized and Non-Standardized Test Machines and Test Methods

In addition to the tribological mechanical–dynamic test machines and test methods described in Sections 8.3.1–8.3.8, several other important test procedures that are currently used for the mechanical–dynamic testing of tribological contacts are summarized in Table 8.7. Although some of these test machines and methods are obsolete, they are still used worldwide in many laboratories [15–24].

8.4

Tribology of the Gearbox, Transmission, and Transfer Case

8.4.1

Variety of Gear and Transmission Types

Using the principle of mechanical advantage, gearboxes, transmissions and transfer cases provide a speed-torque conversion commonly known as “gear reduction” or

Table 8.7 Other standardized and nonstandardized test machines and test methods.

Test machine	Application	Test method
Roll stability test apparatus	Standard test method for roll stability of lubricating grease	ASTM D 1831
SKF (EMCOR) anti-rust rig of lubricating grease	Determination of rust prevention characteristics	IP 220/93 DIN 51 802
Water-washout apparatus	Standard test method for determining the water washout characteristics of lubricating grease	ASTM D 1264 IP 215/93 DIN 51 807, Part 2
ASTM torque test apparatus	Standard test method for low temperature torque of ball bearing grease	ASTM D 1478
IP low-temperature torque apparatus	Determination of low-temperature torque of lubricating grease	IP 186/93
ASTM leakage test apparatus	Standard test method for leakage tendencies of automotive wheel bearing greases	ASTM D 1263
Sonic probe-type apparatus of polymer-containing oils	Standard test method for sonic-shear stability	ASTM D 2603
Shell DeLimon rheometer	Standard test method for determination of delivery resistance using the Shell DeLimon rheometer	E-DIN 51 816, Part 1 ^{a)}
Evaporation loss tester	Standard test method for engine and hydraulic oils for determination of the evaporation loss and sediments	WOLF ^{a)} Specification
Incline tribometer	Standard test method for the determination of friction coefficients	H. Schmidt Specification

a) Obsolete but still in use.

“speed reduction,” from a higher-speed motor to a slower – but more forceful – output, or *vice versa*. Gearboxes have found use in a wide variety of different stationary and mobile applications; for example, gears and transmissions are used in agricultural, industrial, construction, mining, and automotive equipment. In addition to an ordinary gearbox or transmission equipped with gears, such equipment contains many more machine components, including bearings, synchronizers, wet clutches, and seals. Typically, different types of hydrostatic drive and/or electrical adjustable-speed drives are attached to the connecting shafts, in order to transmit power and torque. In many areas of machine design, torque transfer plays a decisive role; an overview of the various types of torque transfer currently used is provided in Figure 8.11.

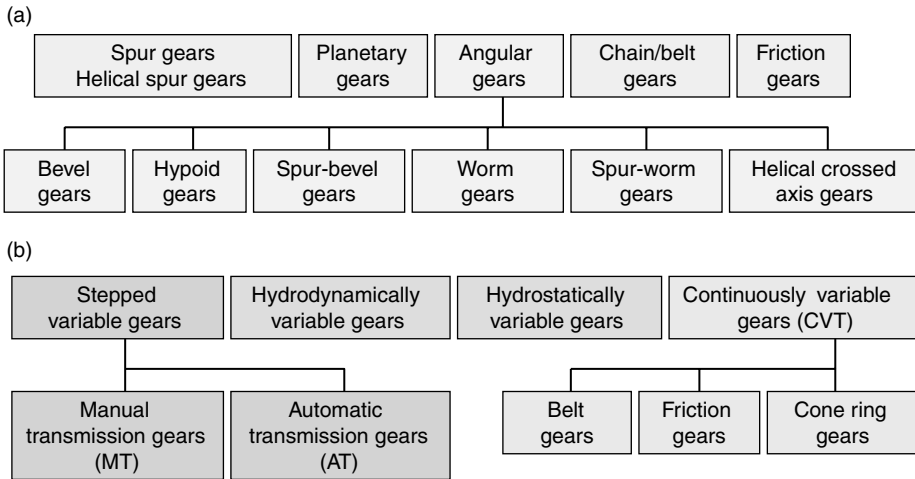


Figure 8.11 Gearbox types, transmission types, and transfer cases. (a) Constant gear ratio; (b) Variable gear ratio.

8.4.2

Gears and Roller Bearings

8.4.2.1 Gears

Significant differences are also apparent between the tribology of gear drives [25, 26] on the one hand, and that of journal and rolling bearings [27] on the other hand, since the lubrication conditions that characterize the sliding/rolling contacts in toothed wheels will differ from those in journal or roller bearings. As noted above in Figure 8.1, the lubrication conditions in tooth contacts and in roller bearings are often difficult, since in general the toothed wheels and roller bearings in a gearbox will have the main requirements for the lubricant and surface treatments. Consequently, the gear type will represent an element of particular concern; frequently, toothed wheels will differ in their gear types, which very often occur in gearboxes in mixed form. In general, the various gear types or arrangements of toothed wheels and axes will determine the classification of the whole gearbox, transmission, or transfer case. Some current, often-used examples of different gear types, with constant gear ratios, are illustrated schematically in Figure 8.12, while gears with variable gear ratios are shown in Figure 8.13a (belt gear) and Figure 8.13b (friction gear).

Each of the above-mentioned types of torque transfer entails specific tribological requirements that must be met in order to ensure the reliable function of both the machines and plant. Consequently, due to the high load of the tooth contacts, the heavily loaded lubricants in hypoid gears will require lubricating oils that are highly oxidation-stable, and which also demonstrate a very good scuffing and scoring and wear load capacity. At the same time, the formation of a load-capable and separating film thickness for sufficient lubrication and cooling of the sliding rolling contacts in hypoid gears will require a lubricant with an adequately high viscosity at the operating

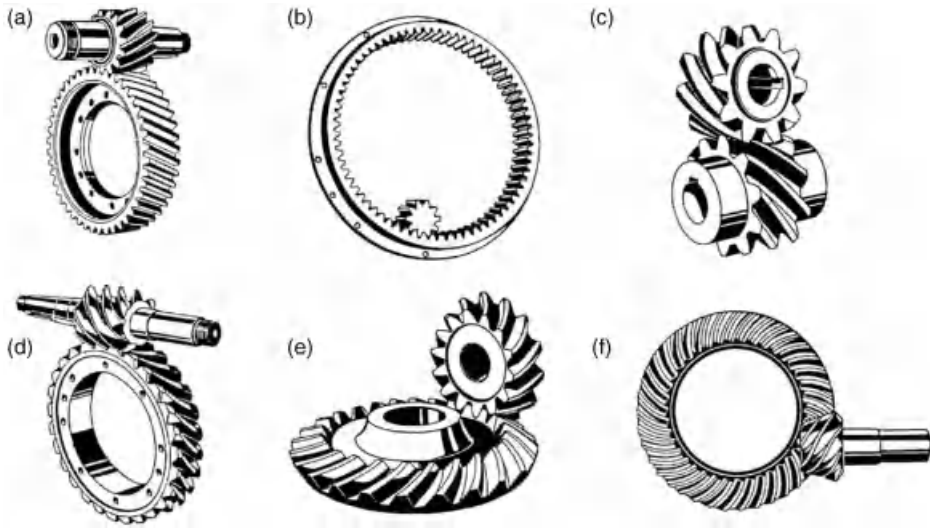


Figure 8.12 Examples of different gear types with constant gear ratio. (a) External helical spur gear; (b) Internal spur gear; (c) Helical crossed-axis gear; (d) Cylindrical worm gear; (e) Bevel gear; (f) Hypoid gear.

temperature. In contrast, whilst the lubricants used in hydrodynamic gears, as in torque converters, hydrodynamic wet clutches or retarders, do not require a good scuffing and scoring load capacity, they must be highly oxidation-stable. Due to the viscosity-dependent losses, those lubricants are used in hydrodynamic gears should have a much lower viscosity at operating temperature when compared to the

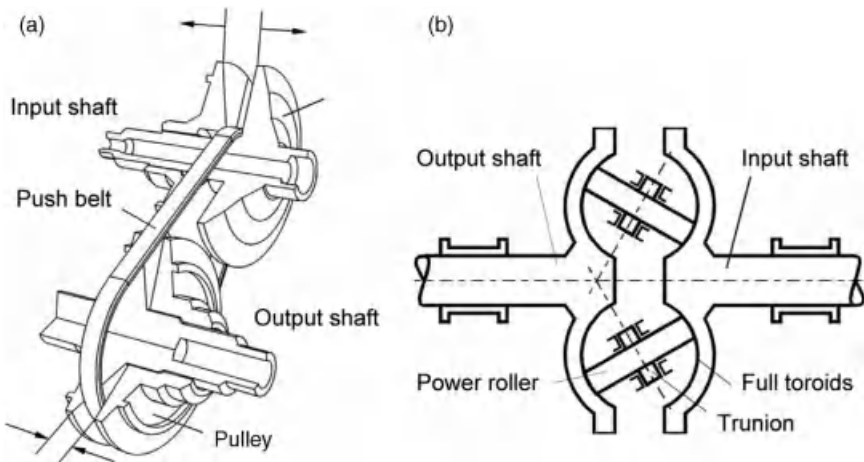


Figure 8.13 Schematics of different gear types with variable gear ratios. (a) Van Doorne push belt drive (belt gear); (b) Torotrak full toroidal traction drive (friction gear).

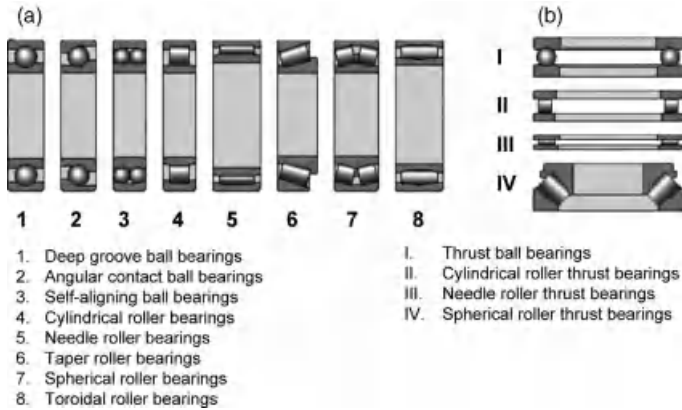


Figure 8.14 Roller bearing types for industrial and automotive gear applications. (a) Roller bearings with radial and axial load capacity; (b) Thrust roller bearings.

lubricants used in hypoid gears. All of the above-mentioned gear types are used in machines and plant construction with variable exposure times. Thus, the demands made on these gears will be closely connected to those made on the gear lubrication oils, and should be viewed from an industry-wide perspective in terms of their service life and oil-drainage intervals.

8.4.2.2 Roller Bearings

The various types of roller bearing found in today's gearboxes, transmissions, or transfer cases often occur in mixed form (see Figure 8.14). Roller bearings are normally composed of two rings, rolling bodies, and a cage. The bearings may be categorized as several basic types, according to their inner design, the shape of the rolling bodies, and directions of the forces that can be retained. The basic types of rolling bearing are standardized internationally [28–30]. Each type of bearing is produced in a variety of designs, the properties of which may differ from the basic form shown in Figure 8.14. From a tribological point of view, when selecting the bearing type during the gear construction phase, certain important facts must be taken into account. The primary consideration is the amount and type of load that is to be transferred. With regards to the reliability of a gearbox, consideration must also be made of the way in which the bearing will be lubricated, the design of the seating, and the bearing's operational parameters (e.g., speed and thermal conditions), as well as requirements for accuracy, installation, and dismantling.

8.4.3

Gear and Roller Bearing Tribo-Performance Test Rigs

8.4.3.1 Older Test Rigs Used for Gear and Axle Application

The IAE Test The Institute of Automotive Engineers (IAE) gear and lubricant test machine is used for load-carrying tests of steam turbine oils. The qualification test

method for evaluating the load-carrying properties of oils in the IAE gear machine is specified as Procedure B of the standard IP 166/77 at a test oil temperature of 70 °C (158 °F) and a drive gear speed of 4000 rpm. The IAE machine could be used to evaluate the extremely important functional properties of transmission, gear, and industrial oils. A good correlation was noted between the results obtained with the IAE machine, and with the four-ball tester. Whilst, today, the test standard IP 166/77 is obsolete, the IAE method is still in use.

The Ryder Test Typically, the Ryder gear-test rig is used to obtain a scuffing or load-capacity rating for aviation oils. The load-capacity rating is derived only from scuffing criteria (scuffing is one of several surface-deterioration mechanisms that affect the life and durability of aircraft bearings and gear hardware). Following its long-term role as a qualification test, the Ryder gear-test method has acquired a large database. Indeed, the US Navy has supported efforts to provide Ryder-like load-capacity data for gas turbine and gearbox oils. As a consequence, these efforts have expanded the scope of oil characterization beyond the perspective of a pass/fail or ranking of oils, such that scuffing performance is considered to be the sole criterion.

In providing continuity between the older Ryder gear load-capacity data and current or future oil-characterization methods, the Ryder method ranks oils with regard to a scuffing failure event. The new gear-oil test methods characterize oils with regards to traction behavior (e.g., friction, gear efficiency). The introduction of high thermal stability (HTS) oils and, in particular, of corrosion-inhibited (CI) oils, has emphasized the need for a greater testing sensitivity for oils with a lower-than-average lubricating performance. A poor lubricating performance, as determined by the Ryder test, becomes apparent as a superficial form of scuffing (“micro-scuffing”). Other gear failures that should be covered by using the new test methods include fatigue life (“pitting”) and superficial pitting (“micro-pitting”).

The L-20 Test The L-20 test is a performance test for gear lubricants at low speed and high torque. This test procedure once covered the GL-4 performance of gear oil, but has since been replaced by the L-37 procedure (although the L-20 is still used for screening and research). The L-20 test is used to determine the load-carrying, wear, and EP characteristics of gear lubricants in hypoid axle assemblies, under conditions of low speed and high torque. The procedure axle is operated at 62 rpm and 68 Nm of torque, with no cooling water until the lubricant temperature reaches 60 °C (140 °F). The axle is then operated for 30 h at 62 rpm and 3650 Nm of torque, with the lubricant temperature being cycled between 93 and 121 °C (200 and 250 °F).

The L-33-1 Test The L33-1 test method checks gear lubricants for American Petroleum Institute (API) category GL-5 performance. This method is used for evaluating rust- and corrosion-inhibiting properties while oils are subjected to water contamination and elevated temperature. An electric motor, specially selected hypoid differential housing assembly, cooling fan, heating lamps, and heated storage box serve as the procedure apparatus. The differential housing assembly is operated for

4 h at 2500 rpm and 82 °C (180 °F) lubricant temperature, with a defined volume of distilled water mixed in the lubricant. The unit under test is then placed in the storage box and stored for 162 h at 52 °C (125 °F). At the end of the procedure, the procedure parts of the assembly are rated for the presence of rust, with all internal moving parts (ring, pinion, bearings, differential gears, etc.) being evaluated.

The L-37 Test The L-37 test is a performance test for gear lubricants at high-speed, low-torque, followed by low-speed, high-torque. This test method is used to determine the load-carrying, wear, and EP characteristics of gear lubricants in hypoid axle assemblies. A specially selected rear axle assembly, engine, and transmission, and two large dynamometers serve as the procedure apparatus. The axle under test is operated for 100 min at 440 rpm, 146 °C (295 °F) lubricant temperature, and 1070 Nm of torque; followed by operation for 24 h at 80 rpm, 135 °C (275 °F) lubricant temperature, and 4720 Nm of torque. The tested parts are evaluated when the procedure has been completed.

The L-42 Test The L-42 test procedure reveals the performance of gear lubricants in axles under high speed and shock loading. The aim here is to evaluate the anti-scoring properties of gear lubricants under high-speed and shock conditions, with the performance of the test lubricants being compared to that of reference oils. A specially selected rear axle assembly, engine, transmission, special axle-mounting assembly, and two large dynamometers serve as the procedure apparatus. A break-in is conducted at moderate speed and load at a lubricant temperature of 107 °C (225 °F); this is followed by a series of moderate accelerations and decelerations with temperatures approaching 138 °C (280 °F). The final series of runs consists of high-speed accelerations with rapid decelerations. The tested parts are evaluated when the procedure has been completed.

The L-60-1 Test The L60-1 test procedure measures the thermal and oxidative stability of gear lubricants. This method is used to determine the deterioration of lubricants under severe thermal and oxidative conditions. A gear-case assembly of two spur gears, two copper strips, a bearing, a temperature-control system, an alternator, a motor, and a regulated air supply serve as major parts of the procedure fixture. The spur gears are rotated under load at 1750 rpm input for 50 h. The lubricant temperature is maintained at 163 °C (325 °F), and airflow through the lubricant is controlled at 22.1 mg min⁻¹ for the procedure's duration. The physical and chemical properties of the oil and deposits on the gears are evaluated on completion of the procedure. The above-mentioned test standards for gear and axle applications are listed in Table 8.8.

8.4.3.2 FZG Gear-Test Rig

The FZG gear-test rig is specified in DIN 51 354 part 1 [31]. The FZG rig (shown schematically in Figure 8.15) is a test machine with a mechanical power circuit, in which the drive (slave) gearbox and test gearbox are connected by two torque shafts, by friction; on one shaft is located a clutch by which to apply the load. The temperature

Table 8.8 Tribo-performance test standards for gear and axle application.

Test machine	Application	Test method
IAE gear machine	Determination of the load-carrying capacity of lubricants – IAE gear machine method	IP 166/77 ^{a)}
Ryder gear-test rig	Load-carrying capacity of lubricating oils – Ryder gear machine	FTMS No. 791 C method 6508.2 ^{a)}
Axle gear	L-20 high-torque test	CRC L-20 ^{a)}
DANA model 30	L-33-1 moisture corrosion test	CRC L-33
Dodge (3/4 ton)	L-37 high-torque test	CRC L-37
	L-42 high-speed axle test	ASTM D 6121
L-60 model two steel spur gear	L-60-1 thermal and oxidative stability test	CRC L-60
		ASTM D 5704

a) Obsolete but still in use.

in both gearboxes can be set and controlled. The test rig is driven by an electric motor with a variable speed (usually 1500 rpm), that can be adjusted from 7.5 to 3000 rpm in two directions of rotation. The load can be applied either by using a weight system, or with the tension ratchet. The FZG gear-test rig has undergone much improvement during the past 10 years, mainly conducted by the Forschungsvereinigung Antriebstechnik (FVA, Frankfurt/Main, Germany) and by the Institute for Machine Elements

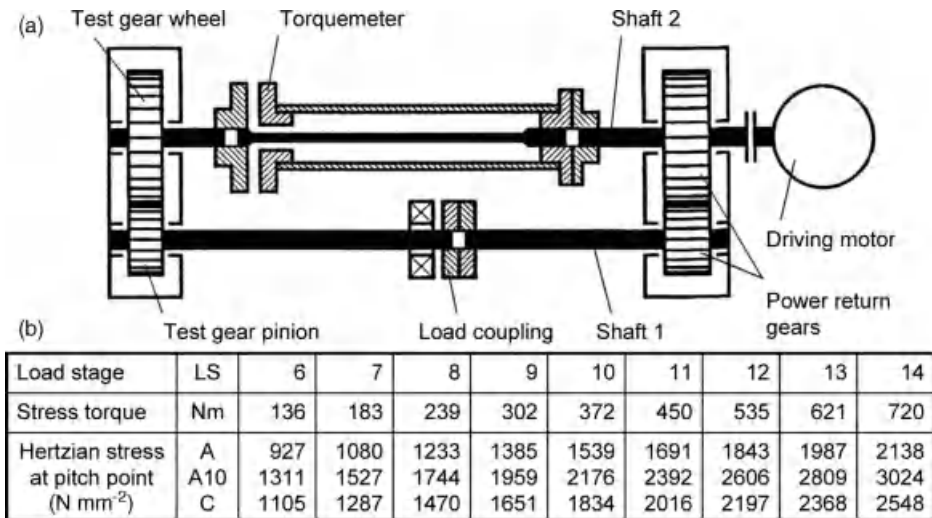


Figure 8.15 FZG gear-test rig. (a) Schematic of the FZG gear-test rig; (b) Maximum Hertzian stress at pitch point of different test gear sets (e.g., A-type, A10-type, and C-type gear sets).

and Gear Research Center (FZG, Munich, Germany). The FZG gear-test rig is currently widespread, and is the most widely accepted of application-related gear-tests. Gear-oil tests are specified by the Coordinating Research Council (CRC) and by the Coordinating European Council (CEC), which are nonprofit organizations that direct, by committee action, engineering and environmental studies on the interaction between automotive equipment and petroleum products. The sustaining members of the CRC are the API, the Society of Automotive Engineers (SAE), and automobile manufacturers (General Motors, Ford, Daimler, Chrysler, Honda, Toyota, and Volkswagen). The CEC is an industry-based organization that develops new test procedures for the performance testing of automotive engine oil, fuels, and transmission fluids. The CEC represents the automotive fuels, lubricants, additives, and allied industries in the development of performance tests, usually via the European industries ACEA, ATIEL, ATC, and CONCAWE.

8.4.3.3 The Micro-Pitting Rig (MPR)

The micro-pitting rig (MPR) test apparatus (Figure 8.16) is a computer-controlled, three-contact disk machine in which three counterface rings of equal diameter are positioned apart. In the middle of these three rings is located a smaller-diameter roller that is in contact with each ring. This arrangement allows the test roller to be subjected to a large number of rolling contact cycles during a short period of time, and leads to significant reductions in testing time. At a typical entrainment speed of 3.5 m s^{-1} , the central test roller will experience approximately one million contact cycles per hour. The rig has an on-board processor, which allows the speed, slide/roll

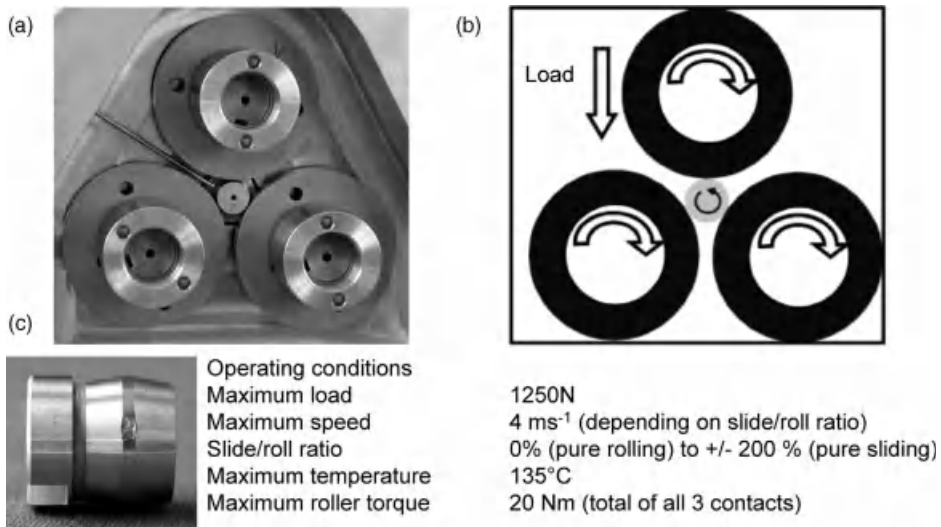


Figure 8.16 micro-pitting test rig (MPR). (a) MPR specimen test set-up, showing three counterface rings and a central roller; (b) Schematic of the MPR; (c) Pitting on specimen after testing.

ratio, temperature and load to be automatically controlled. Two servo-controlled motors are used to control the speeds of the rings and the roller separately, which allows any combination of slide/roll ratio and entrainment speed to be set. As the rig is computer-controlled, it is possible to perform both simple and complicated test steps under precisely controlled conditions. This allows the effect of tribological contacts to be studied, depending on the lubricants, materials and surface treatments, on micro-pitting, macro-pitting, or failure load testing. A dip lubrication system is used to supply lubricant into the contacts. The test requires a relatively small volume of fluid (150 ml), into which the two lower rings are dipped. An electric cartridge heater is used to adjust the temperature of the test chamber, which in turn heats up the test lubricant. A temperature probe is inserted into the test chamber, with the tip of the probe close to the contact region.

8.4.3.4 The High-Temperature Bearing Tester (HTBT)

The high-temperature bearing tester (HTBT) rig (Figure 8.17a) is a modified version of the old Unisteel Roller Bearing Test Apparatus [32]. The test machine drives a standard thrust bearing (deep groove ball or needle bearing) which is lubricated with approximately 180 ml of the test oil. The deep groove ball bearing assembly is shown schematically in Figure 8.17b. The upper half-standard thrust race has a pressed fit onto the drive shaft. In this modified version, the race drives three roller balls that sit in a special cage, while the lower half-standard thrust race is flipped over and press-fitted onto the retainer table. In this way, the flat surface of the lower race becomes the test specimen for the rolling contact of the balls and formation of the fatigue pit (see

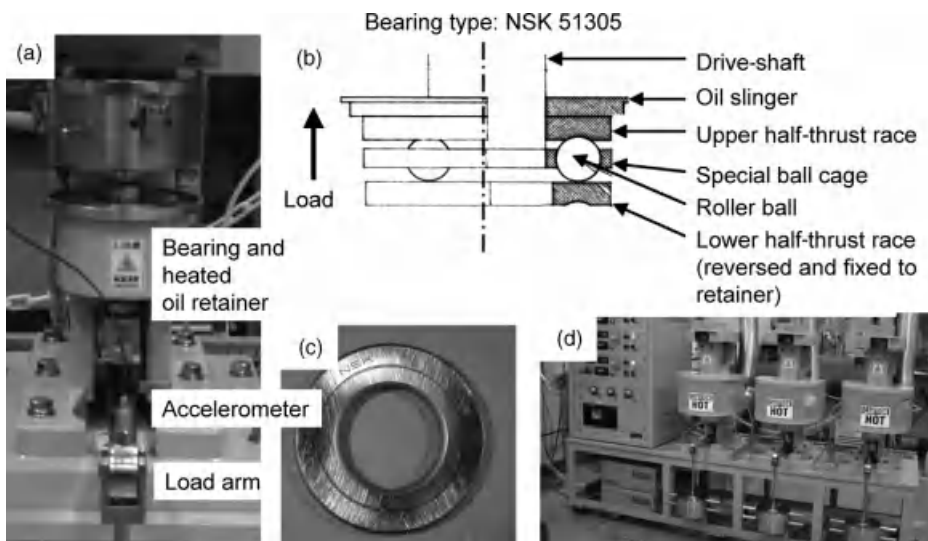
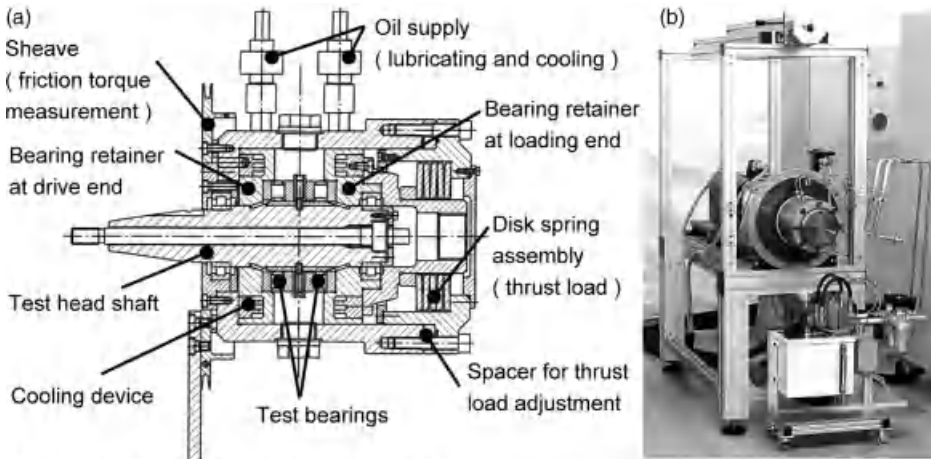


Figure 8.17 The high-temperature bearing tester (HTBT). (a) Accelerometer location; (b) Schematic of bearing assembly; (c) Pitting damage on the lower fixed reversed disk; (d) Test rig with three test units.

Figure 8.17c). A constant load, controlled oil sump temperature and rotation speed are applied to the bearing, and the number of rotation cycles required to produce a fatigue pit is then monitored. These data are acquired by having an accelerometer fixed in the load arm, and setting the vibration meter cut-off limit to stop the rig. Replicate tests are performed and the results analyzed using the Weibull distribution [33]; from this analysis, the fatigue life of the bearing when using a test oil can be obtained. The fatigue test procedures are listed in Table 8.15. Currently, the HTBT is available in which three or five similar test units that can be run simultaneously; a rig with three test units is shown in Figure 8.17d.

8.4.3.5 The Roller Bearing Test Apparatus (FE8)

The FAG Roller Bearing Test Apparatus FF8 (fat finger error) is one of the most versatile test rigs for lubricants; the machine itself is specified in DIN 51 819, part 1 [34]. The method specified serves to test lubricants such as lubricating oils [35] and greases of NLGI classes 1–4 (in accordance with DIN 51 818, part 2 and part 3) [36, 37], and to assess the effect that these lubricants have under service conditions on the frictional behavior and wear of angular contact groove ball bearings, tapered roller bearings, and cylindrical thrust roller bearings. A schematic of the test head and drive unit of the FF8 is shown in Figure 8.18. Two test bearings are mounted in the FE8 test head, subjected to a given axial bearing load (thrust load equivalent to 10, 20, 50, 80, or 100 kN), operated at a given speed (variable from 7.5 to 3000 rpm), and maintained (by means of a heating and/or cooling system) at any required operating temperature between ambient and 200 °C (392 °F). The operating temperature must be a multiple



Test parameters for the examination

Roller bearing type: angular contact ball bearings, taper roller bearings, thrust bearings

Test conditions: speed – temperature – thrust load

Lubricant: oil, grease

Figure 8.18 FAG roller bearing test apparatus FE8. (a) Cross-section view of the FE8 test head; (b) FE8 test rig.

of 10 K. Newer FF8 machines are equipped with an additional cooling device that enables the bearings to be tested at temperatures of -20°C (-4°F). When testing oils or greases with an external heating system, this is switched on after only a short running-in time, and the test is then started. Grease testing is continued until a loading time of 500 h has elapsed, or until lubrication of the bearings has become inadequate and the test bearing friction torque has assumed the switch-off torque for at least 10 s; at this point the apparatus will switch off automatically. For operating conditions beyond a loading time of 500 h, the weight loss in mass of the rolling elements and of the bearing cages (i.e., wear) is used to determine the AW characteristics of the grease. When testing lubricating oils, an external oil circulation system is added. In this case, a defined oil flow rate of $150\text{--}250\text{ ml min}^{-1}$ with a total oil volume of 5 liters is specified for a bearing oil inlet temperature of $80\text{--}120^{\circ}\text{C}$ ($176\text{--}248^{\circ}\text{F}$). The duration of the oil-test procedure is 80 h, using the thrust cylindrical roller bearings. This test is also referred to as the FE8 wear test.

Bearing geometries of 60 mm (bore diameter) have sufficient bearing size and mass to determine the lubricant-dependent weight losses of roller elements, bearing races, and the cage with sufficient accuracy, and with repeatability and reproducibility. By varying the cage material (e.g., polyamide, brass, or steel), the lubricant-dependent wear protection can be determined for different materials on steel contacts for greases and lubricating oils. The current FF8 roller bearing test apparatus is also suitable for monitoring the bearing fatigue life (pitting load capacity) in mixed-lubrication regimes [38, 39]. New test procedures have also been evaluated [39, 40] using modified FE8 test heads.

8.4.3.6 The Roller Bearing Test Apparatus (FE9)

The FAG roller bearing test apparatus FE9 has been developed for testing greases under field-relevant operating conditions. The service life of the grease is determined from the operating temperature, the load, and the rotational speed of the test bearing. A schematic of the FE9 test machine, and details of the cap assembly, are shown in Figure 8.19.

The machine is specified in DIN 51 821, part 1, while the test method A/1500/6000 has been standardized in DIN 51 821, part 2 [41] (see Table 8.9). The angular contact ball-bearing in the test head is filled with approximately 2 ml grease, after which the test bearing is loaded with a thrust load (axial test force) of 1500 N at a speed of 6000 rpm. The test temperature can be selected within the range $120\text{--}200^{\circ}\text{C}$ ($248\text{--}392^{\circ}\text{F}$) (maximum), and is applied to the test bearings via heating elements. These high temperatures of the tested greased bearing facilitate oxidation of the lubricant. The failure of a lubricant in the test bearing causes the required power input of the drive motor to be increased. However, if a given limit is exceeded, this results in an automatic shut-off of one test head, which means that the duration of one test run has been determined. For each FF9 test, a statistical evaluation is performed for five test runs on five different test heads, all operated under identical conditions; five (slightly) different test results (run-times) are used for the statistical determination of the 50% probability value of failure, using the method of Weibull [33]. The average duration is regarded as the service life of the grease. The test

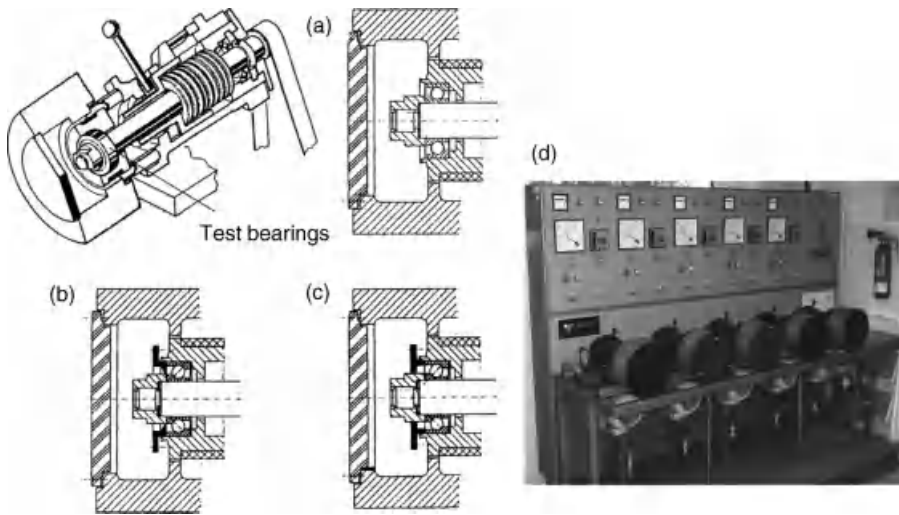


Figure 8.19 Schematic of the FE9 test head (grease test) and cap assembly. (a) Open cap assembly; (b) Covered cap without grease reservoir assembly; (c) Covered cap with grease reservoir assembly; (d) FE9 test rig.

conditions are considered to have been selected correctly if a 50% probability of failure occurs after 100–200 h. After more than 300 h, the test run normally stops automatically.

If a deviation is made from the standard test procedure, the speed can be reduced to 3000 rpm and the thrust load enhanced to 3000 or 4500 N in order to conduct tests under intensified mixed-lubrication conditions. In practice, however, it is accepted that at an operating temperature above 100 °C (212 °F), an increase in the operating temperature by 10–15 K will halve the service life of the grease in roller bearings. There is no benefit in running wear or fatigue endurance tests using the FE9 machine, as the size of the test bearings is too small to determine wear or pitting gravimetrically, and this leads to a relatively large scattering of the test results. Under FE9 (field-related) operating conditions, the nominal bearing fatigue life of the loaded test bearing (both calculated and validated statistically in terms of fatigue life in the catalogues of bearing manufacturers) is much longer than the service life of greases determined in the FE9 apparatus.

Table 8.9 Test standards for FE9 roller bearing applications.

Test method	Test machine	Application
DIN 51 821	FAG roller bearing test apparatus FE9	Test using the FAG roller bearing testing apparatus FE9
DIN 51 821, Part 1		General working principles
DIN 51 821, Part 2		Test method A/1500/6000

Table 8.10 Gear damage characteristics.

Type of damage	Characteristic
Wear	Continuous material wear ^{a)}
Scuffing and scoring	Sudden metal-on-metal contacts ^{a)}
Fatigue	Micro-pitting and pitting ^{a)}

a) Details of the main types of gear damage are provided in Ref. [42].

8.4.4

Types of Tooth Flank and Roller Bearing Damage

When designing a transmission, it is first necessary to ensure that all of the contact points (especially the gears and bearings) are adequately dimensioned and sufficiently supplied with lubricant under all operating conditions. Damage to the gears and bearings may often result from an overload combined with a too-high local stress on the material/lubricant combination being used. When a transmission is concisely designed, a lubricant containing the correct additives can be of great help in preventing damage to the gears and bearings and other transmission components, assuming that the materials and operating conditions are properly matched. Today, the types of damage are standardized and can be divided into three main categories (see Table 8.10). The different types of damage that occur with gears have been extensively documented [42], while details of bearing damage have been summarized by the bearing manufacturer Schaeffler (INA/FAG) [43] (see also Ref. [44]). Today, the need to conduct practical, field-related test procedures will require use of the test machines described in Sections 8.3 and 8.4.3, the aim being to protect roller bearings and tooth flanks in gearboxes, transmissions and transfer cases against the types of damage described in Sections 8.4.4.1–8.4.4.5.

8.4.4.1 Wear and Wear Performance Tests

For maximum gear efficiency and energy savings, low-viscosity lubricants are frequently used, as a greater transmitted power will lead to a higher temperature and thus to a thinner lubricating film. All of these tendencies will increase the probability of failure in gear contacts at low speeds, because of wear. Not only gears [45] but also roller bearings [46] experience continuous wear preferentially at slow circumferential speeds, under mixed or boundary lubrication regimes. Although, at present, there is no standardized wear calculation for gears and bearings, one approach has been proposed for gears [47], and another for bearings [48]. An example of a tooth flank displaying typical symptoms of wear is shown in Figure 8.20a, where the involute flank shape displays significant wear marks on the tooth-tip and tooth-root areas. In the case of more advanced wear, the damage extends to the center of the tooth flank. In bearings which have an inadequate or non-load-bearing or soiled oil film, nonuniform wear will occur in the contacts of raceways and roller elements. In tapered roller bearings, wear is often connected with the

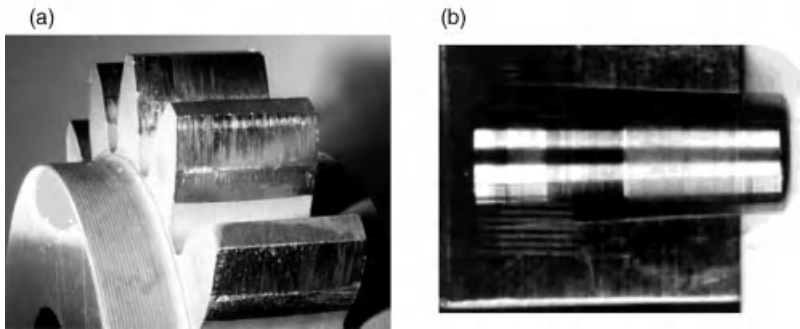


Figure 8.20 Examples of wear damage on tooth flanks and roller bearings. (a) Tooth flank with significant wear damage; (b) Roller element with striation as a result of wear in certain areas.

inadequate adjustment of the bearing arrangement (an example is shown in Figure 8.20b). Hardening processes may have a considerable effect on wear, with nitrided gearwheels displaying the least wear, and pairings consisting of case-hardened pinions and age-hardened wheels showing very high wear under comparable operating conditions. The correct lubricants and additives can have a favorable effect on wear load capacity if the lubricants are of high viscosity and also contain AW additives [49–51]. Some appropriate mechanical–dynamic test methods for evaluating the wear-load capacity of bearings and gears are detailed in Table 8.11.

More recently, new test methods based on a modified FZG gear-test rig have been developed to evaluate the load-carrying capacity of gear surface and lubricants. For low-speed conditions, a wear test using C-type gears at low pitch line velocity of 0.05 m s^{-1} (7.5 rpm) and two different temperatures (90 and 120 °C; 194 and 248 °F), has been developed and applied to many different lubricants to assess the response to different additives at high loadings of load stage 12 (C/0.05/90:120/12; DGMK project no. 377-1; see also Table 8.12 and Ref. [52]). Under such

Table 8.11 Mechanical–dynamic test methods for determining the wear load capacity for transmission applications.

Test method	Test machine	Application
ASTM D 4998	FZG wear gear-test rig	Standard test method for evaluating the wear characteristics of tractor hydraulic fluids
DGMK report no. 377-1		Method to assess the wear characteristics of lubricants – FZG test method C/0.05/90:120/10
DIN 51 819	FAG roller bearing	Test using the FAG roller bearing testing apparatus FE8
DIN 51 819, Part 1	test apparatus FE8	General working principles
DIN 51 819, Part 2		Testing of lubricating greases
DIN 51 819, Part 3		Testing of lubricating fluids

Table 8.12 FZG/DGMK project no. 377-1 wear load capacity test.**Test procedure of the FZG/DGMK wear load capacity test [36]**

Weight loss at	Test conditions	Duration	Load cycles on the test wheel
First test stage	C/0.05/90/12	2 × 24 h	2 × 12 500
Second test stage	C/0.05/120/12	2 × 24 h	2 × 12 500
Third test stage	C/0.05/90/12	1 × 48 h	1 × 25 000
	C/0.57/90/12		1 × 250 000
	C/0.05/120/12		1 × 25 000

Test procedure of the shortened FZG/DGMK wear load capacity test [36]

Weight loss at	Test conditions	Duration	Load cycles on the test wheel
First test stage	C/0.05/90/12	2 × 20 h	2 × 10 400
Second test stage	C/0.57/90/12	1 × 20 h	120 000
Third test stage	C/0.57/120/12	1 × 20 h	120 000

operating conditions, the lubricant's wear-protective additives are of particular importance. The test method according to ASTM D 4998 facilitates identification of the wear-protective capacity of lubricants, by using the FZG gear-test rig. Test method A/0.57/120/10 is also known as the "Chevron test"; in this case, the pitch line velocity is 0.57 m s^{-1} (150 rpm), but using A-type instead of C-type gears. These wear-intensive operational conditions have been developed to examine the long-term wear-protection capacity of universal tractor transmission oils (UTTOs). By modifying the ASTM test system described above, this method has been extended to 60 h duration to serve as a more precise test for vehicle, industrial, and hydraulic oils. By determining (gravimetrically) the weight loss of the test gear after 20, 40, and 60 h, the running-in and long-term wear of lubrication oils can be assessed satisfactorily. An important standardized performance test, which usually is applicable to most roller bearing types, can be run on the FAG Roller Bearing Test Apparatus FE8 (see Section 8.4.3.5).

8.4.4.2 Scuffing/Scoring and Performance Tests

The scuffing and scoring of tooth flanks occurs primarily at medium to high circumferential speeds, and on case-hardened gears. According to Refs [53, 54], the contacting surfaces will briefly weld together under these conditions, but the high relative speed of the contact surfaces one to another causes these welding bridges to be immediately torn back apart, such that the flanks will display the typical appearance of scuffing and scoring (Figure 8.21a). Subsequently, the damage will always appear on corresponding engaging flanks, often on the tooth tip and tooth root, where very high velocities are present. Damage from scuffing and scoring will

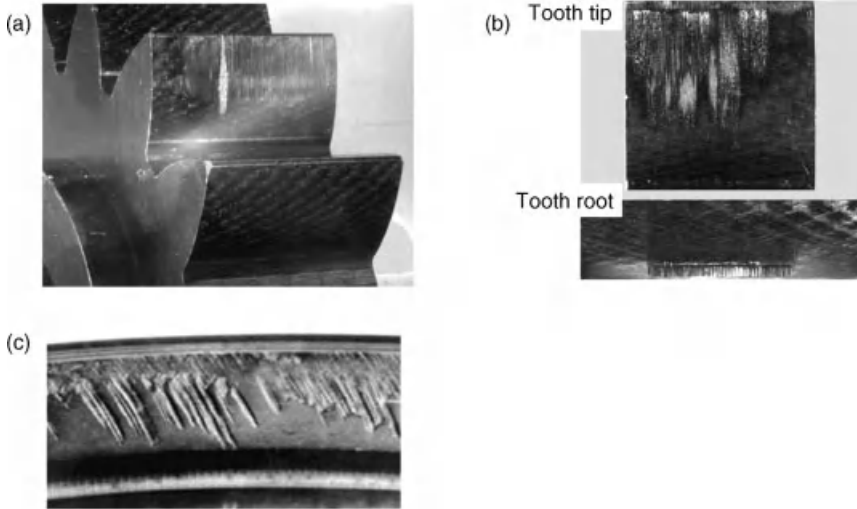


Figure 8.21 Examples of scuffing damage on tooth flanks and roller bearings. (a) Tooth flank with substantial scuffing damage; (b) Tooth flank with combined scuffing and wear damage; (c) Scuffing and scoring marks on the lip of the inner bearing race of a tapered roller bearing.

appear suddenly, and may even occur from a single incidence of overload. Such sudden scuffing and scoring can cause complete destruction of the tooth flanks, with freshly manufactured gearwheel surfaces that have not yet been broken-in being especially vulnerable. In fact, experience has shown that non-run-in gearwheels have only 20% of the scuffing load capacity of gearwheels with well run-in surfaces. Yet, by adding the appropriate EP additives to the lubricant it is possible to increase the scuffing load capacity more than fivefold.

The calculation of scuffing load capacity has been standardized for gears (according to Refs [55, 56]). Typically, the tooth tip will cause a mixture of wear and scuffing during gear tooth engagement (see Figure 8.21b), a phenomenon which is observed primarily in too-heavily stressed, non-profile-corrected gears [57–59]. Appropriate mechanical–dynamic test methods for evaluating the scuffing load capacity of gears are described in Table 8.13. Damage from scuffing and scoring occurs less frequently in roller bearings. Scuffing has been observed on full-type, large-size bearings, for example, in the gearboxes of cement mills. Details of this phenomenon have been reported, where it is referred to as “smearing” [60, 61]. Due to mixed lubricating conditions, or even at boundary regimes, at both high slide/roll contact stresses and at high contact speeds an adequate hydrodynamic oil film will be torn apart from forming between the rollers or roller faces, respectively. If the lubricant does not contain adequate AW additives, or if the operating viscosity of the lubricant is too low, then if the roller seating is too tightly adjusted or if there is warping due to thermal expansion or roller skew, or if the axial load on the cylindrical roller bearings is too high, it might be possible for local or extensive scuffing damage to occur on roller bearings. Likewise, welds and cracks might appear on the raceways and in the roller

Table 8.13 Mechanical–dynamic test methods for determining the scuffing load capacity for transmission applications.

Test method	Test machine	Application
DIN 51 354	FZG (EP)	Standard test method for lubricants using the FZG gear-test rig
DIN 51 354, part 1	gear-test rig	General working principles
DIN 51 354, part 2		Standard test method A/8.3/90 for lubricating oils
DIN technical report 74		Standard test method A/2.8/50 for greases
CEC L-07-A-95		Load-carrying capacity test for transmission lubricants
IP 334/93		Determination of load-carrying capacity of lubricants – FZG gear machine method
ISO 14 635-1:2000		FZG test method A/8.3/90 for relative scuffing load-carrying capacity of oils
ASTM D 5182		Standard test method for evaluating the scuffing load capacity of oils (FZG visual method)
FVA information sheet 243/5 rev.	FZG high-EP gear-test rig	Standard test method for determining the load-carrying capacity of high-EP oils using the FZG gear-test rig
CEC L-84-02		FZG scuffing load-capacity test for high-EP oils
ISO 14 635-2:2004		FZG step load test A10/16.6R/1 20 for relative scuffing load-carrying capacity of high-EP oils
FZG-L-42	FZG L-42 hypoid gear-test rig	Load-carrying capacity of hypoid gear lubricants

face and ring lip areas (see Figure 8.21c) and, in the case of full-type cylindrical roller bearings, also between the roller–roller contacts.

The “FZG EP Scuffing Tests” With the lubricant to be tested, specific gear teeth (A-type) are run at a constant speed with a pitch line velocity of 8.3 m s^{-1} (1500 rpm), and with an established initial lubricant temperature of 90°C (194°F). The test gears of type A used here have been adjusted to a shape which is particularly scuffing-sensitive. The FZG test method A/8.3/90 for lubrication oils has been standardized worldwide by ISO, ASTM, IP, CEC and DIN (see Table 8.13). The stress on the tooth flanks may be increased gradually; consequently, on completion of the test run (or after each load stage if testing is conducted in gradual steps; see Figure 8.15b), any changes on the tooth flank surfaces (e.g., flank damage, scoring) are recorded by description, photographs, tooth surface roughness measurements, or contrast printing. Any changes in the weight of the test wheels may also be determined gravimetrically. These test results can be transferred to other gears, and might even play a role in the design and calculation of gears, according to DIN 3990 [55]. Further procedures, such as A/16.6/90 and A/16.6/140, are also used as variations, but have not yet been standardized.

The “FZG High-EP Scuffing Tests” Oils with a high additive treat-rate (so-called high-EP gear oils, such as hypoid gear oils) are capable of withstanding the standard FZG test procedure for lubricating oils. FVA information sheet no. 243/5 revised and CEC test method L-84-A-02 describe mechanical test procedures for lubricating oils, primarily for use in highly loaded gear systems with and without hypoid offsets. In this case, three procedures have been defined in detail by the FVA [57]:

- the *load stage test*: procedure A10/16.6R/90
- the *shock test*: procedure S-A10/16.6R/90
- the *shock test at increased oil temperature*: procedure S-A10/16.6R/110.

All tests are run under enhanced operating conditions, with the rig being driven by an electric motor running at double speed of 2880 rpm, driving the gear wheel shaft. The direction of the drive is the reverse of that of the standard test method A/8.3/90, giving a corresponding pitch line velocity of 16.6 m s^{-1} , with a driving wheel (this is test 16.6R). Further aggravating test conditions include the use of A10-type test gears with a pinion face width of 10 mm, a required starting temperature of 90, 110, or 120°C (194, 230, or 248°F) in the oil sump, and visual assessment stipulated for these procedures. The test S-A10/16.6R/110 (shock test) can be used as a screening test for the CRC L-42 test [59]. To evaluate the oil’s load-carrying capacity for API GL-5 it is necessary to compare the results for the candidate oil with those from the ASTM reference oil no. 114-1. The ASTM reference oils can clearly be separated by approximately 1.5 load stages (LS). The pass reference oil no. 114-1 does not fail ($\text{LS} > 10$); fail reference oil no. 112-2 fails 100% at LS 9. Candidate oils meet or exceed the scuffing requirement of API GL-5 when the scuffing load stage is higher than that of ASTM reference oil no. 114-1 (see Ref. [62]).

8.4.4.3 Surface Fatigue/Micro-Pitting and Performance Tests

Surface fatigue, which is also termed “micro-pitting” or “gray staining,” is fatigue damage that occurs on the top material layer on the hardened and ground surfaces of machine components that are subject to changing dynamic stresses. Examples of such components are the tooth flanks of gear drives and the raceways and roller elements of roller bearings. The damage consists of the finest material cavities on the surfaces of the above machine elements, and can often be first detected as damage only under the microscope or by using a surface-measuring instrument. As the damage advances, however, these surface cavities become visible in the form of gray stains on the surface, and lead to profile shape deviations on the surfaces. This results in higher dynamics and further consequential damage, such as pitting, wear and breakage of the tooth or roller element. For case-hardened gears, gray staining can be observed on tooth flanks at almost all speed ranges, but tooth flanks with raw surfaces are particularly susceptible. Gray staining appears preferentially in the range of negative sliding velocities, or as fatigue damage when there is slippage underneath the pitch circle (surface fatigue failure) [63]. A tooth flank damaged by gray staining is shown in Figure 8.22a, while the effects of surface roughness and of the grinding process (Maag, Höfler, Reißauer) on the micro-pitting load capacity are detailed in Ref. [64]. In this case, tiny, very flat cavities also occur in roller bearings at relatively

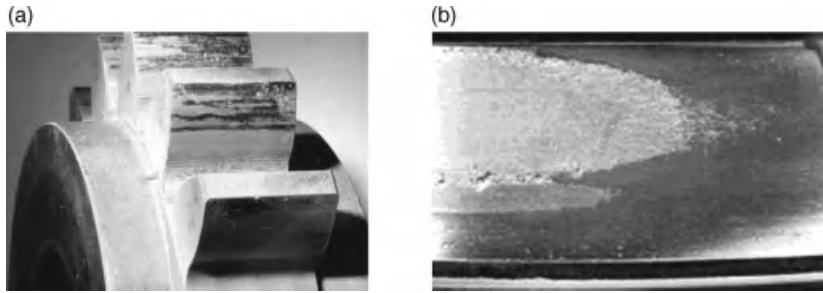


Figure 8.22 Examples of micro-pitting damage on tooth flanks and roller bearings. (a) Tooth flank damaged by gray staining or micro-pitting; (b) Roller bearing raceway damaged by gray staining or micro-pitting.

low loads when sliding/rolling ratio (slippage) is also present and, as they appear in large number, they resemble stains on the raceway. In this machine element, this effect is also referred to as gray staining or micro-pitting (see Figure 8.22b).

An appropriate lubricant that might have a favorable effect on gray staining must have both a sufficiently high viscosity and an appropriate lubricant additive system. The operating viscosity and operating temperature of the transmission are of exceptional importance when choosing a suitable additive system. Practice has shown that, although some lubricant additive systems have a high load-carrying capacity at a transmission operating temperature of 90 °C (194 °F), for example, their load-carrying capacity is low at an operating temperature of 60 or 120 °C (140 or 248 °F). Caution is necessary in the choice of an appropriate lubricant. At the instigation of the affected transmission manufacturers, the FVA developed the FZG micro-pitting load capacity test [65, 66] and a micro-pitting short test [67]. The most important of these test methods (see Table 8.14) have been developed as a decision aid in choosing the correct surface, surface treatment, and lubricant. The methods described in Table 8.14 are used to determine the micro-pitting load capacity. During

Table 8.14 Mechanical–dynamic test methods for determining the micro-pitting load capacity for transmission applications.

Test method	Test machine	Application
FVA information sheet no. 54/I-IV	FZG micro-pitting gear-test rig	Standard test method for determining the lubricants effect on the formation of micro-pitting – test method GF-C/8.3/90
DGMK-FVA project no. 259/4 Flender test		DGMK/FZG micro-pitting short test GFKT – C/8.3/90 GG-V 378, Flender test, determination of the lubricants effect on gear micro-pitting
MPR Test	MPR Test Rig	PCS instruments, micro-pitting in rolling contact bearings [68]

the coming years, the intention is to submit the test method as an ISO draft standard, driven by the wind-power industry, although there is as yet no standardized calculation procedure available.

The “FZG Micro-Pitting Tests” The FVA-FZG micro-pitting test is well established as the standard test method GF-C/9(10)/8.3/90 (FVA information sheet no. 54/I-IV for evaluating the micro-pitting characteristics of lubricants used in gear drives [65]). The FZG micro-pitting test consists of two phases: a load-stage (LS) test, followed by an endurance test. The LS test is used to evaluate the ability of the gear-lubricant in a tribological system to resist micro-pitting; this is determined under specified operating conditions (lubricant temperature, circumferential speed) in the form of a failure load stage. Subsequently, the endurance test provides information regarding the progress of damage after a large number of load cycles. This test is conducted at relatively high loads (failure LS 5–10), using C-GF-type gears as test gears, with a defined surface roughness ($R_a \geq \pm 0.5 \mu\text{m}$) [66]. This greater surface roughness facilitates the formation of micro-pitting on the test gears [65]. The test method provides accurate results, though at a relatively high cost, and is also quite time-consuming (up to 520 h). This FVA-FZG micro-pitting test has been supplemented by a standardized short-test method that enables the classification of candidate lubricants in a manner analogous to the FVA-FZG micro-pitting test [66]. Within the scope of the research project (FVA no. 259/4), the DGMK-FZG micro-pitting short-test method GFKT-C/8.3/90 was developed, and tested with lubricants for which the classification in the standard FVA-FZG micro-pitting test was well known. The new DGMK-FZG micro-pitting short test groups the candidate lubricants into classes of micro-pitting load capacity, analogous to the FVA-FZG micro-pitting test. The classes were seen to correlate well with those of the FVA-FZG micro-pitting test, with a good correlation between the average maximum profile deviation after running the DGMK-FZG micro-pitting short test, and the failure-LS of the FVA-FZG micro-pitting test. Moreover, the DGMK-FZG micro-pitting short test is considered to be a standardized short-test method suitable for differentiating the micro-pitting load capacity of the different candidate lubricants.

The “MPR Micro-Pitting Tests” Micro-pitting, as a rolling contact surface fatigue failure mechanism which occurs in rolling element bearings, can be also tested on the PCS Instruments MPR (see Section 8.4.3.3). Both, the test procedure and test specimens have been designed to reproduce the lubricated contact conditions which can lead to either micro- or macro-pitting [68].

8.4.4.4 Sub-Surface Fatigue/Pitting and Performance Tests

As in the case of micro-pitting, the formation of pitting on the surfaces of rolling contacts relates to a fatigue damage that can be observed on both age-hardened and case-hardened gears [69] or roller bearings [43] in all transmission types, and at all circumferential speeds [70]. In case-hardened gears, pitting occurs on few or often on only one damaged tooth flank (see Figure 8.23a), while the remaining tooth flanks show no sign of damage. In contrast to case-hardened gears, age-hardened gears very

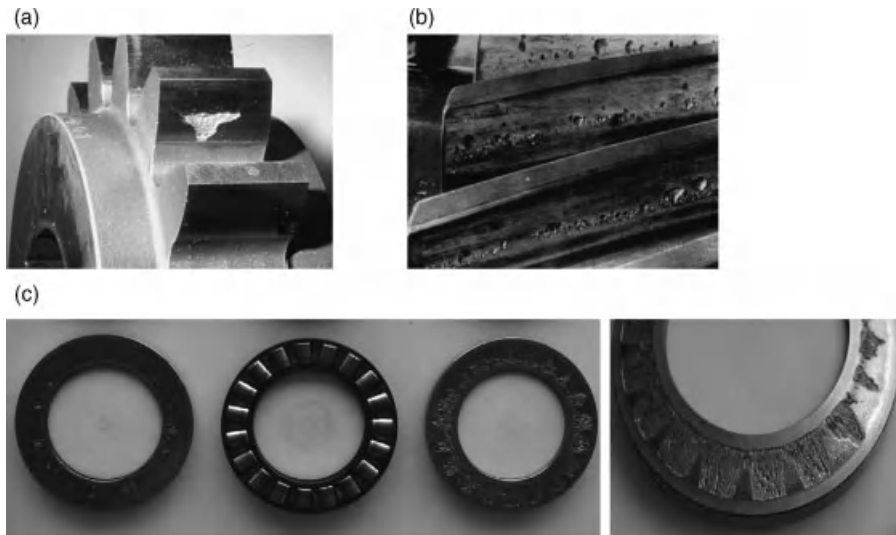


Figure 8.23 Examples of pitting damage on tooth flanks and roller bearings. (a) Case-hardened tooth flank; (b) Age-hardened tooth flank; (c) Cylindrical thrust roller bearings damaged by pitting.

frequently exhibit uniformly distributed pitting damage over the entire tooth width, and on all tooth flanks on the circumference (see Figure 8.23b). On gearwheels, pitting appears preferentially on the center of the tooth flank at the height of the pitch circle, but on bearings it appears mostly on rotating bearing rings in the load zone (see Figure 8.23c), where the greatest stress and largest stress cycle amplitudes are present. The fatigue limit values of the gear material or bearing material, and the stress cycle that falls within the material's fatigue and endurance limits, today serve as the basis for the calculation of the fatigue and endurance limits of the gear [43], and also for the design of bearings, in accordance with Refs [71, 72].

The results of recent studies have shown that the lubricant can, in principle, affect fatigue capacity [73, 74]. Indeed, in general an increase in the lubricant viscosity will lengthen the durability although, because of higher churning losses, it is not always possible nor practical to increase the viscosity of the lubricant in the transmission arbitrarily. At present, lubricants with much lower viscosity, such as “low-viscosity oils,” are increasingly being used in order to reduce churning losses, and thereby increase the transmission efficiency. This trend is most strongly observed in transmission fluids, such as automatic transmission fluid (ATF), manual transmission fluid, and axle oils [75–77]. Today, standardized test methods are available to study the effect of lubricants on pitting load capacity. In addition, some transmission manufacturers, including ZF Friedrichshafen [40], Volkswagen [78], and a large Japanese manufacturer, specify new transmission fluids based on test methods and test specifications that they have developed themselves. The most common test methods used for measuring the fatigue capacity of bearings and gears are listed in Table 8.15 and Table 8.16, respectively.

Table 8.15 Mechanical–dynamic test methods for determining the fatigue capacity of bearings for transmission applications.

Test method	Test machine	Application
IP 300/82	Four-ball apparatus	Rolling contact fatigue failure – modified four-ball machine method
VW-PV-1444		Pitting load capacity of liquid lubricants
Evonik RohMax		The effect of lubricating oils on bearing fatigue-life using the Evonik RohMax
Pitting Test		Pitting Test procedure
SNR LC106 101 N	SNR Roulements	Determination de l'endurance des matériaux à la fatigue de roulement (Determination of the durability of materials caused by fatigue of roller bearings)
Procedure 3	(French bearing manufacturer)	
Modified IP 305/79	HTBT – High-Temperature	Determination of the effect of lubricants on rolling fatigue resistance of bearing steels (deep-groove ball bearing test)
ball bearing test	Bearing Tester	
Modified thrust needle bearing test		Fatigue test of lubricating fluids (thrust needle bearing test)
ZF 702 232/2003	FAG FE8	ZF bearing pitting test
VW-PV-1483		Determination of oil influence on pitting load capacity of cylinder roller thrust bearings on mixed-lubrication

Table 8.16 Mechanical–dynamic test methods for determining the fatigue capacity of gears.

Test method	Test machine	Application
Gear pitting test		
FVA Information Sheet	FZG gear-test rig	Standard test method for determination of the effect of lubricant on fatigue capacity:
No. 2/IV	(standard)	PT C/9/90, PT C/10/90 (one-stage test) PT C/LLS/90, PT C/HLS/90 (load spectrum test)
CEC IT 067		PT C/9/120 (PT C/8/120 – Asian gear manufacturer)
FVA Information Sheet		Field-relevant pitting test (PTX gear type)
No. 371		PTX C/9/90 (120), PTX C/10/90 (120)
Gear micro-pitting test → terminate upon to pitting or fatigue damage		
FVA Information Sheet	FZG gear-test rig	Standard test method for determination of the lubricant on micro-pitting formation – GF C/8.3/90
No. 54/I-IV	(micro-pitting rig)	
DGMK-FVA Project		DGMK-FZG micro-pitting short test
No. 259/4		GFKT C/8.3/90

The “FZG Pitting Tests” For automotive applications, load-spectrum testing is often required at low (PT-C/LLS/90) and high (PT-C/HLS/90) loads [79]. The “field-relevant pitting test” has proved to be an appropriate method for testing pitting load capacity with regard to practical relevance, test duration, and reproducibility of the results [80]. Depending on the application profile, the test method is defined as either a single-stage test (for lubricant developers), or as an extended application test (for lubricant users). It is recommended that helical gears are mounted in the slave gearbox, and that lubrication is implemented as temperature-controlled splash lubrication. Each test run must be conducted with fresh oil, and with the oil level at the middle of the shafts. Gears of type PTX-C are specified in Ref. [81]; these are manufactured by ZF Friedrichshafen in a large production batch, within the specified tolerances. The results of the test procedures require at least three or more tests to be conducted under identical conditions, in order to determine a 50% failure probability of fatigue-life. For this, two procedures have been defined in detail by the FVA:

- Pitting test PTX-C/10/90: this is a single-stage test, LS 10, oil temperature of 90 °C (194 °F).
- Pitting test PTX-C/SNC/90: this is an application test as an extension of the single-stage test.

The PTX C/10/90 is carried out with additional test runs of the lubricant at LS 9 or 11, depending on the result of the previous stage test; the oil sump temperature is 90 °C (194 °F).

For special tests at different temperatures, the test designations for both procedures are modified appropriately.

8.4.4.5 Tooth Fracture

Until today, tooth fracture has been based exclusively on fracture mechanics, which are themselves dependent on the material (steel) of a toothing. Tribology does not have a direct influence on tooth fracture, and tooth fracture is mentioned here only for reasons of completeness. Indirectly, however, the lubricant can facilitate tooth fracture. If, for example, an overheating of the gear or lubricant (accelerated oil aging) leads to lubrication failure (or something similar), then any changes that occur in the metal structure of the toothing due to the overheating will, sooner or later, cause tooth fracture. Tooth fracture may also occur with teeth which have been pre-damaged by micro-pitting or pitting.

8.4.5

Gear Efficiency and Fuel Economy

Today, the major targets of transmission design are a higher efficiency, a higher torque capacity, and a reduced size under fuel economy aspects. Unfortunately, however, increasingly smaller transmissions with higher torques lead to higher operating temperatures. As friction in the transmission is responsible for temperature increases and efficiency losses, a reduction of such friction represents the main

means of improving efficiency and keeping the operating temperature low. The main features of transmission design to increase efficiency are a reduction of friction of the bearings and the rotary shaft seals, a reduction of sliding of the gear flanks, and a reduction of splashing and pumping losses of the lubricant. Losses in a gear system are classified as either load-dependent or speed-dependent, for example churning or sealing losses. In order to identify and compare the effects of lubricants on gear efficiency, two test methods are commonly used. For roller bearing applications, the VW-PV-1454 test (see Table 8.1) [82], which uses a modified four-ball apparatus adapter, whilst for a gear-test method the VW-PV-1456 test can be used [75, 76, 83], which employs a modified FZG gear-test rig. Both tests have proven successful for monitoring the efficiency of lubricating oils and additives.

The “FZG Gear-Efficiency Test” All FZG test methods measure and compare the torque loss which the driving motor imports into the mechanical power circuit to sustain the rotational movement during the operating conditions. To achieve this, another torque meter must be installed behind the input shaft of the driving motor; in these tests, the same gear-set types are used in the slave gearbox and test gearbox, and both gearboxes are filled with the same oil at an identical level. By using this method, the total losses in the no-load and load modes of operation can be measured to determine their dependence on gear type, oil and additive formulation, viscosity grade, oil fill level, rotational speed, and load. Both test gears have, furthermore, been equipped with an adjustable heating system which maintains equal oil sump temperatures in both gearboxes, separately [77, 84]. The main advantage of the above-mentioned procedure, in comparison with the older so-called “Ecotrans” test method (GFC-T-014-T-85) [85], is a more precise measurement of torque loss when using a torque meter. In the “Ecotrans” test method, the friction torque in the mechanical power circuit is calculated by measurement of the electrical input power of the driving motor; however, the rotational speed and load-dependent power input of the often different systems of electrical power input may lead to significant inaccuracies. An excellent comparison of the common FZG gear-efficiency methods currently in use is described in Ref. [77].

8.4.6

Transmission Trends with Regard to Tribology and Oil Aging

The reduction of oil aging in order to lengthen oil-drain intervals represents a major challenge in the design of new transmissions. At this point, gear manufacturers such as Daimler, Volkswagen, MAN, Volvo, Jatco, ZF, Eaton, Dana, and Getrag should be mentioned, as they have all played important roles worldwide in setting trends for both commercial vehicles and passenger cars. These companies have produced, and continue to produce, a wide variety of very different transmission types, and deliver them to other manufacturers of motor vehicles not mentioned here. The special transmission requirements set by these companies have major influences on the development of new driveline fluids, which must meet the specific requirements of different gearboxes, transmissions, transfer cases, and axle gears (differential gears)

in order to transmit, reliably, the power to the wheels. In Europe, most gearboxes that serve to change the gear ratio are manual transmissions, with synchronization, whereas in America and in the Asian Pacific they are mostly automatic or semi-automatic transmissions, or continuously variable transmissions (CVTs). With respect to these automatic or CVTs, the tribological aspect of the lubricant is responsible not only for the gear drive lubrication but also for the function-related operation of wet clutches, wet brakes, torque converters, retarders, or chains and push-belts. With respect to the current transmission and driveline component development for motor vehicles, the following trends – which are mainly customer-driven – have been observed:

- Drivers of motor vehicles expect modern cars to ensure an improved performance, a reduced noise emission, and a reduced fuel consumption. This trend is reflected in the increasing use of lubricants with a low viscosity, together with a reduced fill volume. Furthermore, multigrade oils are now used on a large scale, leading to a considerable reduction in fuel consumption.
- Vehicle operators welcome an improving reliability of the vehicles and increasing oil-drain intervals, so as to reduce the operative costs incurred.
- The requirements and specifications issued by the motor, transmission, and vehicle manufacturers intend to considerably extend the oil-drain intervals. Today's trend is to supply all transmissions with "fill-for-life" fluids and, indeed, many of today's manual transmissions and axle gears in passenger cars are operated with fill-for-life fluids (>300 000 km; >185 000 miles). With regards to automatic transmissions in passenger cars, these long oil-drain intervals will soon be achieved. For commercial vehicles, the oil-drain intervals required by manufacturers are currently experiencing an extension. The plan is to achieve transmission service lives of 500 000–750 000 km (310 000–435 000 miles) up to 1 000 000 km (620 000 miles), without draining.
- Legislation in industrialized countries has a major influence on lubricant formulations, mainly for reasons of environment-friendly fluids and disposal. Hence, the use of mineral-based oils is decreasing. Today's environmentally friendly, synthetic and ester-based base oils are often used for reasons of environmental protection. Due to their improved thermal oxidation stability, ester-based oils may be used together with polyalphaolefins (PAO) and hydrocracked (HC) base oils.

Thus, from the tribological aspect, the requirement for a better knowledge of the oil-aging process in gearboxes and transmissions has led to the creation of tools such as the modified FZG gear-test rig with oil-aging test set-up, and also field-based oil-aging test procedures.

The "FZG Synthetic Oil-Aging Test" A faster oil aging of lubricants can be simulated in a modified FZG back-to-back gear-test rig [86], the arrangement of which is shown schematically in Figure 8.24. For applications with long oil-drain intervals, an oil-aging test was developed using C-type gears under different loads, speeds, and temperature conditions. In this case, the lubricants are exposed to conditions of load

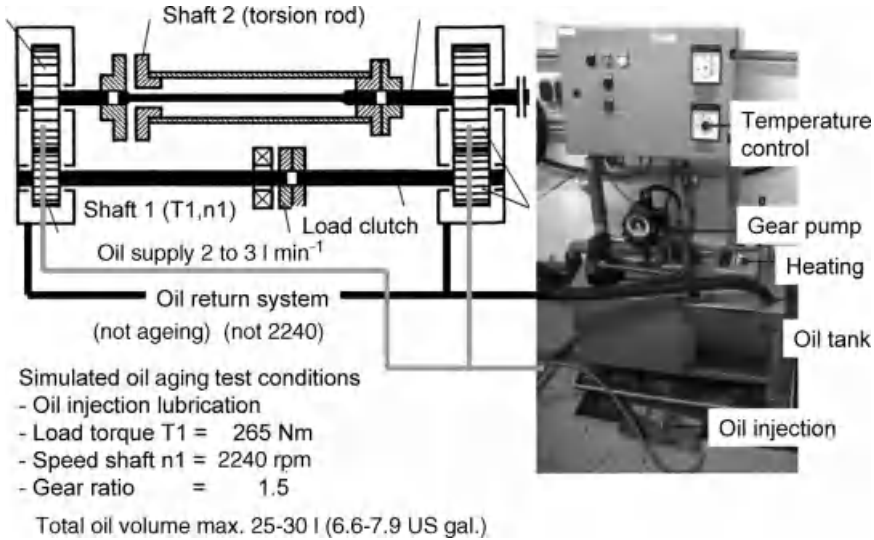


Figure 8.24 FZG gear-test rig with modified oil-aging test set-up.

and speed of bearings and gears encountered in standard transmissions and, in a spray lubrication device, to elevated oil temperatures of 110–130 °C (230–266 °F) to produce an enhanced thermal degradation over the run time. The oil-aging properties, and their effect on performance under these high-temperature conditions and in other component tests after aging, are correlated with those of reference oils. The different oil application-related aging test methods are described in Ref. [87]. Following a shortened duration of oil aging in the FZG rig, the same oil is further tested to determine the characteristics of any critical components. The different component test results for commercial oil brands are discussed in Refs [88, 89].

Further correlations of ATFs that have been aged synthetically using FZG test methods to evaluate wet clutch friction stability, compared to results obtained from field trials, are provided in Ref. [90]. The data in Figure 8.25 reveal that, by using these test results, oil-specific and application-specific lifetime limits (e.g., “logarithmic oil temperature/aging time curves”) can be derived, enabling determination of the effect of temperature on the lifetime of each of these critical components. When using the FZG oil-aging procedure, the analytical figures must be taken as an indication of oil modifications that can result in different possible effects on lubricant performance, and the capacity in the different components. These effects are heavily dependent on the oil type and the additives. For a specific investigation of the effects of extended oil-drain intervals, it is essential that the oil-specific and application-specific lifetime-limiting criteria are known, for example, from damage or from long-term investigations of the application. Aged samples from the application, run under known temperature and duration conditions, are also necessary to calibrate the aging conditions in the test rig described in Ref. [90].

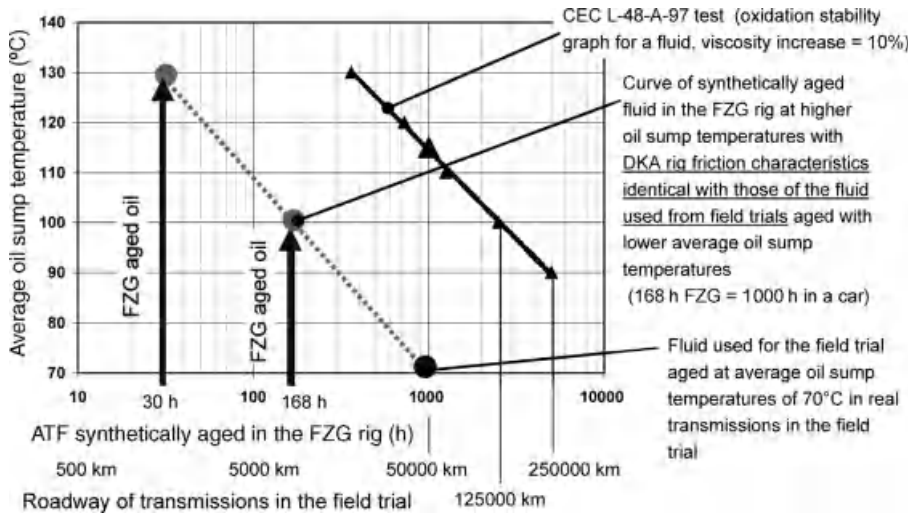


Figure 8.25 Shortened duration of field-related oil aging conducted with the modified oil-aging test set-up at the FZG gear-test rig.

8.4.7

Synchronizer Applications and Performance Tests

8.4.7.1 Area of Application

Manual transmissions are a common source of complaint from car drivers, because of poor or hard gearshifting. For that reason, the OEMs pay increasing attention to the friction properties of the synchronizing elements. Component harmonization and mass production imply that the same gearbox model must accommodate a wide range of different driving patterns. Within the field, there are very large variations between minimum and maximum operating conditions and, therefore, different expectations of shifting characteristics. More compact vehicles with smaller engines and better fuel economy require a wider range of gear ratios; as a consequence, larger gears are used for the lower ratios, thus increasing the demand for synchronizers to operate between shifts. Clearly, although there is more inertia to be stopped, there is less space to accommodate the synchronizer, and this has led to the development of double- and triple-cone synchronizers which multiply the number of friction surfaces and enable the design to be kept compact. However, the demand on stable friction coefficients will be increased, because there is more energy to dissipate in a tighter volume [91–93].

8.4.7.2 Function and Tribology of the Synchronizer

In a synchronized gearbox, the synchronizer components play a vital role in the shifting process. For example, they are used to accelerate the gear to be engaged, so that it can quietly mesh with the driving gear when the rotating speeds are synchronized. Synchronizers can be described as “mechanical brakes”; they are

commonly conical in shape, and have grooves to break the oil film, to provide some cooling, and to furnish a complicated surface pattern for the best braking grip. Whilst many different designs have been developed over the years to enable smooth and rapid gear engagement, several factors play (potentially) clear roles in their performance, including the machining and manufacturing processes used in their creation. The synchronizer material is certainly an important factor for providing the correct frictional properties in constant evolution and, indeed, the details of its composition, component geometry and manufacturing conditions are jealously guarded by the different commercial suppliers. Typical shifting times will range from a few tenths of a second in a passenger car, to less than 50 ms in racing vehicles. As comfort is less of a priority in the latter application, it enables the use of more direct systems that would otherwise be rejected as too harsh by the average driver. Although, the details of the operation are complex, they are totally transparent to the driver, except when the synchronizer does not perform its duty properly, causing gear clashing [94, 95]. The customer's expectations increase as rapidly as the technology improves, and new solutions must constantly be developed or further enhanced to provide faster and smoother shifting. There is, therefore, a need for standardized test rigs. Some examples of synchronizer systems currently in use are shown in Figure 8.26.

The design of synchronization requires an adjustment of the same friction or friction characteristic during a required gear service life of approximately 100 000 single gearshift operations, with different material/lubricant combinations, but without significantly changing the other chemical/physical and dynamic–mechanical properties. The following example (see Figure 8.27) provides an overview of a tribological system development which complies with most of the required chemical and dynamic–mechanical limits, including excellent gearshifting characteristics in a



Figure 8.26 Synchronizer systems currently in use. (a) Single- and double-cone synchronizers; (b) Triple-cone synchronizers.

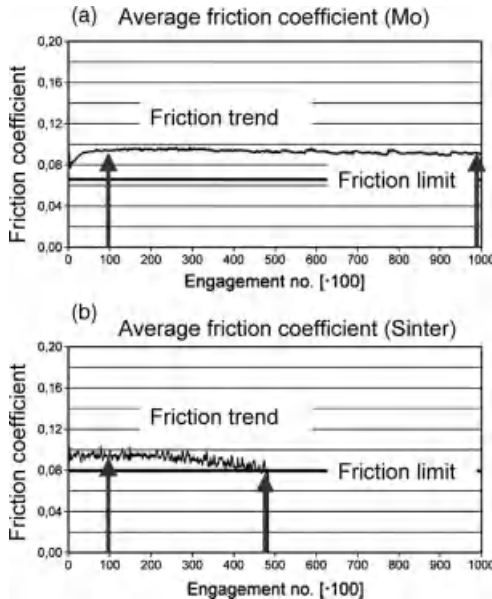


Figure 8.27 FZG SSP180 test run, average friction coefficient with the same fluid and different synchronization materials. (a) Upshift, molybdenum-synchronizer; The vertical arrows show the friction trend at 100 and at 1000

engagements (after breaking-in); (b) Upshift, sinter-synchronizer. The vertical arrows show the friction trend at 100 engagements (breaking-in) and at 485 engagements (failure, after falling below the friction limit).

molybdenum–steel synchronization. This is demonstrated by the individual gearshift operations, which show a constant friction coefficient during the entire synchronization time (the shift time and friction trend are shown in Figure 8.27).

The trend shown in Figure 8.27a, in which the average friction coefficient has been applied during the required service life of 100 000 gearshift operations, remains almost constant and sufficiently high during all such operations. The gearshifting characteristics of the gear oil with this molybdenum–steel synchronization is to be considered excellent, when compared at gearshift no. 10 000 (Figure 8.28a) and at gearshift no. 100 000 (Figure 8.29a). Different material combinations such as sinter–steel, which is used by the manufacturer for the same gear family, display inferior synchronization characteristics in the bench test. The individual gearshift operation at the start of the test at gearshift no. 10 000 (Figure 8.28b) still shows the desired stable friction coefficient during the entire synchronization time (engagement time). However, this curve changes after some time and shows a sharp increase in friction towards the end of the gearshift operations. The large difference between the static and sliding friction coefficients leads to a jolting during the gearshifting operation, which is perceived as an undesirable phenomenon. This effect will increase during subsequent gearshift operations, and result in a clashing of the synchronization at gearshift no. 48 500 (Figure 8.29b). Thus, as shown by the trend figure in comparison to the molybdenum–steel synchronization, the required

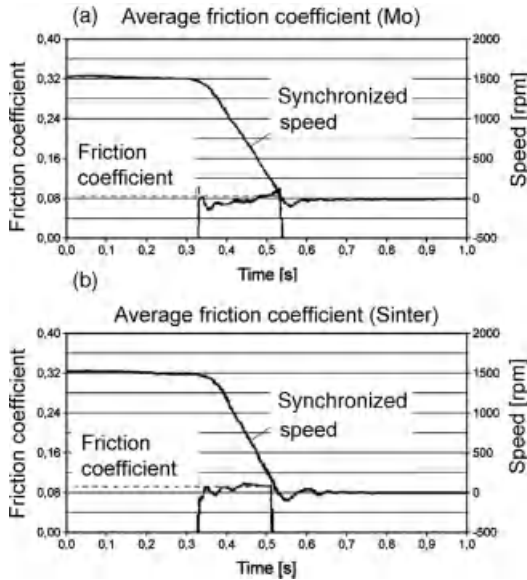


Figure 8.28 FZG SSP180 test run, engagement no. 10 000 with the same fluid and different synchronization materials. (a) Upshift, molybdenum-synchronizer; (b) Upshift, sinter-synchronizer.

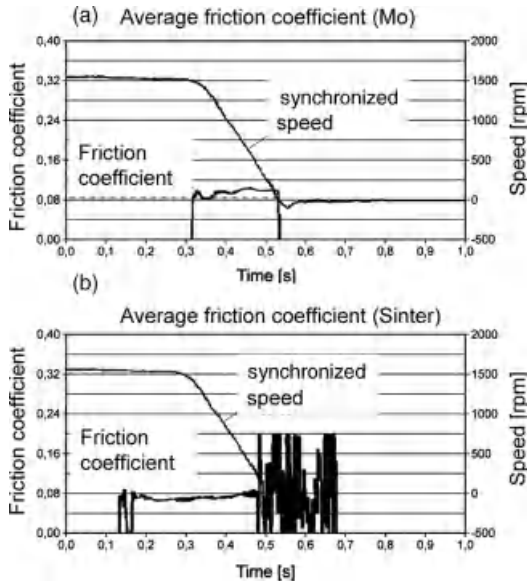


Figure 8.29 FZG SSP180 test run, with the same fluid and different synchronization materials. (a) Upshift, molybdenum-synchronizer engagement no. 100 000; (b) Upshift, sinter-synchronizer engagement no. 48 500.

number of gearshift operations of 100 000 is not achieved, and the test must be stopped after 48 500 operations. A second test, conducted under the same operating conditions, confirmed the results that had been obtained and, as a consequence, the material/lubricant technology was rejected by the gear manufacturer as unsatisfactory. Additional information regarding the friction characteristics required and the shifting operation that influences the tribological parameters in synchronizers are provided in Refs [96, 97].

8.4.7.3 Standardized Test Rigs and Test Methods

A very limited range of three standardized rigs, called “Synchromesh,” for performance evaluation are currently available commercially; these are the μ -comb rigs and the FZG SSP180 rig. Testing conditions with this equipment always attempts to match today’s gearbox operating environment, particularly in terms of dynamic performance and performance optimization. For both types of rig, the test components can either be taken out of regular production, or accurate pre-measured and selected parts may be used. The use of a hardware set of known performance (e.g., the Audi, New Venture Gear, ZF or Daimler synchronizers) enables determination of the effects of different lubricants on synchronizer endurance for manual and dual-clutch gearboxes in automotive applications, as defined by wear and changes in the coefficient of friction. As materials or fluid formulations are changed to address new or greater performance requirements in other areas of the transmission, information provided by these test procedures will enable tribologists to determine whether the synchronizer performance will remain acceptable. Subjecting these units to thousands of engagements also serves to test synchronizer durability. Different types of synchronizer and friction material are used by the OEMs and, at present, the area of application affects the service life. It is not possible to create one general standard test procedure for approval purposes. The OEMs require a common test procedure which would provide an understanding of the oil and synchronomaterials manufacturers’ test results. The test procedures described by CEC L-66-T-99 for the FZG SSP180 are suitable for use as “screening tests” for this purpose [98]. Different types of synchronizer can be used, and a variety of procedures are available depending on the application (passenger car or heavy-duty vehicles, and/or materials, as summarized in Table 8.17). Gear clashing, synchronizer wear, or synchronizer seizure are the main types of failure observed for this equipment, in agreement with most field experience [99].

The μ -Comb Synchronizer Testing Machine The μ -comb synchronizer test machine was developed by the Hörbiger Company in Schongau (Germany) [100]. The test rig uses a single synchronizer set and operates upshifts during testing. In order to maintain the operating conditions as close as possible to a “real” gearbox, the direction of the rotational speed changes direction every 200 revolutions. Different types of synchronizer can be used, and different procedures are available depending on the application, whether passenger car or heavy-duty vehicles, and/or materials. The rig characteristics are well suited for the measurement and development of double- and triple-cone synchronizers. Although the most widely recognized version

Table 8.17 Test standards and synchronizer materials for tribological tests.

Test method	Test machine	Application
ZF, Audi, VW, New Venture Gear, Getrag, BMW, Ford, GM, Fiat	μ -Comb synchronizer testing machine	Audi ML 285 brass, single-cone Audi ML 310 molybdenum, single-cone Audi ML 310 Carbon 5010, double-cone OEM Specifications VW DK 67, HS45, double-cone ZF TK 89, triple-cone, HS45 AUDI B 80 brass, single-cone
CEC L-66-T-99	FZG SSP180 synchronizer testing machine	ZF BK 117 HS45, single-cone, light truck ZF BK 119 molybdenum, single-cone, light truck DC AK 177 molybdenum, single-cone, heavy-duty application

is the small μ -comb option, a larger version – the μ -comb truck – is used to test the synchronizers of commercial vehicles. The main technical data are listed in Table 8.18, and a schematic of the operating system is shown in Figure 8.30.

The FZG SSP180 Synchronizer Testing Machine The most widely recognized synchronizer testing machine is the FZG SSP180, which was developed by the Hurth Company and is now built, distributed, and supported by the ZF Company in Passau, Germany [101]. This machine uses a complete synchronizer set, and operates full up- and down-shifts during testing. The test machine comprises an electric motor, two

Table 8.18 μ -Comb synchronizer test machines.

Technical data	μ -Comb	μ -Comb truck
Synchronizers	50–120 mm	100–200 mm
Speed difference	0–4500 rpm	–3500–3500 rpm
Axial force	0–5000 N	0–5000 N
Inertia	0.013–0.036 kg m ⁻²	0.015–2.5 kg m ⁻²
Cycle time	>3 s	>3 s
Oil temperature	Room temperature to 120 °C (248 °F)	Room temperature to 120 °C (248 °F)
Oil flow rate	0–3.5 l min ⁻¹	0–3.5 l min ⁻¹
Total oil volume	4–6 l	4–6 l

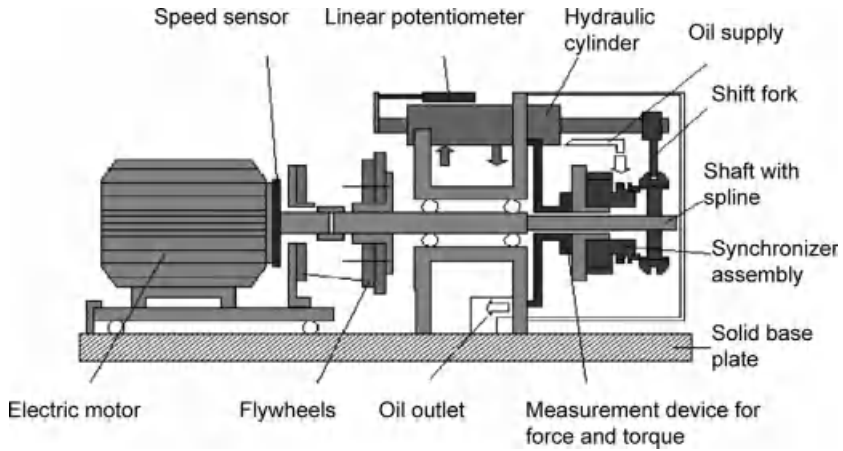


Figure 8.30 Schematic of the μ -Comb synchronizer testing machine.

flywheels, actuating hydraulics, an oil-heating and -circulation system, and a test box. The large main flywheel is connected to the electric motor via a belt-and-pulley combination, to ensure a constant and stable source of speed. The small flywheel realizes the load that the synchronizers either bring to zero speed (shift to “up (A)” position; see Figure 8.31), or accelerate to a constant speed (shift to “down (B)” position). This is accomplished by the two ring-and-cone synchronizers mounted in the test box; the rear unit accelerates the load flywheel to synchronous speed, while

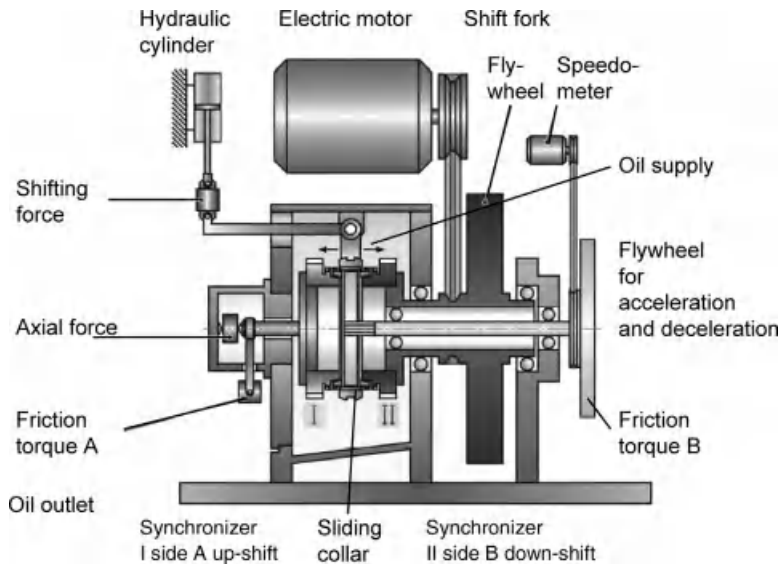


Figure 8.31 Schematic of the FZG SSP180 synchronizer testing machine.

Table 8.19 FZG SSP180 synchronizer testing machine.

Technical data	FZG SSP180
Synchronizers	40–200 mm
Speed difference	0–5000 rpm
Axial force	0–4000 N
Inertia	0.04–0.12 kg m ⁻²
Cycle time	>4 s
Oil temperature	10–120 °C (50–248 °F)
Oil flow rate	2–9 l min ⁻¹
Oil volume	8–10 l

the forward unit decelerates the flywheel to zero speed. The actuating hydraulic moves a shift fork that engages one unit and disengages the other. During shifting, heated lubricant is sprayed onto both synchronizer units. The technical data for the machine are listed in Table 8.19, and a schematic of the FZG SSP180 machine is shown in Figure 8.31. Typical synchronizer engagement traces showing individual shift performance data are illustrated in Figures 8.27–8.29. Data from the engagements are plotted during the course of the test, and the trends observed show whether performance is degrading, or not.

8.4.8

Wet Clutch Applications and Performance Tests

8.4.8.1 Area of Application

The testing of components for application in automatic and semi-automatic transmissions, or in axle gears with limited-slip differentials, is another aspect of the study of friction and friction materials, and especially of friction disks operating under wet or lubricating conditions. To ensure today's requirements for smooth gearshifts and braking with limited-slip differentials or wet brakes, self-excited vibration or shudder, which may occur, must be avoided. The wet friction coefficients and the constant wet friction durability of the friction characteristics in the sliding contacts of the rotating friction disks are important aspects of Driveline's effective and comfortable torque-transfer process. The most common use of these friction disks is in the wet clutches of automatic transmissions used in automobiles and trucks. The disks are also used in all other applications, including wet brakes (speed-controlled brakes), lock-up clutches, continuously slipping torque converter clutches (CSTCC), electronically controlled converter clutches (ECTCC), launch clutches in motor cycles, and limited-slip differentials. Modern all-wheel drive (AWD) systems, which originally were used to improve the off-road capacity of military and other off-road vehicles, have friction disks. During the early 1980s, however, a new market for AWD performance vehicles emerged with the introduction of the Audi Quattro. The working principle of transmitting torque by the use of friction disks is always the same. In all such applications where friction disks operate at low sliding velocities for long periods of

time, it is important to control the friction characteristics. Consequently, many test machines have been designed, especially for testing the fluids and their friction characteristics.

8.4.8.2 Function and Tribology of the Friction Disks

Friction disks basically function under fully lubricated conditions, with the single-disk or multiple-disk wet clutch configuration being used most often (see Figure 8.32a). This consists of one or more friction disks attached to one shaft fixed by splines; one or more separator disks are similarly connected to the other shaft. When disengaged, the clutch transmits only a small drag torque because of viscous friction, and thus both shafts are free to rotate independently. The clutch is engaged by applying a normal force from the hydraulic cylinder (mechanical or electromechanical actuators are also commonly used), clamping the friction and separator disks together, and thereby enabling torque to be transmitted between the input and output shafts. As a result, most research on friction is related to this application. The fluid must cool the disks and maintain their friction characteristics of constant dynamic and static friction coefficients. The typical friction characteristics for three different fluids, but with an identical friction material, are shown in Figure 8.32b (similar differences can be seen for a single fluid with different friction materials). To avoid vibrations (commonly referred to as “shudder” in clutch applications and “squeal” in brake applications), the relationship between friction and velocity (μ - v relationship) should have a low static coefficient of friction and a higher dynamic coefficient of friction that increases as the sliding velocity increases [102, 103]. In the case shown in Figure 8.32, fluid A will suppress vibrations, whereas oils B and C may be susceptible to vibrations because they have a negative slope in some regions. The effect of the relationship between friction and velocity on the anti-shudder

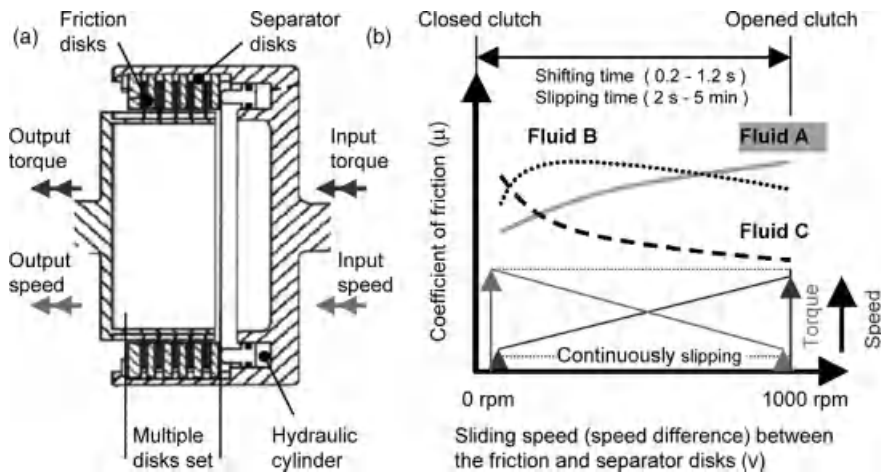


Figure 8.32 Wet clutch application. (a) Schematic diagram of a multiple-disk wet clutch; (b) Fluid-dependent friction characteristics in a multiple-disk wet clutch system.

performance of wet clutches is well established. The advantage of a positive μ - ν slope can easily be shown mathematically from engineering vibration calculations; it should, however, be noted that a positive slope is neither a necessary nor sufficient condition to guarantee friction stability.

8.4.8.3 Standardized Test Rigs and Test Methods

The Low-Velocity Friction Apparatus (LVFA) In Section 8.3.7, a tester was introduced which demonstrates the ability to measure sliding-friction characteristics in tribological contacts. The low-velocity friction apparatus (LVFA) provides a simple means of determining the friction characteristics of arbitrary paper on steel contacts, using only small volumes of fluid. The dependence of friction on sliding speed, contact pressures, and temperatures can be measured relatively quickly with especially designed specimens. Figure 8.33 shows some examples of measured friction characteristics for different ATFs as a function of the sliding speed under constant temperature and contact pressure. Tests with friction disks and plates taken from regular production can be performed better by using a much larger friction test bench (as described below). In comparison to the LVFA, these larger machines function dynamically with given centrifugal masses that reduce the speed of the disk-plate blocks under defined test conditions; this situation is more field-related, but requires much larger fluid volumes than does the LVFA. A variable or gradually shifting inertia of these test machines permits the measurement of realistic-dynamic shifting characteristics of wet clutch/brake when opening or closing the clutch/brake, as well as under continuous slip.

The SAE No. 2 Machine The SAE No. 2 machine, which has been used for over thirty years, is probably the most widely used instrument for evaluating friction

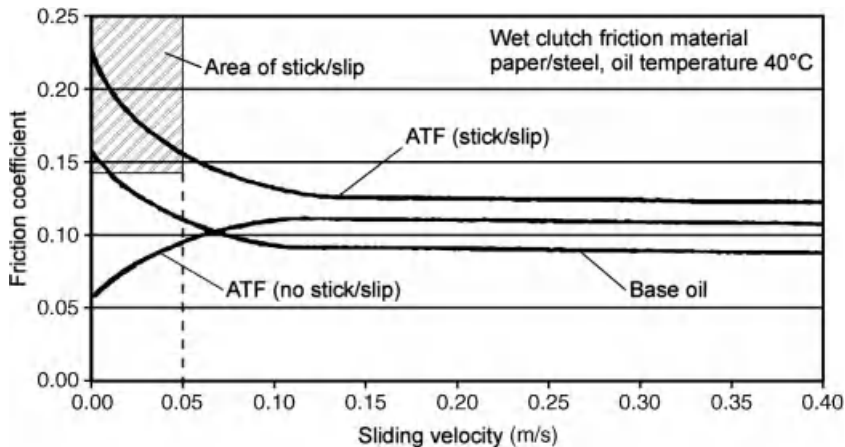


Figure 8.33 LVFA (low-velocity friction apparatus) and determination of the dependence of friction on sliding speed to avoid stick-slip behavior.

performance in North America and Asia Pacific [104–108]. The rig tests a full clutch pack, enabling an assessment of the overall performance of lubricant–friction material combinations. The SAE No. 2 machine can be used in two different operating modes. For the first test mode, the large drive motor accelerates the flywheel to 3600 rpm and then turned off; the clutch is then engaged to stop the flywheel. This procedure is repeated several times each minute for 50–100 h to investigate the durability of the fluid. In the second operating mode, to determine torque capacity, the clutch is engaged and the low-speed drive is run at 0.72 or 4.37 rpm. Typical data obtained include the maximum break-away friction and the friction coefficient after some seconds of continuous slip. The applied normal force in the SAE No. 2 machine is usually well below 10 kN. The JASO M394-95 test procedure is a Japanese standard for friction evaluations using the SAE No. 2 or similar apparatus [107]. Research groups have also used modified SAE No. 2 machines, with some success, to evaluate friction characteristics at low speeds [109] or the friction characteristics of synchronizers.

The DKA Machine (ZF Friction-disk Test Bench) The DKA machine, which operates in very similar fashion to the SAE No. 2 machine, was developed in Europe [110] for research, development, and quality control in the production of additives and finished fluids. A schematic diagram of the DKA machine (ZF friction disk test bench) is shown in Figure 8.34 [111]. Technical data for the different types of DKA-1A/1B rig are compared in Table 8.20. For test runs on DKA machines, PC test

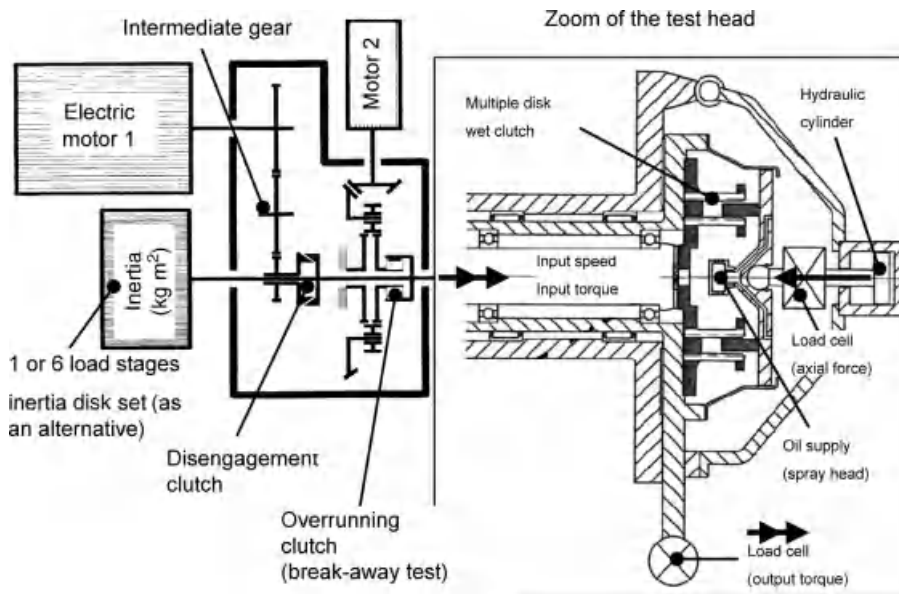


Figure 8.34 Schematic of the DKA-1A/1B rig for evaluation of the coefficients of friction of transmission fluids.

Table 8.20 DKA Machine (ZF friction disk test bench).

Technical data	27KW DKA-1A	50KW DKA-1B
Power supply	50 kVA	125 kVA
Speed difference	20–7000 rpm	20–7000 rpm
Break torque	1500 Nm	2000 Nm
Break-away torque	1500 Nm	2500 Nm
Inertia (var. mass set)	0.053–0.78 kg m ⁻²	0.053–0.78 kg m ⁻²
Oil temperature	40–150 °C (104–302 °F)	40–150 °C (104–302 °F)
Oil flow rate	0.2–6.0 l min ⁻¹	0.2–6.0 l min ⁻¹
Total oil volume	12–25 l	12–25 l

programs are prepared to control the test bench in automatic mode, including the break-away test where the actuated disk package is accelerated from standstill to a defined break-away speed for measurement of the static friction coefficient. During each test run, the friction disks are permanently supplied with a temperature-controlled lubricant; the oil is delivered into the center of the shaft to simulate the operating conditions found in a vehicle transmission. The friction disks are actuated by means of a servo-cylinder, with direct thrust load measuring which enables simulation of the shift pressure characteristics found under actual field conditions. The DKA-1B rig is equipped with two sets of flywheel masses which can be independently connected and disconnected. The measurement accuracy for the DKA machine is substantially higher than for other systems.

Figure 8.35 shows the typical friction coefficients of a four-stage load-spectrum test, measured on a DKA-1B machine, with variable inertia for building up different shifting torques at each load stage. The data in Figure 8.35 compare the friction characteristics at the first and at the 50th run-throughs (one run-through comprises 66 single clutch-shifting cycles). Using this set-up, two different ATF technologies have been tested and compared. In order to achieve smooth and comfortable wet clutch shifting, the best approach is to reach a relatively high dynamic friction coefficient at the start of the shifting operation, which will decrease during braking-in and then fade to an even slightly lower static friction coefficient. However, this behavior will have a negative influence on the shifting comfort. During the test, oil A initially shows such a desired friction curve in each first shifting cycle at load stage 1–4 (see Figure 8.35a). However, the tribological friction disk/plate-contact of oil A is not able to maintain the required friction characteristics, as seen in the 50th run-through (see Figure 8.35b). As the durability of the friction coefficient of oil A towards the 50th run-through is not maintained, the user would prefer oil B which, even after the 50th cycle, does not display such a high increase in static friction, while its long-term friction characteristics show a relatively constant behavior. Subsequently, in order to test the clutch/brake shifting and friction characteristics, especially in the case of continuous slip of friction partners, the gear manufacturer ZF has developed another test bench, which is described in the following subsection.

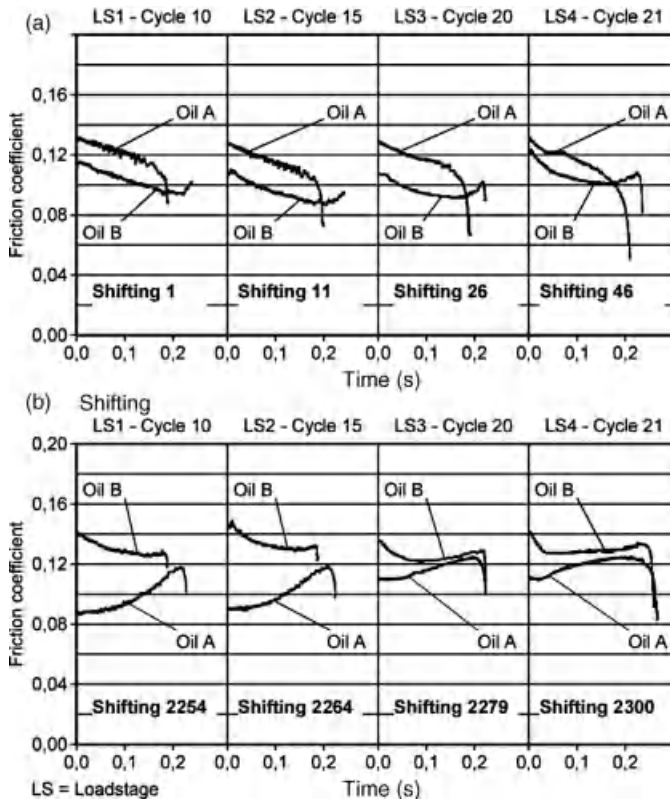


Figure 8.35 Evaluation of a DKA-1B test run, with different ATF additive technologies. Wet clutch loadstage test. (a) First run-through, first shifting at each of the four loadstages; (b) 50th run-through, last shifting at each of the four loadstages.

ZF GK Test Benches (Nos 1, 2, and 3) The ZF GK test benches have undergone constant development, from version No. 1 to an advanced version No. 3. All three test benches can be used for testing wet clutches, torque converters, and their friction partners and fluids, for example ATF, UTTOs, and Super Tractor Oil Universal (STOU), engine oils and oils for CVT applications [112, 113]. The newest rig simulates DKA/SAE No. 2 operation modes that enable limited measurements of the dynamic shifting, quasi-static test and the break-away procedure. The test units are used for research, development, and quality control in production (additive packages, friction disks and plates from regular production in reference oil and finished fluids). Figure 8.36 shows a schematic of the GK rig with the hydraulic system and a separated test oil system enabling oil tempering down to -20°C (-4°F), using a refrigeration unit for cold-start tests. This compact test system has a minimum oil volume of 5 liters (1.3 US gallons), which enables it to be used for aged/used oils from transmissions, or from other test rigs or synthetically aged fluids (see Section 8.4.6).

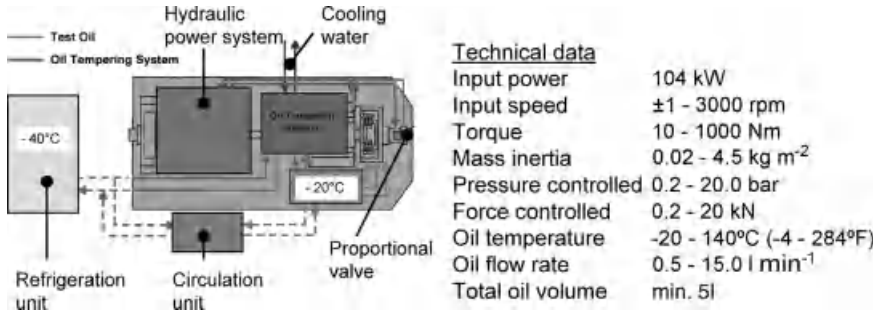


Figure 8.36 Schematic of the ZF GK test bench no. 2, and technical data.

The modes of operation of the GK rig are summarized in Figure 8.37, while Figure 8.38 shows an example of changes in the friction characteristics of an ATF running a combined oil aging and speed-controlled opening and closing procedure in a wet clutch on the GK rig. The μ - ν relationship reveals a dramatic decrease in the dynamic coefficient of friction at controlled shifting no. 15 000. This corresponds to a real transmission in a car having been driven for 60 000 km (37 280 miles), under enhanced driving conditions.

8.4.9

Variator Applications and Performance Tests

8.4.9.1 Area of Application

A CVT is a system that enables a progressive variation of the transmission ratio by means of a variator. It thus enables selection of an infinite number of ratios between minimum and maximum values. Other transmissions only enable the use of a limited set of fixed gear ratios. A manual transmission usually enables the use of five to six gear ratios, although some gearboxes have seven or eight. It is advantageous and more comfortable to use a CVT rather than other transmissions, because the engine will always operate under the optimum conditions and throttle-positions, adapted to varying road conditions and power demands. CVTs in motor vehicles enable the

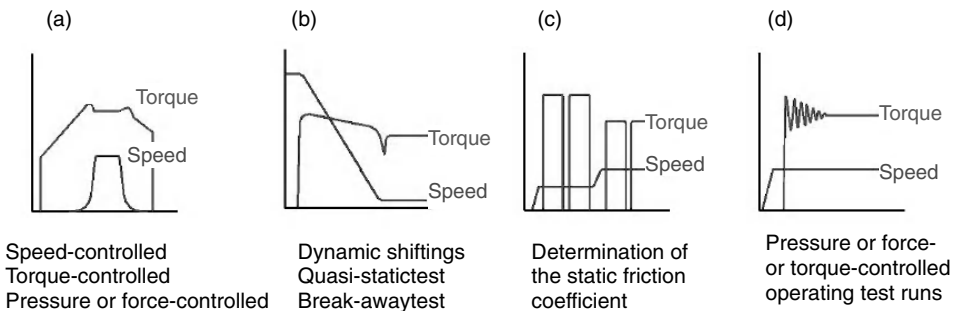


Figure 8.37 Operating modes of the GK test bench No. 2. (a) Opening and closing; (b) DKA-operation; (c) LVFA-operation; (d) (Green-) shudder.

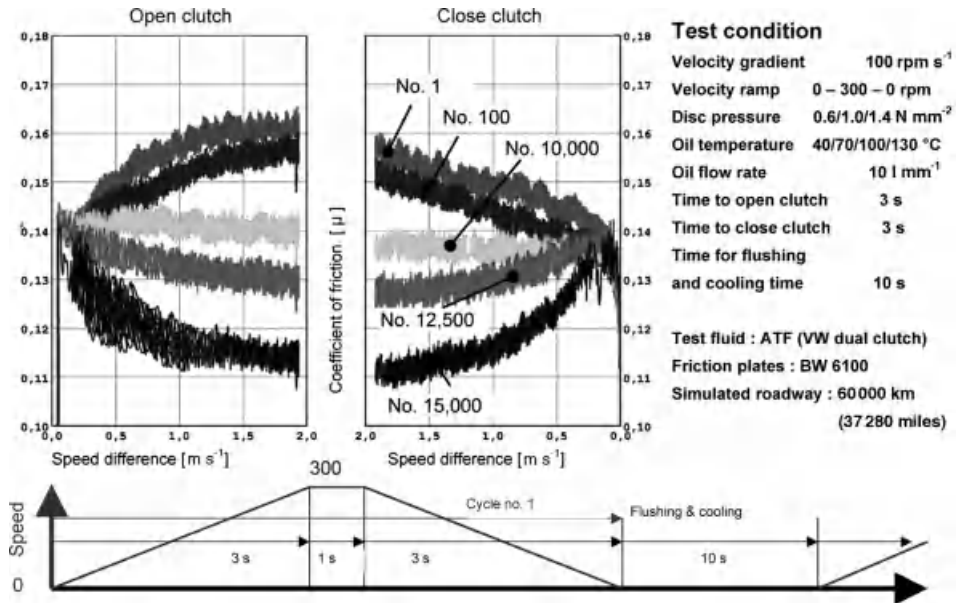


Figure 8.38 Example of an oil test result run on GK test bench no. 2.

operation of a combustion engine along certain preferred characteristic curves in the engine's ignition map. In contrast to all other vehicle transmissions, the variator enables an ideal alignment of the input torque of a combustion engine with the requested output torque of the driving vehicle. The resulting benefits of using a variator in comparison to all other vehicle transmission types include:

- Exploitation of the engine's torque at any speed, through the operation along the engine's characteristic operation mode driving at the maximum of available torque ("sporty" driving).
- Achieving a very economical performance through the operation mode along the engine's characteristic curve of minimum fuel consumption (economic driving, fuel economy).

Figure 8.39 shows the ignition map of a passenger car's 101 kW gasoline engine. This map displays the two characteristic modes: Mode 1 (the upper broken line) as the driving at maximum torque available; and mode 2 (the lower broken line) as driving the curve along the minimum fuel consumption.

Only a correspondingly adjusted, optimally designed and controlled variator enables the driving operation along the shown characteristic curves of mode 1 or 2, as shown in Figure 8.39. Nowadays, three different variator concepts have proven to be successful to meet these requirements:

- B-CVT, belt or chain gear drives (see Figure 8.13a, Section 8.4.2)
- T-CVT, friction gear drives (see Figure 8.13b, Section 8.4.2)
- H-CVT, hydrostatic-dynamic powershift drives.

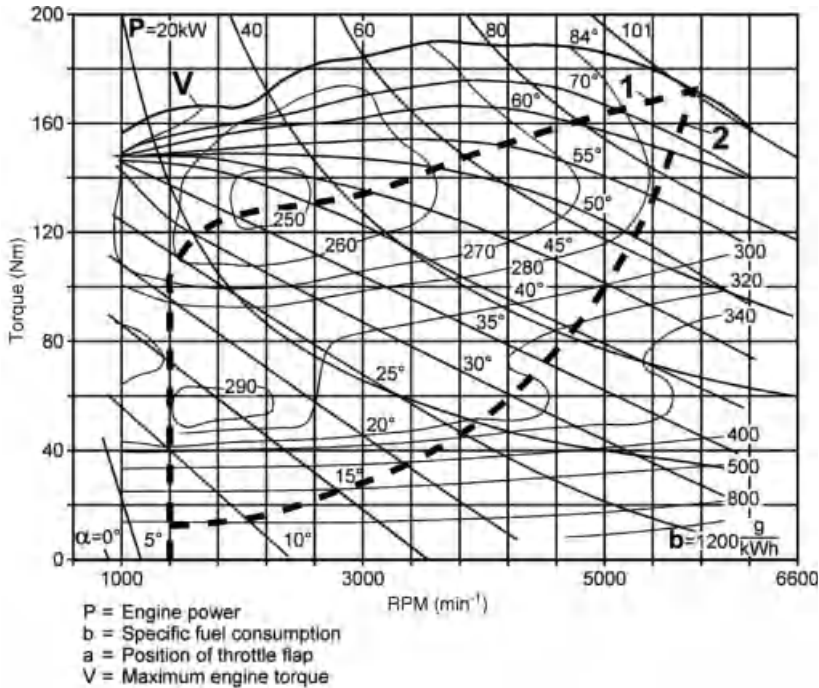


Figure 8.39 Ignition map of a passenger car's 101 kW gasoline engine.

With regards to a certain vehicle performance, the belt or chain gear drive variator system's mechanics has reached its limits in powerful transmissions at output torques of about 450 Nm. Today, this limit is reached at an output power of slightly more than 350 kW – that is, in mid-range passenger cars or limousines. In this respect, friction gear variator concepts allow the transfer of input torques up to 1000 Nm at engine powers of up to 450 kW. Hydrostatic–dynamic powershift drives are used in agricultural and tracked vehicles which usually have a very high engine input power of more than 300 kW and up to 1200 kW. In these transmission systems, planetary gear stages branch the input power into a closed hydrostatic circuit which consists of a hydraulic pump (mostly an axial piston pump) and a hydrostatic motor (generally an axial piston pump of bent axis design). Branching of the power and control of the output speed, depending on the volume flow rate, is achieved by making adjustments to the axial piston pump. Using the same car and engine, a CVT variator will take only 75% of the time taken by a manual transmission to accelerate from 0 to 100 km h⁻¹. Perhaps, the most remarkable practical proof of CVT performance, was its use in the 800 cV Formula One Canon-Williams-Renault in 1993 when, with much less development than the manual transmission version, the experimental CVT Formula One car was 1 s faster per lap.

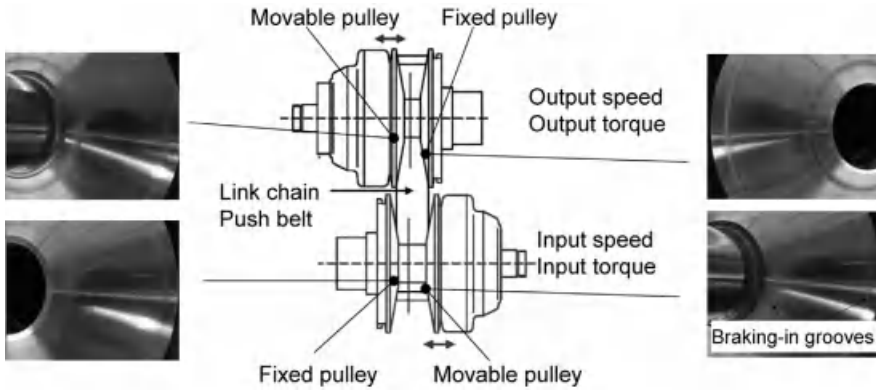


Figure 8.40 Schematic of a push belt variator in a CVT gearbox.

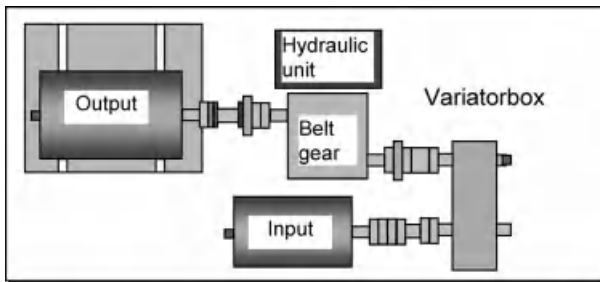
8.4.9.2 Function and Tribology of Chain, Push Belt, and Fluid

As indicated in the schematic shown in Figure 8.40, a CVT variator system such as a linking chain or push belt consists of a first pair of pulleys (input shaft) and a second pair of pulleys (output shaft). Each shaft has a fixed pulley, a pulley which is movable in the axial direction, and a chain or a push belt that is wrapped around these pulleys. The following considerations apply in particular to gears with wrapping elements, for example push belts, or link chains, which have a finite number of contacts with the pulleys. In such a CVT, the torque is transmitted through friction forces in lubricated contacts between the chain and the cone pulleys. Under these circumstances, the friction coefficients (μ) are in the range $0.07 < \mu < 0.11$, depending on the lubricant and on surface roughness. Thus, very high contact thrust forces are necessary for a high torque capacity. These high contact forces deform the pins of the chain links and the pulleys, which should be light compared to the weight of the gears. Because of these deformations, the chain does not wrap around the pulleys in a circular arc, but rather moves around the pulleys with additional radial motions inwards or outwards; a circumferential slip can be added to these sliding movements in the radial direction, which arises from the longitudinal elasticity of the chain and the changes of the contact radii caused by the radial movements. Additional sliding movements will also occur if the ratio is changed. Together, these sliding movements add up to a total slip between the chain or belt and the pulleys [114]. The local friction forces counteract the local sliding movements, causing a change of forces within the chain and thus transmitting the torque through the gear. Such relationships for stationary operating states have been very well known for a long time, based on measurements and theoretical studies [115–129]. The construction, optimization, and design of future CVTs by means of available calculation algorithms [121, 128] requires the analysis of the operating points; this is based on measurements on appropriate CVT variator test rigs, as described in the following subsection.

8.4.9.3 Standardized Test Rigs and Test Methods

All approval tests for current CVTs and advanced developments of new designs are conducted with variator components taken from regular production and housed in the test gearbox. Two different test rigs are available commercially, with each rig being used to test a complete variator; these rigs are the ZF universal variator test bench [130], and the Van Doorne test bench (VDT) [131]. The more versatile ZF rig can be used to test both push belt and link chain systems, whereas the VDT rig is specified for the VDT push belt system only. Both rigs cover fluid-durability tests and functionality items running different multiple-block programs. The durability items include wear of the belt/chain and pulleys, fatigue of the belt/chain and pulleys, and/or the degradation of the fluid (friction characteristics). The functionality items include torque transmittance (maximum torque capacity), variator efficiency (“KpKs-evaluation” of input and output thrust force/pressure on the movable pulley and the stability of the tribological contact), noise and vibrations, and the cooling properties and/or heat dissipation.

The ZF Universal Variator Test Bench A schematic of the test rig, test set-up, and technical data is shown in Figure 8.41. The arrangement of the electric motors and belt gear is variable for different variator systems (push belt or link chain). This test machine can run with a minimum of 8 liters (2.1 US gal.) of test fluid only, and enables cold-start testing at -20°C (-4°F) by use of an additional cooling device. A 130 h fluid test procedure has been developed by LUK (a German manufacturer of link chains for CVT applications) and ZF for the approval of CVT fluids in CFT 23 and 30 gear series for Ford.



Electric motor 1 – Input machine

Input power	240 kW
Input speed	5500 / 6500 rpm
Torque	400 / 380 Nm
Torque impact	560 Nm (< 5500 rpm)

Hydraulic and cooling unit

Oil temperature	$-20 - 140^{\circ}\text{C}$ ($-4 - 284^{\circ}\text{F}$)
Pressure	1- 80 bar
Oil flow rate	5 - 9 lmin ⁻¹
Total oil volume	8 - 55l

Electric motor 2 – Output machine

Input power	255 kW
Input speed	1,350 / 6700 rpm
Torque	1 800 / 349 Nm
Torque impact	2,520 Nm (< 1350 rpm)

Figure 8.41 Schematic of a ZF universal variator test bench, and technical data.

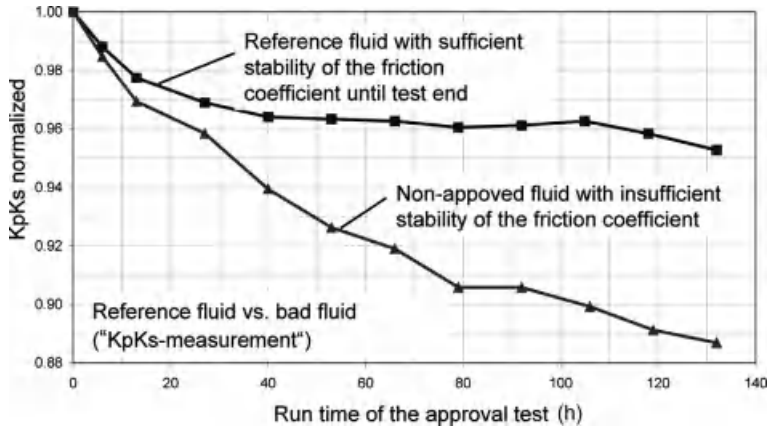


Figure 8.42 Test result from the ZF CVT tribological contact, and fluid approval run.

After braking-in, where a preconditioning of the tribological contact takes place, the “KpKs-measurement” is conducted temporarily to evaluate the force/pressure input/output stability of the tribological contact. A so-called “Zeta-max-measurement” is also made to identify the maximum input/output gear ratio (Zeta), in order to define torque capacity on the basis of a non-destructive test method. For a comparison of the friction coefficient determined by the slip-curve test method, a “Zeta-slip-force-measurement” can also be used to determine the coefficient of friction in gear ratio “LOW” (start-up). This value will be used for the calculation and evaluation phase of the tribological contact and fluid test (as illustrated in Figure 8.42), to demonstrate friction stability by running at constant gear radii with “Zeta-measurement.” In between the temporal “Zeta-measurements,” additional high-load and high-speed test phases are implemented in this test procedure for 20 h each. This is the so-called “steady-state test,” which is run alternately at minimum and maximum gear ratios.

The Van Doorne Test Bench The fluid test procedure entails a 100 h period of full load testing at nominal torque in three fixed ratios, 40 h at “TOP” (highway), 40 h at “OD” (overdrive), and 20 h at “LOW” (start-up). In this case, LOW and OD are the two most extreme ratios of the variator, while TOP is the ratio at which the vehicle top speed is reached. This durability cycle is supplemented with wear inspections, wear measurements, and functionality-related measurements. To judge the suitability of the tribological contacts and fluids tested, all of the test results obtained for one combination under investigation are compared with results obtained with a reference test piece and a reference fluid (ESSO EZL799 is currently used as the reference fluid). The fluid tests are performed with VDTs 24 mm push belt-type 901 018 (24/9/1.5/208.8) and ZFST (P811/Alaska) pulleys, using VDT belt boxes and test rigs. A fluid sump volume of approximately 30–40 liters (7.9–10.6 US gal.) is used. The tests are performed with regular production belts and pulleys from a single production batch, so as to minimize variation in hardware. Whenever belts or pulleys from other production batches are used, reference tests must be performed with the reference

test pieces and fluid. A schematic of the test arrangement, together with a more detailed description of the fifteen steps of the VDT test method, are provided in Ref. [131].

8.5

Tribology of Internal Combustion Engines

8.5.1

Variety of Internal Combustion Engines

The most commonly used power source for mobile propulsion as required in most types of cars, trucks, off-road equipment, tractors, motorcycles, boats, in a wide variety of aircraft and locomotives, and in other portable machinery, is the internal combustion engine (ICE). In general, these engines use petroleum; this is advantageous, as petroleum can provide a high power-to-weight ratio, together with excellent fuel energy-density. All ICEs depend on the exothermic chemical process of combustion – that is, the reaction of a fuel, typically with the oxygen from the air – although other oxidizers such as nitrous oxide may be employed. The most common modern fuels are composed of hydrocarbons, and are derived from mostly petroleum. These include fuels known as diesel-fuel, gasoline and petroleum gas, and the rarer use of propane gas or alcohol. Most ICEs designed for gasoline can run on natural gas or liquefied petroleum gases, without major modifications except for the fuel delivery components. Liquid and gaseous biofuels, such as ethanol and biodiesel (a form of diesel fuel produced from crops that yield triglycerides such as soy bean oil, rapeseed oil or palm oil) can also be used; some ICEs can also run on hydrogen gas. Especially these new biofuels represent an increasing challenge with regards to the tribological contacts over the mechanical parts of the ICEs. These biofuels have very poor evaporation losses during the combustion process, and tend to forming layers or to leave deposits on surfaces that cause thinning of the lubricating oils.

All ICEs must achieve ignition in their cylinders to create combustion [132]; typically, the engines use either a spark ignition method or a compression ignition system. Today's most commonly used ICEs worldwide are based on the four-stroke cycle or traditionally so-called "Otto cycle" (gasoline engines); several variations of these cycles have been developed, most notably the Atkinson and Miller cycles [133]. Today, most truck and automotive diesel engines use a four-stroke cycle, but with a compression heating ignition system; this is the so-called *Diesel cycle* [134]. Although all four-stroke engines are generally quieter, more efficient and larger than their two-stroke counterparts, today's largest compression-ignition engines are in fact two-stroke diesel engines, and are used in some locomotives and large ships. These types of engine are not naturally aspirated to scavenge the cylinders.

A further development of the internal four-stroke combustion engine is based on five- or six-stroke cycles. The fifth cycle, as added by Delautour, is that of refrigeration, and the five-stroke engine is up to 30% more efficient than an equivalent four-stroke engine. The six-stroke engine captures the waste heat from the four stroke Otto cycle and creates steam which simultaneously cools the engine while providing a free

power stroke. This not only removes the need for a cooling system but also makes the engine lighter; it also provides a 40% increased efficiency over the Otto cycle.

The *Bourke engine* has two opposed cylinders with the pistons and a Scotch Yoke mechanism instead of connecting rods to translate the linear motion to a rotary motion. Because the motion of the pistons is a perfect sine wave with regards to time versus displacement, the fuel burns in a smaller volume. Hence, the Bourke engine's combustion phase more closely approximates a constant volume combustion than do either four-stroke or two-stroke cycles.

The *Controlled Combustion Engine* uses two counter-rotating cams instead of a crankshaft to drive two horizontally opposed pistons, while retaining an identical cylinder head assembly to conventional engines. This engine is about one-fourth the size and weight of a conventional engine of similar output, and uses fewer moving components. A four- or two-stroke cycle can be used, and it can run on petrol, diesel, compressed natural gas, or ethanol.

The *Wankel rotary engine* is a type of ICE, which uses a rotor instead of reciprocating pistons [135], and is more properly called a “four-phase” than a four-stroke engine [136]. This design delivers smooth, high-speed power from a compact, light-weight engine which, today, is most notably used by several car manufacturers.

From a tribological point of view, the two-stroke, four-stroke and Wankel engines deserve closer attention, based on a deeper consideration of the different mechanical–dynamic surface contacts and operating conditions that are similar to most other ICEs and their applications described above. Where very high power is required, however, such as in jet aircraft, helicopters, tanks and large ships, the power sources appear mostly in the form of turbines [137–140]. Turbines are also used to power electric generators, and also widely for industrial purposes. The tribological requirements of turbines incorporate most of the tribological issues of automotive combustion engines with respect to a wide range of different other applications not mentioned here.

8.5.2

Area of Application and Operation of Two-Stroke Engines

The smallest gasoline engines are usually two-strokes. These are popular due to their simple design, low cost, and very high power-to-weight ratios, and are still widely used in high-power, handheld applications where light weight is essential. Typical examples include chainsaws, string trimmers, lawn mowers, and small, portable or specialized machine applications such as outboard motors, jet-skis, mopeds, scooters, snowmobiles, and karts. These engines also provide the propulsion for small-capacity, high-performance motorcycles, and for all types of model airplanes and other model vehicles. In the past, two-stroke cycles were created for use in diesel engines with opposed piston designs, for example, as low-speed units such as large marine engines [141], locomotives, and V8 engines for trucks and heavy machinery. Until their production was stopped during the late 1980s, several passenger cars that used two-stroke engines were also manufactured, including Saab in Sweden, Syrena in Poland, and some German manufacturers such as DKW, Auto-Union, Trabant, and Wartburg.

Carburettor – crankcase, cylinder with spark ignition – exhaust pipe (two-stroke emission)

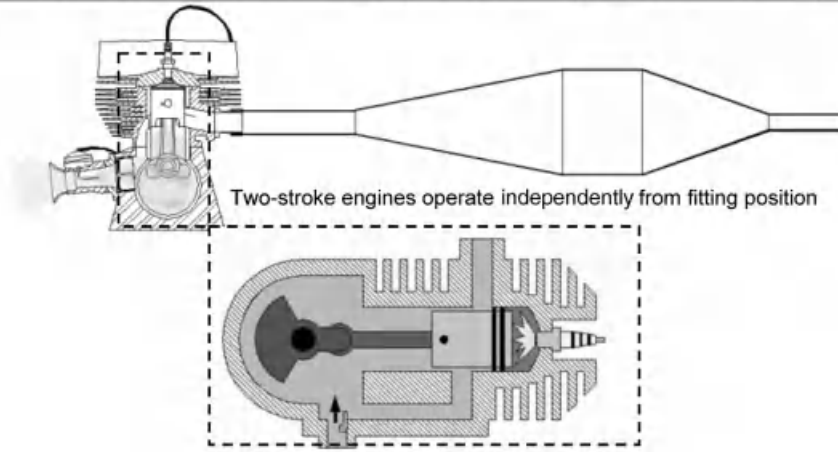


Figure 8.43 Schematic of a two-stroke engine.

The design types of the two-stroke cycle engine vary according to the method of intake of fresh air/fuel mixture from the outside, the method of exchanging the burned exhaust for fresh mixture, and the method of exhausting the cylinder. An example of a two-stroke gasoline engine design is shown in Figure 8.43. Unlike a gasoline engine, which requires a spark plug to ignite the fuel/air charge in the cylinder, a diesel engine relies solely on the heat of compression for ignition. Fuel is injected at high pressure into the superheated compressed air and instantly ignites; hence, scavenging is performed with air alone. A two-stroke diesel is supplied with air from a blower or turbocharger alone, and is considered not to be naturally aspirated.

The two-stroke cycle engine operates in two strokes, allowing a power stroke for every revolution of the crank:

First stroke – power/exhaust: This stroke occurs immediately after the ignition of the charge. The piston is forced down; after a certain point, the top of the piston passes the exhaust port, so that most of the pressurized exhaust gases can escape. As the piston continues down, it compresses the air/fuel/oil mixture in the crankcase. When the top of the piston passes the transfer port, the compressed charge enters the cylinder from the crankcase and any remaining exhaust is forced out.

Second stroke – compression/intake: The air/fuel/oil mixture has entered the cylinder, and the piston begins to move up. This compresses the charge in the cylinder and draws a vacuum in the crankcase, pulling in more air, fuel, and oil from the carburettor. The compressed charge is ignited by the spark plug, and the cycle begins again. In these engines some of the exhaust and intake charge are in the cylinder simultaneously; but the gases are kept separate by careful timing and aiming of the transfer ports. In this way, the fresh gas has minimal contact with the exiting exhaust, which it is pushes ahead of itself.

8.5.3

Tribology of Two-Stroke Engines and Performance Tests

The demands of two-stroke engines are closely affiliated to a simple lubrication system in which a special two-stroke oil is mixed with the fuel, and therefore reaches all moving parts of the engine. Devices using this method of lubrication have the advantage of operating in any orientation, as there is no oil reservoir which would depend on gravity for its correct function. Depending on the design of the engine system, the oil can be mixed with the fuel manually each time fuel is added; the ratio of the oil and fuel mixture may range from 1 : 20 to 1 : 100. More advanced designs use an oil pump, which can automatically mix fuel and oil from separate tanks, or they may use indirect fuel injection with an oil/fuel mixture between 1 : 50 and 1 : 400. The engine block is typically cast from aluminum or iron before precision features are machined into it. The cylinder (the space in which a piston travels) forms the central working part of the reciprocating engine (see Figure 8.43) [142]. The purpose of the piston is to compress the air/fuel volume enclosed by the cylinder and, after combustion, to exert a force on the crankshaft so as to transfer the combustion energy into a spinning motion. In general, the lubricated pistons may be lined with sleeves or liners of a harder metal, or be given a wear-resistant coating. The two-stroke engine uses cylinder port valves which are incompatible with piston ring seals inside the cylinder, and which cover and uncover the ports. This causes the lubricant (the air/fuel/oil mixture) from the crank to work its way into the combustion chamber, where it is burned. The charging and emptying process causes about 30% of the fresh mixture to be exhausted without burning [143]; this is in addition to a partial burning of the oil, and this leads to a significant increase in the emission of pollutants. As about one-fourth of the oil is exhausted as an unburned oil mist [144], in highly populated areas where there are large numbers of small motorcycles (as in many Asian cities), this leads to severe odor, smoke, and noise pollution. Various investigations have been conducted into designs that attempt to reduce combustion of the lubricant. Yet, in recent years, these disadvantages have been countered by several advances in two-stroke technology, and the development of direct or indirect fuel injection has led to significant reductions in emissions and to improved fuel efficiencies. Further research might potentially lead to the production of a two-stroke engine with very valuable properties of high specific power and low pollution. Nonetheless, today's two-stroke engines require correspondingly high-quality oils for reliable operation and durability. From the tribological point of view, the principal criteria for the quality and durability of a two-stroke engine are the surface material, the manufacturing process, the surface treatment, and the engine oil.

The principal criteria for maintaining quality inside a two-stroke engine at all moving surfaces include:

- lubricity and antiwear properties
- cleaning function (detergent/dispersant properties)
- avoidance of deposits in the exhaust system
- low smoke emissions

- spark plug and/or ventilation or cleanliness
- avoidance of pre-ignition
- good fuel miscibility, even at low temperatures
- corrosion protection
- good flowing properties.

Most of these goals can be achieved using modern base-oil and additive technologies, which are usually matched to the requirements of the engines by specified engine tests. The operating conditions of engine tests are mostly field-related; such engine tests identify and rate performance levels for tribological issues in line with the engine oils tested. The API currently lists three categories that cover all engines, from low-power lawn mowers to high-performance motor cycles (see Table 8.21). Although engine performance tests are officially no longer performed because the specified test engines are no longer manufactured, the test methods can still be used for screening tests and component development with similar or comparable two-stroke engines. The Japanese Automotive Standards Organization (JASO), to which all major Japanese vehicle manufacturers belong, classifies three two-stroke engine performance levels as FA, FB, and FC with regard to the oil (see Table 8.22). Four different two-stroke engines are used to evaluate the tribological aspects of lubricity, detergent effects regarding oil, surfaces and appearance of moving wear parts, exhaust smoke, smoke particles and deposits. The International Standards Organization (ISO) mainly classifies two-stroke oils into three categories – ISO-L-EGB, -EGC and -EGD – although a fourth category (-EGE) is currently being drafted with strong European representation. The categories ISO-L-EGB and -EGC mirror the requirements of the JASO categories FB and FC, while requiring additional proof of piston cleanliness. The ISO-L-EGC and -EGD also require proof of low smoke output, similar to the JASO FC. The performance categories of two-stroke engine tests for outboard engines were developed primarily by the American National Marine Manufacturers Association (NMMA), to which all important American outboard engine manufacturers belong. The engine types and respective test criteria are listed in Table 8.23.

Table 8.21 API classification, tribo-performance tests with two-stroke engines.

API	Application	Test engine	Test criteria
TA	Mopeds, lawn mowers, electricity generators, pumps	Yamaha CE 50 S (50 cm ³)	Piston seizing, exhaust system deposits
TB	Scooters, small motorcycles	Vespa 125 TS (125 cm ³)	Pre-ignition, power loss due to combustion chamber deposits
TC	High-performance motorcycles, chainsaws	Yamaha Y 350 M2 (350 cm ³) Yamaha CE 50 S	Pre-ignition, power loss due to combustion chamber deposits Piston seizing, ring sticking

Table 8.22 JASO classification, tribo-performance tests with two-stroke engines.

Test engine	Test criteria	Test parameters	FA	FB	FC
Honda Dio AF 27	Lubricity	Piston ring wear, ring scuffing, piston seizing	>90	>95	>95
Honda Dio AF 27	Detergent effect	Piston ring sticking as a result of lacquering, coking, deposits on piston and in combustion chamber	>80	>85	>95
Suzuki SX 800 R	Exhaust smoke	Smoke particles	>40	>45	>85
Suzuki SX 800 R	Exhaust deposits	Back-pressure in exhaust system	>30	>45	>90

Table 8.23 NMMA classification, tribo-performance tests with two-stroke engines.

Test engine	Test criteria
Yamaha CE 50 S	Lubricity (seizures)
Yamaha CE 50 S	Power loss due to pre-ignition
Mercury 15 HP (2 runs)	Compression losses, ring jamming, piston cleanliness
OMC 40 HP	Ring jamming, piston cleanliness
OMC 70 HP	Ring jamming, piston cleanliness

8.5.4

Area of Application and Operation of Four-Stroke Engines

Today, the four-stroke ICE is the predominant power source for most types of cars, trucks, motorcycles, construction machinery, and many others. Four-stroke engines for lighter applications include all gasoline and light diesel engines with direct or indirect injection. The light diesel engines, which today are gaining popularity in passenger cars in Europe, are becoming increasingly the dominant European engine. Although, four-stroke engine can have various numbers of cylinders, and arrangements of those cylinders, the most common arrangements are V6, V8, and inline-four [132–134]. In recent years, the “cam-in-block engine” has become less prevalent than the overhead cam engine, as it requires stiffer springs in combination with a higher load on the surface contacts, which in turn incorporates a much higher mass inertia of the reciprocating engine parts. A lighter load on the engine components will tend to reduce both wear and energy consumption, prompting new developments in this direction. Today, the large majority of commercial vehicles, including trucks, buses, farm and tractors, harvesters, construction machines and stationary machinery, are all powered by

diesel engines. Apart from the pre-chamber diesels engines (which have largely been superseded in Europe), the engines are normally highly turbocharged, direct-injection motors. Both, economic and ecological aspects, along with high injection pressures, have led to improved combustions and thus reduce emissions. In addition, for long-haul vehicles, the typical oil-drain intervals have been extended to 150 000 km (93 200 miles). Whilst the general requirements of four-stroke engines differ between diesel and gasoline engines, their technical working principle is very similar, and only the ignition processes will differ.

A schematic cross-sectional view of a four-stroke gasoline combustion engine with spark ignition and overhead camshafts is illustrated in Figure 8.44a. This engine operates with the following four-stroke cycles:

First stroke – Intake: On the intake stroke, the intake valve opens (at this point, gasoline engines take in a mixture of air and gasoline). The piston is moved down, such that a mixture of air and vaporized fuel is pushed by atmospheric pressure into the cylinder, through the intake valve port in the expanding cylinder. Diesel engines will take in air only, while homogeneous charge compression ignition (HCCI) engines will take in both air and fuel, but continue to rely on an unaided auto-combustion process, due to higher pressures and heat.

Second stroke – Compression: When the piston begins to move upward again, both valves are closed, such that the cylinder is sealed; the air or vaporized air/fuel mixture is then compressed. By the time the piston reaches the top of its travel, compression of the air or air/fuel mixture not only increases the pressure in the cylinder but also causes the air or air/fuel mixture to increase in temperature. Gasoline engines compress to less than 12.5 bar (185 psi) and use a spark plug (see Figure 8.44a), so as to ignite the mixture when it is compressed by the piston head in each cylinder. Compression in a diesel engine is usually higher than

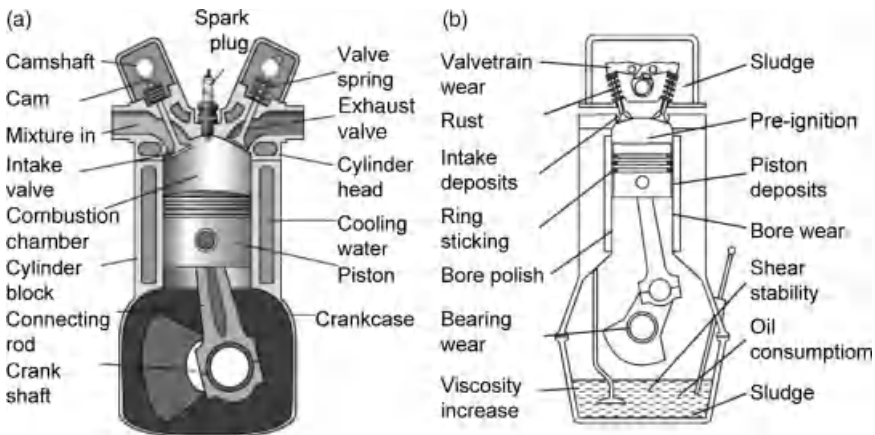


Figure 8.44 (a) Cross-section view of a four-stroke engine; (b) Tribological-relevant issues of four-stroke combustion engines.

37.5 bar (550 psi). Shortly before peak compression, a small quantity of diesel fuel is sprayed into the cylinder via a fuel injector, and this causes the fuel to ignite instantly (see Section 8.5.5.8).

Third stroke – Power: As the piston nears the top of the compression stroke, ignition and combustion of the fuel takes place. The mixture burns rapidly, and the burning fuel creates carbon dioxide, water vapor, and other compounds. The force created by the combustion gases pushes the piston down again. The cylinder pressure increases to 40 bar (600 psi), causing the piston to be forced down in the cylinder. This power impulse is transmitted down through the piston, through the connecting rod, to the crankshaft, which is rotated due to the force. A “gasoline ignition process” uses electrical/gasoline-type ignition systems that can also run on fuel types other than petroleum. Generally, the ignition process relies on a combination of a lead-acid battery and an induction coil to provide a high-voltage electrical spark to ignite the air/fuel mix in the engine’s cylinders. During operation, this battery is recharged using an electricity-generating device driven by the engine, such as an alternator or generator. A “diesel engine ignition process” relates to compression ignition systems, such as the diesel engine and HCCI engines which, for ignition, rely solely on the heat and pressure created by the engine during its compression process.

Fourth stroke – Exhaust: As the piston reaches the bottom of the power stroke, energy from the expanding gases has been transferred from the piston to the crankshaft via the connecting rod. At this point, the exhaust valve opens and the piston then rises and sweeps most of the combustion products out of the cylinder. When the piston is near the top of the exhaust stroke, the exhaust valve closes and the intake valve opens. The cycle repeats again with the next intake stroke. The sequence of four strokes is continuously repeated during operation of the engine.

8.5.5

Tribology of Four-Stroke Engines and Performance Tests

The internal four-stroke combustion engine, as illustrated in Figure 8.44a, is much more complex and has more tribological requirements than its two-stroke counterpart. The purely tribological challenge consists of guaranteeing the functional reliability of all points with tribological relevance over the whole range of operating conditions. The points of tribological relevance are shown in Figure 8.44b. Various conditions influence the engine design, such as the desire for a high power output, legislative requirements for reduced emissions (e.g., Euro 5 and Euro 6), increased fuel economy (reduced CO₂ emissions), and minimal generation of hazardous substances (exhaust after-treatment systems). Loads on engine components tend to influence wear and energy consumption. Many diverse surfaces will interact and have the potential to experience wear when converting the chemical energy of the fuel into the mechanical energy of the crankshaft.

Apart from this classical tribological duty, the engine oils are especially of high tribological relevance as they must perform a number of additional functions. This

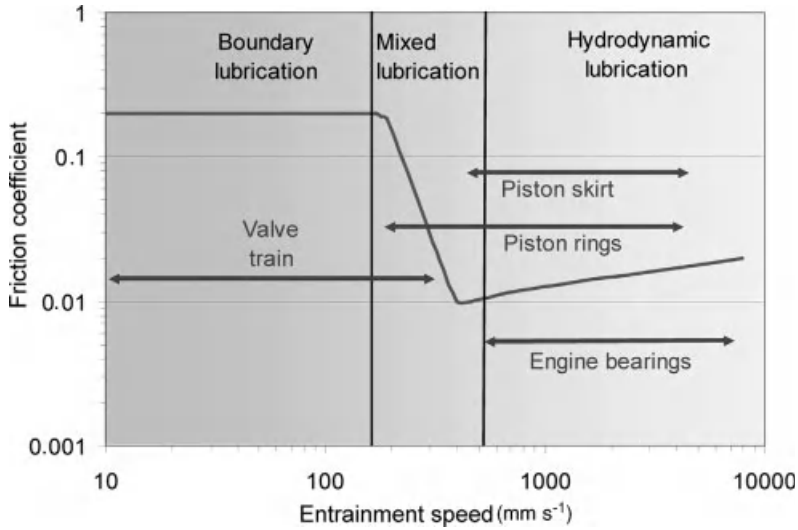


Figure 8.45 Stribeck graph, including the operating regions of several four-stroke engine components.

begins with sealing the cylinder and its ends, and the transport of sludge, soot, and abraded particles to the oil filter (this is termed “soot-handling”). Starting with the tribological functions, the three classic sections of the Stribeck graph are satisfied, from hydrodynamic full-lubrication regimes to the elastohydrodynamic lubrication (EHL) regimes, to the boundary friction conditions (see Figure 8.45). All friction pairings and a whole series of parameters are covered compared to the driveline losses in Figure 8.46 [145]. Sliding friction speeds range from simple a linear up-and-down movement of the piston in the cylinder through to extreme rotational move-

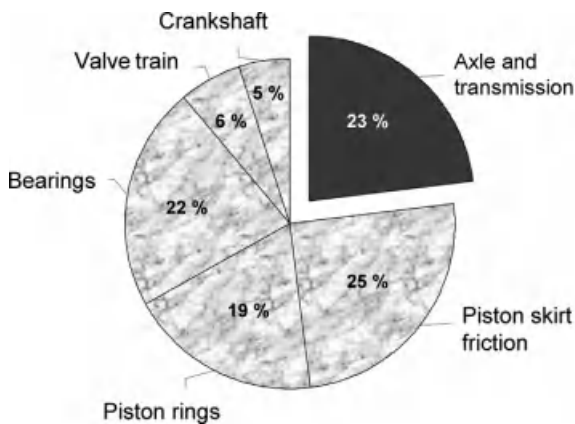


Figure 8.46 Typical values for energy loss in a light-duty vehicle.

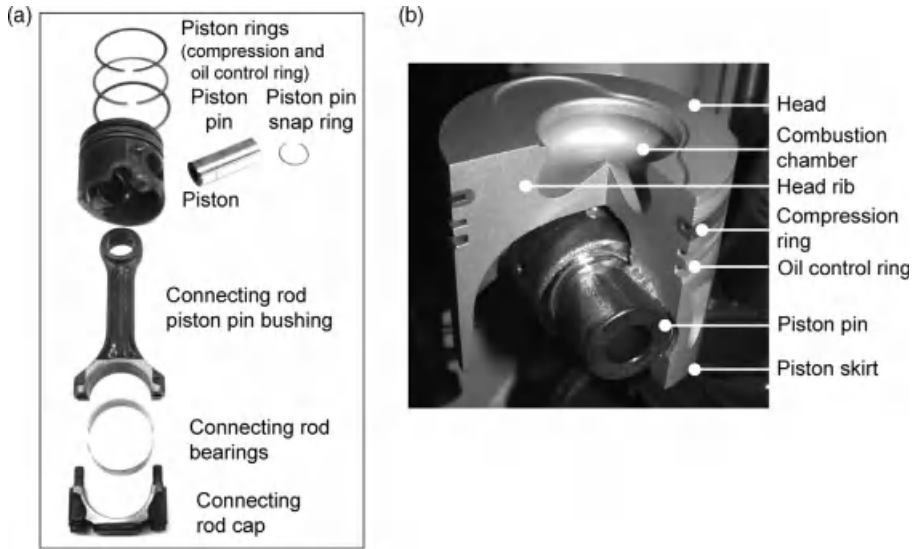


Figure 8.47 The moving parts of a four-stroke engine. (a) Piston and connecting rod (exploded view); (b) The parts of a piston.

ments in the floating needle roller bearings found in advanced turbochargers which rotate at up to 20 000 rpm with micron tolerances. The temperatures encountered will range from ambient in the Arctic (-40°C ; -40°F) to oil sump temperatures of $>130^{\circ}\text{C}$ ($>266^{\circ}\text{F}$) to peak values of over 300°C (572°F) under the surface of the piston crown.

The moving parts of an engine serve an important function in converting not only heat energy into mechanical energy, but also a reciprocal motion into a rotary motion. The principal moving parts in an engine are the piston assembly, connecting rods, crankshaft assembly (which includes the flywheel and vibration dampener), camshaft, valves (includes fuel injection), and gear train (see Figure 8.47). These interacting parts, all of which are of tribological relevance, are described in greater detail in Sections 8.5.5.1–8.5.5.13.

8.5.5.1 Piston

The pistons of an engine serve several purposes: (i) they transmit the force of combustion to the crankshaft, through the connecting rod; (ii) they act as a guide for the upper end of the connecting rod; and (iii) they also serve as a carrier for the piston rings which are used to seal the compression within the cylinder. During the engine cycle, the piston must come to a complete stop at the end of each stroke, before reversing its course in the cylinder, and in order to withstand this rugged treatment and wear the piston must be constructed from a tough material yet be light in weight. In order to overcome inertia and momentum at high speed, the piston must be carefully balanced and weighed, while all of the pistons used in any one engine must be of similar weight to avoid excessive vibration. To help achieve these functions, the

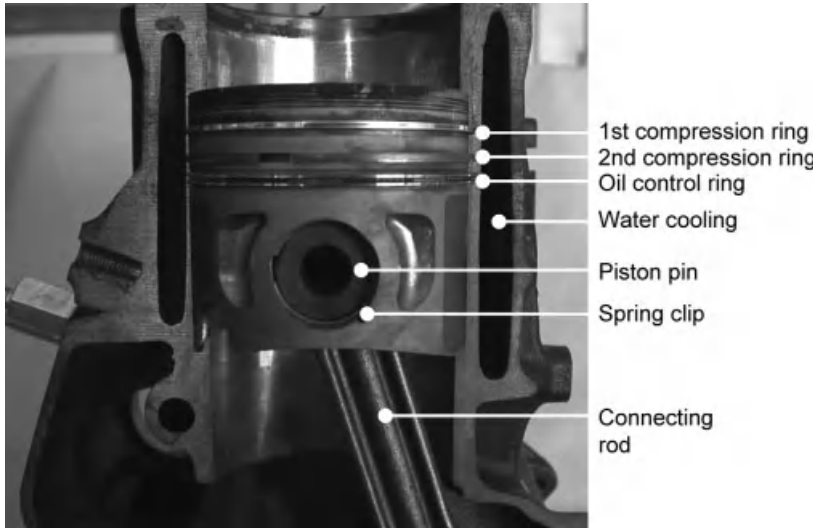


Figure 8.48 Example of a piston assembly of a four-stroke engine.

underside of the piston head is generally reinforced with ribs, which also help to conduct heat away from the piston head to the piston rings, and out through the cylinder walls. The structural components of the piston are the head, skirt, ring grooves, and land (the region between the top and second rings). Not all pistons resemble the typical from shown in Figure 8.48; some will have differently shaped heads, while diesel engine pistons usually have more ring grooves and rings than do gasoline engine pistons. In this case, some of these rings may be installed below as well as above the wrist or the piston pin.

The correct fitting of pistons is extremely important. Because metal expands when heated, and space must be provided for a lubricant between the piston and the cylinder wall, the piston must be fitted to the engine with a specified clearance. Such clearance will depend on the size or diameter of the piston, and on the material from which the piston is made. Cast iron does not expand either as rapidly or as extensively as aluminum; however, aluminum pistons require a greater degree of clearance to prevent binding or seizing when the engine becomes hot.

8.5.5.2 Piston Pin to Piston Contact

The piston pin transfers force from the piston to the connecting rod. The piston is attached to the connecting rod by piston pins (wrist pins), each of which passes through the piston pin bosses and through the upper end of the connecting rod. The interface between the pin and the piston forms a type of journal bearing, although in this case the motion is not a full rotation. Three methods are commonly used to fasten a piston pin to the piston and the connecting rod: the fixed pin, the semi-floating pin, and the full-floating pin (see Figure 8.49a–c). The anchored, or fixed, pin attaches to the piston by a screw running through one of the bosses, while the connecting rod oscillates on the pin. The semi-floating pin is anchored to the connecting rod and

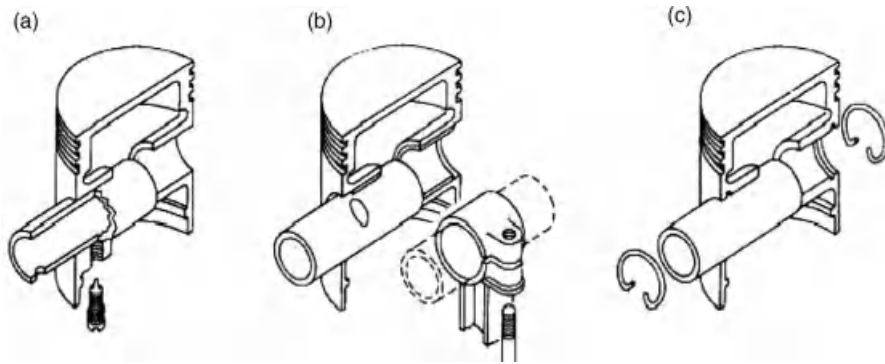


Figure 8.49 Piston pin design. (a) Fixed pin; (b) Semi-floating pin; (c) Full-floating pin.

turns in the piston pin bosses. The full-floating pin design is free to rotate within both the rod and the piston, and the motion is indeterminate. The floating pin has been shown to reduce the operating temperature of the piston pin boss, and is therefore the preferred design [146]. In either case, the velocity of the pin is not sufficient to generate a full fluid film between the surfaces, and a condition of boundary lubrication results. The tribological properties in the pin to pin bore interface are primarily controlled by the material properties of these parts. Automotive pistons are usually made of aluminum–silicon alloys, and the piston pins from low- or medium-carbon steel, which is formed into a hollow cylinder and then carburized. The carburization process results in very high hardness of the pin surface, and helps minimize the adhesion between the pin and piston. The piston pins are manufactured with a high-precision finish, and sometimes are chromium-plated to increase their wearing qualities. Their tubular construction provides them with maximum strength but minimum weight, and they are lubricated either by splash from the crankcase, or by pressure through passages bored in the connecting rods. Increasing the oil supply to this interface has been shown to reduce the tendency for scuffing [145, 146].

8.5.5.3 Piston Skirt to Cylinder Block

The piston skirt to cylinder block interface is one of the primary contributors to total engine friction [145, 147]. The design challenge in this case is to maintain a small clearance between the piston and the block in order to avoid seizure, while minimizing noise and vibration [148]. The aluminum–silicon alloys used for most automotive pistons are lighter than the cast iron pistons of the past, which leads to a reduction in both engine mass and vibration. The higher thermal conductivity of aluminum also helps to prevent any overheating of the top of the piston. Two types of piston skirt are found in most engines: (i) the “full trunk” type is more widely used, and has a full cylindrical shape with bearing surfaces parallel to those of the cylinder, giving more strength and a better control of the oil film; and (ii) the “slipper-type” (cutaway) skirt, which has considerable relief on the sides of the skirt, thus leaving less area for possible contact with the cylinder walls, and thereby reducing friction.

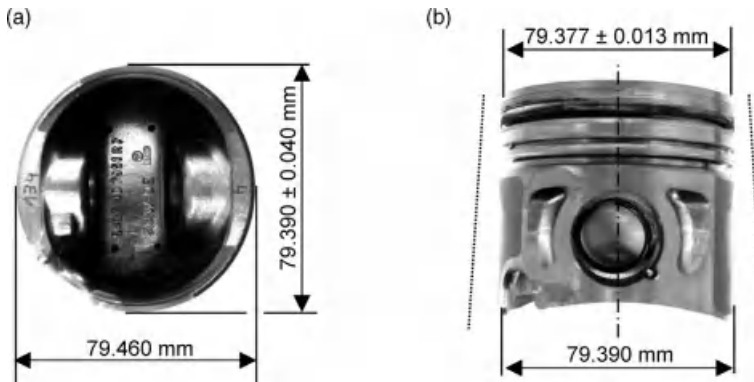


Figure 8.50 Cam-ground piston and piston skirt shape. (a) The elliptical shape of the piston; (b) The taper shape of the piston.

In general, the skirt or bottom part of a piston runs much cooler than the top, and so require less clearance than the head. The piston is kept in alignment by the skirt, which is usually cam-ground (see Figure 8.50). An elliptical shape allows the piston to fit the cylinder, regardless of whether the piston is cold or is at operating temperature. The narrowest diameter of the piston is at the piston pin bosses, where the piston skirt is thickest; the piston skirt is thinnest at the widest diameter of the piston. The piston is fitted to close limits at its widest diameter so that piston noise (termed “slap”) is prevented during the engine warm-up. As the piston expands due to the heat generated during combustion, it will become round as the expansion is proportional to the temperature of the metal. The walls of the skirt are cut away as much as possible to reduce weight and to prevent excessive expansion during engine operation. In fact, many aluminum pistons are produced with split skirts so that, when the piston expands, the skirt diameter will not be increased.

Any additional cooling required by the piston is usually provided by adding devices to direct a jet of oil onto the underside of the piston. In this case, the engine oil is acting as a coolant. However, as the cylinder bore is usually made from gray cast iron, which has a lower coefficient of thermal expansion than aluminum, this may create a design challenge as a piston with adequate clearance at the running temperature may become too loose (and hence noisy) at low temperature. In order to reduce friction and prevent scuffing of the piston, oil must be supplied to the cylinder bore walls. Yet, the clearances are so tight that special coatings are applied to most pistons, such as nickel ceramic composites or molybdenum disulfide. These coatings also reduce friction at the interface of the piston rings, and of the piston skirt with the cylinder walls [145, 149, 150].

8.5.5.4 Piston Rings to Cylinder Block

Piston rings are used on pistons to maintain gastight seals between the pistons and cylinders, to aid in cooling the piston, and to control cylinder-wall lubrication.

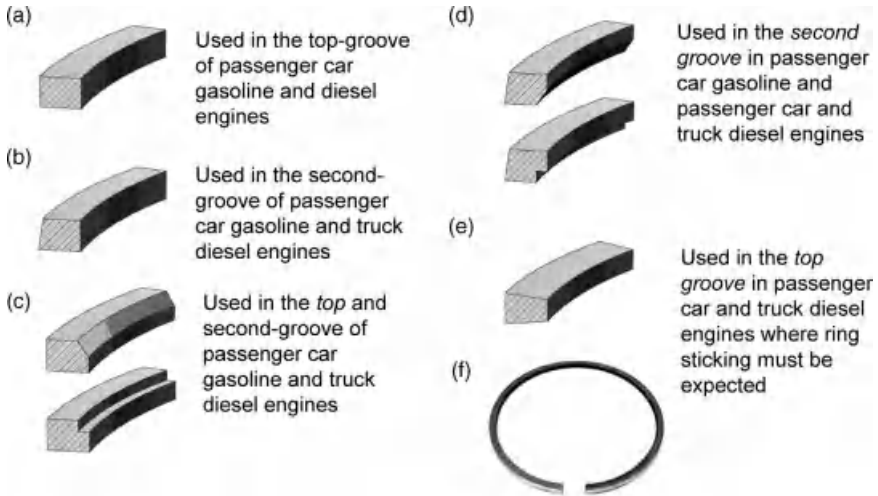


Figure 8.51 Piston compression rings. (a) Rectangular ring; (b) Taper-faced ring; (c) Internally beveled or stepped ring; (d) Taper-faced ring with inside bottom bevel or step; (e) Keystone ring; (f) Compression ring.

The rings operate as set of sliding seals, the aim of which is to separate the combustion gases above the piston from the crankcase environment below. In general, piston rings are of two distinct classifications, namely compression rings (see Figure 8.51) and oil-control rings (see Figure 8.52).

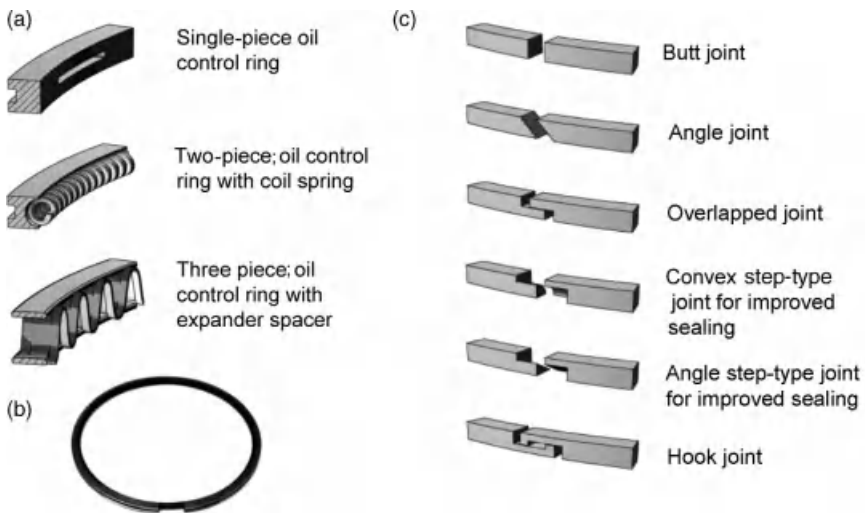


Figure 8.52 Piston oil control rings and joints. (a) Typical types of oil control ring; (b) Two-piece oil control ring; (c) Different types of joints for all forms of piston ring.

The principal function of a compression ring is to prevent gases from leaking past the piston during the compression and power strokes. All piston rings are split to permit assembly to the piston, and to allow for expansion. However, when the ring is in place the ends of the split joint do not form a perfect seal, and therefore more than one ring must be used, with the joints staggered around the piston. The most common arrangement is a set of three rings: the upper compression ring, lower compression ring, and the oil-control ring. About one-third of the heat absorbed by the piston passes through the rings to the cylinder wall. Piston rings are often complicated in design, are heat-treated in various ways, and are plated with other metals. The ring-block sliding interface has been estimated to account for 20% of the total engine mechanical friction [145, 151]. Oil usually reaches the cylinder bore surface by being thrown from the crankshaft after flowing through the bearings. Although some oil is necessary in order for the compression rings to function properly, any oil that escapes past the compression rings will be lost. Hence, the oil-control ring ensures that only the necessary amount of oil will reach the compression rings. The upper compression ring, which experiences the highest loads and oil temperatures, must provide a good seal to the cylinder surface, but in the presence of very little engine oil. To provide an acceptable durability, this ring is usually made from nitrided stainless steel or from steel which has been coated with molybdenum. If the cylinders become worn, ring expanders may sometimes be used so as to ensure a perfect seal. The bottom ring, which usually is located just above the piston pin, is an oil-regulating ring; this scrapes any excess oil from the cylinder walls and returns some of it, through slots, to the piston ring grooves. The ring groove under an oil ring has openings through which the oil can flow back into the crankcase, although in some engines additional oil rings are used in the piston skirt, just below the piston pin.

8.5.5.5 Crankshaft and Crankshaft Bearings

The crankshaft (crank) is the part of an ICE which transfers the reciprocating linear piston motion and pressure force into rotation and torque. This conversion requires so-called “crank throws” or “crank pins” on the crankshaft; these are additional bearing surfaces, the axes of which are offset from that of the crank, and to which are attached the “big ends” of the connecting rods from each cylinder. The crankshaft’s output typically connects to a flywheel (e.g., dual-mass flywheel; see Section 8.5.5.11), to reduce the pulsation characteristics of the two- or four-stroke cycles. Sometimes, torsional or vibrational damping systems are used to reduce the torsion vibrations that often are caused along the length of the crankshaft by the cylinders acting on the torsional elasticity of the metal. In this case, sliding will occur between the crankshaft and the engine block structure, as well as between the crankshaft and the connecting rod as the crankshaft turns (see Figure 8.53a). The pressure forces from the pistons are transferred through journal bearings that are designed to run primarily under hydrodynamic conditions. A correct clearance between the shaft and the bearing is important for good engine performance. Both, the shaft and the bearings, are usually composed of a hard, stiff material, such as cast iron or steel, to minimize deformation [145].

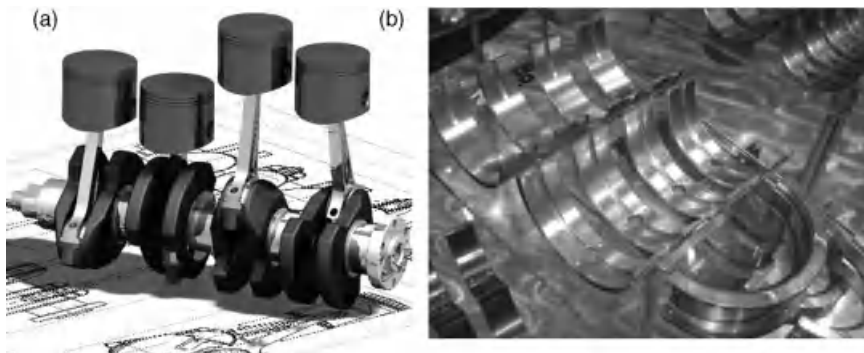


Figure 8.53 Four-cylinder gasoline engine. (a) Crankshaft with pistons and connecting rods; (b) Hydrostatical crankshaft bearings.

For strength and stability, the bearing is made using a steel backing and coated with a soft alloy for better embedability (see Figure 8.53b). Modern engine bearing coatings are usually made from aluminum–tin alloys, which are stronger than lead-based alloys which today are forbidden by legislation in many applications. The low strength of the lead compared to aluminum–tin alloys also limits the output of engines, although when compared to lead, the aluminum–tin alloys have a poorer embedability, so that engine and oil cleanliness become critical for long-term engine durability. The crankshaft bearings are wear components, with heat, pressure, chemical attack, abrasion and loss of lubrication all contributing to their deterioration. Consequently, if an engine is rebuilt, new bearings must always be installed. At the bearing interface, the engine oil will act mainly as a viscous fluid, while the friction in the bearings will be directly related to the viscosity of the engine oil (this is important to maintain fuel efficiency). Correct clearances are extremely important for bearing longevity and oil pressure; typically, crankshaft bearings require at least a $2.5\ \mu\text{m}$ -thick oil film between themselves and their journals in order to prevent metal-to-metal contact. This requires the assembly clearances to be sufficiently loose to allow oil to flow into the gap between the bearing and journal to form an oil wedge that can support the crankshaft. The clearance must also be sufficient so as to allow enough oil flow to cool the bearings. However, such clearance must not be too great, or the oil will escape before it can form a supporting wedge.

When dirt or other abrasive material finds its way between the crankshaft journal and bearing, it can become embedded in the soft bearing material. A close examination may reveal some scoring or wiping, dirt or other debris embedded in the surface of the bearings, or pitting or flaking. Solid particles (e.g., residues from manufacturing, contamination, wear, etc.) can also be entrained in the engine oil, and break in the upper and lower compression rings and the oil control ring, especially when the engine has been inoperative for long periods of time [152]. A shaft will then settle into contact with its bearing until the engine is restarted.

Heat is another factor that accelerates bearing wear, and may lead to failure if the bearings become hot enough. Bearings are primarily cooled by an oil flow between

the bearing and journal, and anything that disrupts or reduces such oil flow will lead to a rise in the bearing temperature. Conditions that may reduce oil flow and cause bearings to run hot include a worn oil pump, a restricted oil pick-up screen, internal oil leaks, a low oil level in the crankcase, aerated oil (oil level too high), fuel-diluted oil from excessive blow-by or coolant-contaminated oil from internal coolant leaks. Surface temperatures in excess of 620 °C (1050 °F) can also melt away the lead in copper/lead bearings, and in those with babbitt layers.

Corrosion may also play a role in bearing failure, as it often results when acids accumulate in the crankcase and attack the bearings, causing pitting in their surfaces. This is much more problematic with heavy-duty diesel engines that use high-sulfur fuels rather than with gasoline engines, although the situation may occur in gasoline engines if the oil is not changed often enough and acids are allowed to accumulate within the crankcase. Other factors that may contribute to acid build-up include engine operation during extremely cold or hot weather, excessive crankcase blow-by (due to worn piston rings or cylinders), or the use of poor-quality oil or fuel. Misalignment can also accelerate bearing wear; for example, if the center main bearings are worn more than those towards either end of the crankshaft, the crankshaft may be bent or the main bores may be out of alignment.

8.5.5.6 Camshaft to Cam Follower, Valves, Valve Mechanisms, and Valve Train

In the ICE, the *cam-and-follower system* is required to control the opening and closing of the valves to the cylinder head. As the camshaft rotates, it presses against a flat or roller surface, which reciprocates to open and close the valves. Most engines have two valves for each cylinder – one intake valve, and one exhaust valve. Since each of these valves operates at different times, separate operating mechanisms must be provided for each valve, and this implies that the followers must open the valves to which they are connected once during the four-stroke cycle. For instance, the follower which is in contact with the inlet valve will open the inlet valve for the induction stroke, and close it for the other three strokes. The follower for the exhaust valve must open the exhaust valve for the exhaust stroke, and close it for the other three strokes. Valves are normally held closed by heavy springs and by compression in the combustion chamber. The purpose of the valve-actuating mechanism is to overcome the spring pressure and open the valves at the correct time. The valve-actuating mechanism includes the engine camshaft and camshaft follower, the so-called “tappets,” push-rods, and rocker arms (Figure 8.54a and b).

The *camshaft*, which is enclosed in the engine block, has eccentric lobes (cams) ground on its surface for each valve in the engine. As the camshaft rotates, the cam lobe moves up under the valve tappet, exerting an upward thrust through the tappet against the valve stem or a pushrod. This thrust overcomes the valve spring pressure and also the gas pressure in the cylinder, causing the valve to open. When the lobe moves from underneath the tappet, the valve spring pressure causes the valve to be reseated.

In V-type engines, the camshaft is usually located directly above the crankshaft. The camshaft of a four-stroke cycle engine turns at one-half engine speed, and is driven off the crankshaft through timing gears or via a timing chain (see Section 8.5.5.7). In

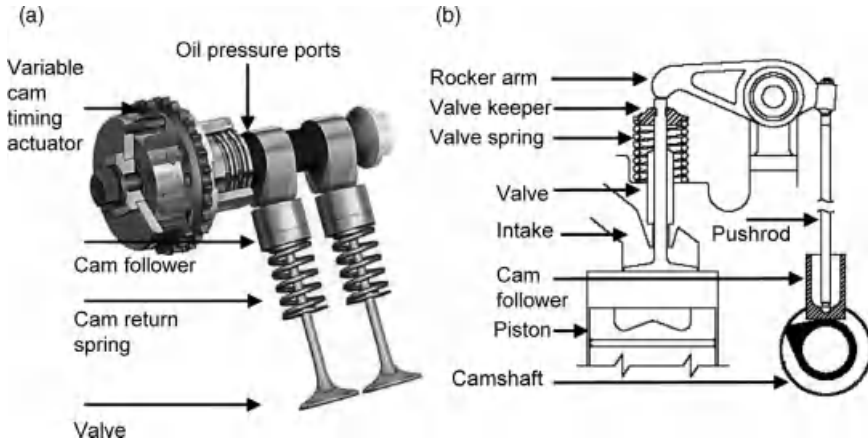


Figure 8.54 Cam-and-follower systems of an internal combustion engine. (a) Camshaft with plate cams imparting on flat followers and valves; (b) Camshaft of an engine incorporating a rocker arm.

most cases, the camshaft will do more than operate the valve mechanism; notably, it may have extra cams or gears that operate fuel pumps, fuel injectors, the ignition distributor, or the lubrication pump. Camshafts are supported in the engine block by journals in bearings, and the camshaft bearing journals are by far the largest machined surfaces on the shaft. The bearings are usually made from bronze, and are bushings rather than split bearings; the bushings are lubricated by oil circulating through drilled passages from the crankcase. Typically, the stresses on the camshaft are small, and the bushings are not adjustable; rather, they are often replaced when the engine requires a complete overhaul.

The *camshaft followers* represent the parts of the valve-actuating mechanism that contact the camshaft, and are termed “valve tappets” or “valve lifters.” In the L-head engine, the followers directly contact the end of the valve stem and contain their own adjusting device (see Figure 8.54b). By contrast, in the overhead valve engine, the followers contact the pushrod that operates the rocker arm, and the end of the rocker arm opposite the pushrod contacts the valve stem. In this case, the valve-adjusting device is in the rocker arm. Many engines have self-adjusting, hydraulic valve lifters that always operate at zero clearance; the operation of one such type of hydraulic valve tappet mechanism is shown in Figure 8.55. In this system, oil under pressure is forced into the tappet when the valve is closed, and the pressure extends the plunger in the tappet so that all valve clearance is eliminated. When the cam lobe moves around under the tappet and starts to raise it, there is no tappet noise. The movement of the tappet then forces the oil upwards into the lower chamber of the tappet; this action closes the ball check valve so that oil cannot escape. The tappet then acts as though it were a simple, one-piece tappet, and the valve is opened. When the lobe moves out from under the tappet and the valve closes, the pressure in the lower chamber of the tappet is relieved. Any slight loss of oil from the lower chamber is replaced by the oil pressure from the engine-lubricating system. This oil pressure

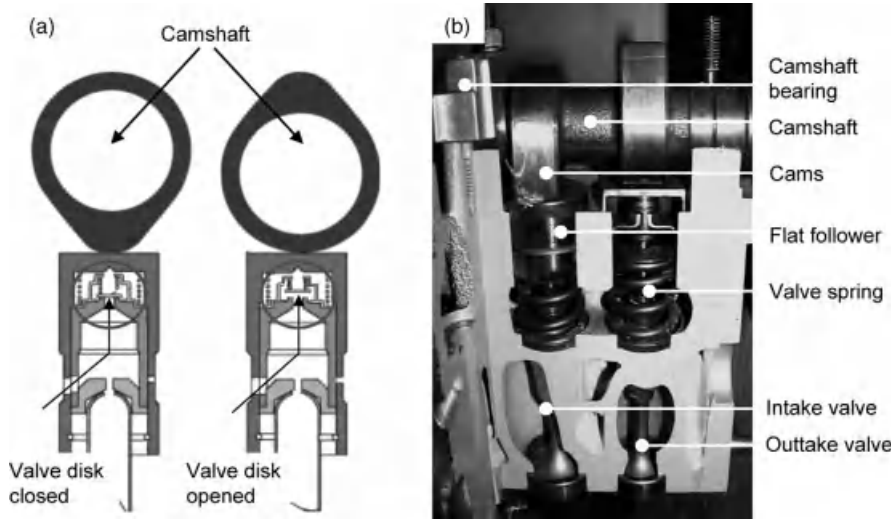


Figure 8.55 Camshaft-and-follower system. (a) Operation of a hydraulic valve lifter; (b) Engine with an overhead camshaft and hydraulic valve adjustment.

causes the plunger to move up snugly against the pushrod, so that any clearance is eliminated.

The interface between the camshaft and follower is unidirectional sliding between nonconformal surfaces. Although engines are designed to provide oil to this interface, it is likely that oil will be scarce at times; for example, when starting a cold engine the cams will begin turning before the pressure is sufficient to pump oil to the top of the engine. A few material combinations have been used successfully in this application, and even those have been shown to wear sufficiently during the life of an engine as to require periodic adjustment, or the use of self-adjusting hydraulic elements. The severity of these various surface interactions is reduced by the presence of engine oil. As friction reduction is an important means for conserving energy and preserving nonrenewable fuel sources, techniques to reduce friction will continue to become increasingly important [145].

8.5.5.7 Gear Trains: Timing Gear Chain and Timing Belt

The relationship between the rotation of the camshaft and that of the crankshaft is of critical importance. As the valves control the flow of air/fuel mixture intake and exhaust gases, they must be opened and closed at the appropriate time during the stroke of the piston. The *gear train* is needed to synchronize the camshaft to the crankshaft position, so that the valves will open and close at the correct time in relation to the position of the pistons. The camshaft rotates at exactly half the speed of the crankshaft, and for this reason it is connected to the crankshaft either directly, via a gear mechanism, or indirectly, via a belt or chain called a “timing belt” or “timing chain.” In some designs, the camshaft also drives the distributor and the oil and fuel

pumps; in some early fuel injection systems, cams on the camshaft would also operate the fuel injectors. In general, a *timing chain* is used in medium and large size cars, where the gears or sprockets of the camshaft and crankshaft are keyed into position, so that they cannot slip. By contrast, a *timing belt* is a toothed belt that connects the engine crankshaft to the camshaft or camshafts, and is mainly used in small and medium-sized passenger cars. The timing belt must be replaced, as specified by the vehicle manufacturer, at intervals varying from 96 000 km (60 000 miles) to 170 000 km (100 000 miles). The timing belt must also be replaced if it sustains any damage such as cracks, cuts, or excessive wear. If the belt is not replaced and breaks, then serious engine damage will be caused, because the camshaft will stop turning (leaving some of the valves in the open position) while the crankshaft continues to rotate, by inertia.

8.5.5.8 Fuel Supply System

In order for an engine to operate efficiently, the fuel must be vaporized into the incoming air in as a fuel/air mixture. Two main methods are used to vaporize fuel into the air: (i) the carburettor; and (ii) fuel injection.

Although, for simpler reciprocating engines, a carburettor is used to supply fuel into the cylinder, an efficient and exact control of the correct amount of fuel supplied to the engine is impossible. A fuel will burn faster and more completely when it has a large surface area in contact with oxygen. Consequently, larger gasoline engines, such as those used in automobiles, have mainly switched to fuel injection systems which, in the case of a diesel engine, can also be used to control the ignition timing. Today, the main injection systems used are gasoline direct injection (GDI) or turbo-diesel direct injection (TDI). Such fuel injection systems are designed and calibrated specifically for the type (or types) of fuel that will be handled, such as gasoline (petrol), autogas (liquid petroleum gas; LPG, also known as propane), ethanol, methanol, methane (natural gas), hydrogen, or diesel. Today, the direct injection has been further developed to the “common rail technology.”

Whilst the designs of fuel injection systems may vary in the way they supply fuel to the combustion process, the way in which any particular system is optimized is very much a matter of design decision. Very often, several objectives may be conflicting, such that it becomes impractical for any single engine control system to fully optimize all of the criteria, simultaneously. In practice, the modern digital electronic fuel injection system is far more capable at optimizing the following competing objectives than would be a carburettor:

- power output
- fuel efficiency
- emissions performance
- ability to accommodate alternative fuels
- reliability
- driveability and smooth operation
- initial cost
- maintenance cost

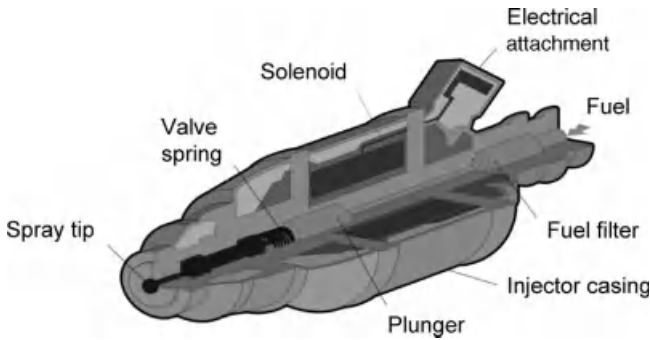


Figure 8.56 Typical fuel injector, a device used to deliver fuel to the internal combustion engine.

- diagnostic capability
- range of environmental operation.

A typical electronic fuel injector (EFI) is shown in Figure 8.56. The operation requires further components, such as further injectors, fuel pump, fuel pressure regulator, and an engine control module (ECM) that includes a digital computer and circuitry to communicate with sensors and control outputs. A wiring harness and various sensors are also required, such as crank/cam position (Hall effect sensor), airflow sensor, exhaust gas oxygen (Oxygen sensor, EGO sensor, UEGO sensor). Central to any EFI system is a computer termed the Engine Control Unit (ECU), which monitors engine operating parameters via various sensors. The ECU interprets these parameters in order to calculate the appropriate amount of fuel to be injected (among other tasks), and controls engine operation by manipulating the fuel and/or air flow as well as other variables. The optimum amount of injected fuel depends on conditions such as engine and ambient temperatures, engine speed and workload, and exhaust gas composition. The electronic fuel injector is normally closed, and opens to inject pressurized fuel as long as electricity is applied to the injector's solenoid coil. The duration of this operation, called the *pulse width*, is proportional to the amount of fuel desired. The electric pulse may be applied in a closely controlled sequence with the valve events on each individual cylinder (in a sequential fuel injection system), or in groups of less than the total number of injectors (in a batch fire system). As the nature of fuel injection dispenses fuel in discrete amounts, and since the nature of the four-stroke engine has discrete induction (air-intake) events, the ECU calculates fuel in discrete amounts. In a sequential system, the injected fuel mass is tailored for each individual induction event. Every induction event, of every cylinder, of the entire engine, is a separate fuel mass calculation, and each injector receives a unique pulse width based on that cylinder's fuel requirements.

8.5.5.9 Oil Pump

An adequate distribution of lubricant through the engine, and sufficient flow to maintain hydrodynamic conditions in engine bearings of automotive engines,

require a pressurized lubrication system. The oil flows in a closed circuit, beginning with the oil sump, from which the oil is drawn into an oil pump which itself then delivers pressurized fluid through a filter. The oil then passes through passages in the block and head, to the crankshaft and camshaft bearings, as well as flowing to the (hydraulic) valve lifters in engines. The oil is then thrown from the rotating components onto the cylinder walls, valve lifters, and all other components. As the oil runs off these surfaces, gravity directs it back to the sump, during which time it serves to cool the pistons, connecting rods, cylinder head, and the whole engine block. Today, two types of oil pump are mainly used: the *spur gear pump* and the *gerotor* (the name is derived from “generated rotor”). Whilst a spur gear pump is of an older design, and is relatively quiet in operation, a gerotor is more efficient and takes up less space in the engine compartment; consequently, most recent designs prefer the gerotor. The oil pump should also incorporate a relief valve for pressure regulation.

The *gerotor* (Figure 8.57) utilizes a positive-displacement pump mechanism, and delivers a predetermined quantity of fluid in proportion to the vehicle’s speed. The inner rotor has one tooth less than the outer rotor, one rotor is located off-center, and both rotors rotate. During part of the assembly’s rotation cycle, the area between the inner and outer rotor increases, creating a vacuum that creates suction; it is this part of the cycle that the intake is located. The area between the rotors is then allowed to decrease, causing compression, at which time the fluids can be pumped. The designers of engines, compressors, machine tools, tractors and other equipment that require hydraulic systems, can build the pump components integrally into these mechanisms at a fraction of the cost of a complete, separately allocated oil pump. The main advantage of stacking compact gerotor elements along a single shaft is that this replaces multiple pump functions. Currently, a wide variety of gerotor sizes are available, covering capacities of up to 380 l min^{-1} ($100 \text{ US gal. min}^{-1}$) and 70 bar (1000 psi). Details of other engine oil pump designs are provided in Section 8.6.4.

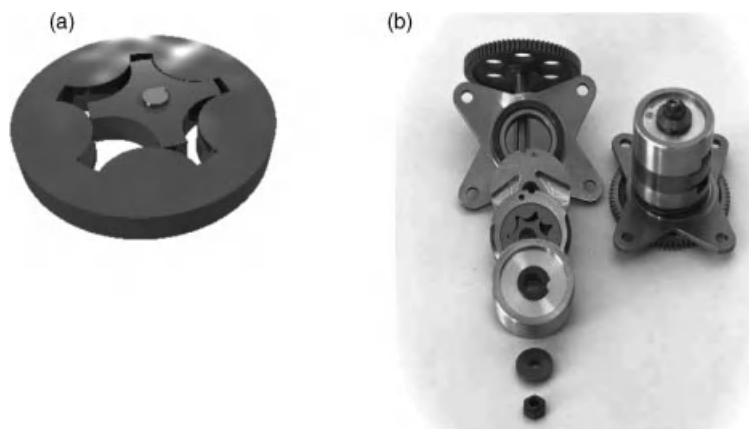


Figure 8.57 Gerotor – engine oil supply system. (a) Cross-section of a gerotor; (b) Parts of a gerotor.

8.5.5.10 Oil Filter

Oil filters and lubricating oils are closely related, and are interdependent. Both are tribologically of crucial relevance for the working life of the lubricated parts of an engine or of the driveline components. Oil filters are intended to remove solid impurities (particles) from lubricants in circulation, the filter element or cartridge generally being either a pleated paper or metal mesh. The primary filter materials may be composed of micro-fiberglass, metal meshes, and/or cellulose paper.

Generally, oil filters are rated by a variety of tests, including industry standard methods and proprietary assays, with the most commonly reported performance figures being for particle removal and flow restriction. The main target is to obtain the highest level of particle removal while causing the least flow restriction. As the flow is known to decrease as the quantity of trapped material increases, filter systems will in general include a bypass circuit that opens when the pressure ahead of the filter reaches a predetermined level. This will allow the oil to continue circulating if the filter becomes plugged, although contaminants will then be allowed to circulate through the engine. The most important characteristics of oil filters are the mesh and retention sizes; for example, the designation $\beta_3 > 200$ describes a filter of $3\ \mu\text{m}$ mesh size and a separation rate of 200 (which means that only one particle among 200 particles will pass the filter). In addition, the initial pressure difference (ΔP_{max} , 0.1–0.2 bar or 1.5–4.5 psi) and the maximum output pressure difference (ΔP_{max} , 3–5 bar or 43.5–72.5 psi) in relation to the flow rate, oil viscosity, and density are of importance. When using filters with micron ratings of, for example, $1\ \mu\text{m}$, $3\ \mu\text{m}$, and $6\ \mu\text{m}$, special care must be taken, since high-molecular-weight components of the oil (viscosity improvers) and contaminations (grease, corrosion preventives) can, in particular, cause the filters to be blocked.

8.5.5.11 Single- and Dual-Mass Flywheel Systems

The principle of the piston-stroke engine, the internal combustion processes of which excite torsional vibrations in the drive train, can lead to unpleasant consequences such as gear rattles and body booms, especially when modern engines are driven at extremely low rotation speeds. The flywheel reduces driveline oscillations by mechanically decoupling the crankshaft from the transmission. The flywheel is mounted at the rear of the crankshaft, close to the rear main bearing; the latter is usually the longest and heaviest bearing in the engine, as it must support the weight of the flywheel. Today, in many passenger cars and light trucks, the conventional driveline is extended by either a single-mass flywheel (SMF) or a dual-mass flywheel (DMF) (Figure 8.58a). Present-day engine control systems are generally designed for use with conventional SMF systems, although in order to facilitate the optimal control of engines, increasing numbers of vehicles are today being equipped with advanced DMF systems. In this case, one mass will continue to belong to the engine's mass moment of inertia, while the other mass will increase the mass moment of inertia of the transmission. These two decoupled masses are linked by a spring/damping system (see Figure 8.58b), in which the arc spring is filled with grease so as to reduce the inner friction. A single clutch disk, without a torsion damper and located between the secondary mass and the transmission, handles the engaging and disengaging

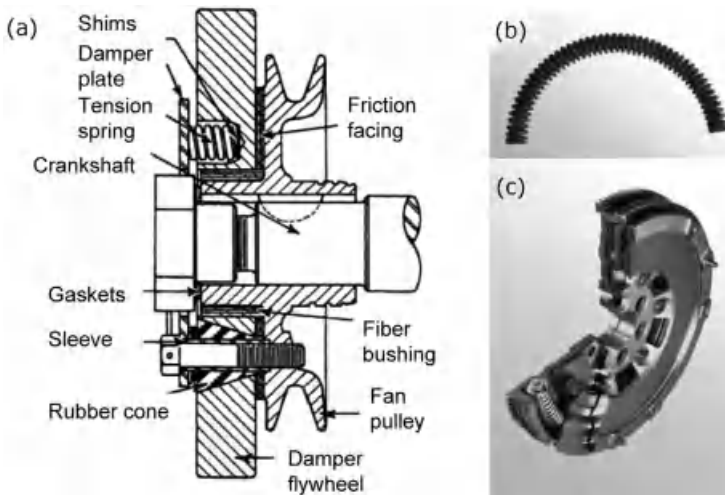


Figure 8.58 Dual-mass flywheel. (a) Sectional view of a typical vibration dampener; (b) Rotational damping arc spring; (c) Dual-mass flywheel.

functions, while shifting gears. One positive effect of the DMF is that the transmission is easier to shift because of the low mass to be synchronized, and there is also less synchronization wear. During the power impulses of the engine, the flywheel stores up rotation energy which is then released between the power impulses, thus assuring less fluctuation in engine speed and a smoother engine operation [153]. The size of the flywheel will vary with the number of cylinders and the general construction of the engine. With a large number of cylinders and a consequent overlapping of power impulses, there is less of a need for a flywheel, and consequently the flywheel itself can be relatively small. Generally, the flywheel rim carries a ring gear (either integral with or shrunk onto the flywheel) that meshes with the starter driving gear for cranking the engine (see Figure 8.58c). The rear face of the flywheel is usually machined and ground, and serves as one of the pressure surfaces for the clutch, thus becoming a part of the clutch assembly.

From the tribological point of view, it is tempting to achieve functional improvements by reducing the friction between the arc spring and the shell. Whilst the friction necessary for start-up is then clearly reduced, this can be compensated by using friction control plates or by using two-stage arc springs with their favorable low first rate. The coefficient of friction can be reduced, in theory, by changing each of the three components of the tribological system, namely the arc spring shell, the grease, and the arc spring. Coatings can be used to influence the behavior of the arc spring shell and, indeed, trials with very different coatings have been shown to deliver sufficient wear resistance. In addition to the standard grease, a friction-optimized type of grease can be helpful, although it was found that increasing the amount of grease did not bring about an improvement in the static to sliding friction ratio. To summarize, the benefits of the dual-mass flywheel include enhanced driving

comfort, the absorption of vibrations, and noise prevention, all of which permit comfortable driving at low speed, fuel savings, and the physical relief of the crankshaft and gearbox.

8.5.5.12 Auxiliary Assemblies

Auxiliary assemblies – those other parts of the engine that are essential for engine operation – very often have a major influence on the tribology of engines and transmissions. Such assemblies are not normally built into the engine itself, but rather are attached to the engine block or cylinder head. They often include the fuel pump, which may be mounted on the engine (see Section 8.5.5.9), or an electrical system to supply power for starting the engine and for igniting the fuel during operation. Typically, the operation of an ICE requires an efficient cooling system, with water-cooled engines requiring a water pump and fan, while air-cooled engines use a blower to force cool air around the engine cylinders. An exhaust system is provided to carry away the burned gases exiting from the engine's cylinders.

8.5.5.13 Engine Testing

Field-related engine tests cannot be performed only over extensive field trials; rather, a number of international committees have created methods for testing engines under defined, reproducible and practically relevant conditions. In Europe, the Coordinating European Council (CEC) for the Development of Performance Tests for Lubricants and Fuels is responsible for testing, approval, and standardization. Performance requirements are set-up in the form of ACEA (Association des Constructeurs Européen d'Automobiles) oil sequences, which are decided together with the additive and lubricant industries. In the USA, this task is performed by the automobile industry and the API, which lays down test procedures and limits. In Asia, the Asian ILSAC has largely adopted the American specifications for automobiles where, in principle, the test engines and procedures focus on general performance criteria for passenger cars (as listed in Table 8.24) and for trucks (heavy-duty applications; see Table 8.25). The test criteria description is closely related to that described in the Sections 8.5.5.1 to 8.5.5.9.

8.5.6

Rotary Engines

8.5.6.1 Application and Operation of Rotary Engines

During the 1950s and 1960s, considerable effort went into the design of rotary engines. Such engines were of special interest for passenger cars, because this design delivers smooth, high-revolution power from a compact, lightweight engine. They are also very quiet-running and have a high reliability that results from their simplicity. The “Wankel” rotary engine, as developed by Felix Wankel during the 1950s [136], utilizes a rotor instead of reciprocating pistons, while having also the four strokes of a typical gasoline cycle (the “Otto” cycle). The first working prototype DKM 54 (see Figure 8.59) was run in 1957 at the research and development department of NSU Motorenwerke AG, Neckarsulm, while in Great Britain, during the 1960s, Rolls

Table 8.24 Passenger car performance tests for four-stroke engines.

Test engine	Test procedure	Test criteria
BMW N52 B25	BMW inhouse	Chassis dyno fuel economy effects of engine lubricants.
BMW N52 AE	BMW inhouse	Air entrainment of engine lubricants using the BMW M52 B30.
BMW N42 RNT	BMW inhouse	Engine lubricant-related wear behavior of the BMW Valvetronic System, using the BMW N42 B18 engine and radiotracer technique
Mercedes OM 364 LA	CEC L-42-T-99	Evaluation of diesel engine oils using the OM 364 LA diesel engine.
Mercedes OM 602 A	CEC L-51-A97	Average cam wear (new tappet), viscosity increase at 40°C, bore polishing, average cylinder wear, oil consumption.
Mercedes OM 646 LA	CEC L-99-08	Development of a passenger car diesel engine wear test using the DC OM 646 DE 22 LA engine (300 h wear test).
Mercedes M 111 Sludge	CEC L-53-T-95	Gasoline engine, low-temperature wear and sludge, determination of average engine sludge (black sludge) and cam wear.
Mercedes M 111 FE	CEC L-54-T-96	Fuel economy effects of engine lubricants, improvement vs. reference oil RL 191 (15W-40)
Mercedes M 271 Sludge Test	Mercedes in house	The evaluation of engine lubricants with respect to sludge formation using the Mercedes M 271 KE18 engine, black sludge.
Mercedes M 271 Wear Test	Mercedes inhouse	The evaluation of engine lubricants with respect to wear using the Mercedes M271 KE18 engine, wear, cleanliness, oxidation, oil consumption.
Opel OP 1 (X20XEV)	GMPTE-T DUR020	Gasoline long-drain properties, oil-aging test.
Opel RNT Valve Train Wear (X20XEV)	GMPTE-T DUR021	Radionuclide wear test, gasoline engine wear.
Opel Aeration	GMPTE-T MEC024	Gasoline engine wear, fresh, used reference oil.
Opel Fuel Economy	GME 8331 TP	Chassis dyno test, chassis dynamometer test using 1.8l, 85kW Opel Astra, test candidate and reference oil.
Opel DI Performance Test	GMPTE-T DUR 019	400 h engine test using Y22DTR engine.
PSA DV4 Test	CEC L-93-04	Oil dispersion test at medium temperature for passenger car direct injection diesel engines, absolute viscosity increase at 100°C and 3% soot, piston merits.

PSA TU3 M-KDX VTS	CEC L-38-A-94	Gasoline engine valve train scuffing, average engine sludge, rocker cover sludge, piston skirt varnish, compression ring (hot stuck), oil screen clogging.
PSA TU3 M-KDX HTDT	CEC L-55-T-95	High-temperature deposits, ring sticking and oil thickening.
PSA TU5 JP HTDT	CEC L-88-02	Evaluation of oil oxidation, high-temperature deposits and ring sticking in gasoline engines, ring sticking (each part), piston varnish (six elements, average of four pistons), absolute viscosity increase at 40 °C between, minimum and maximum values during test, oil consumption.
PSA XUD11 BTE	CEC L-56-T-95	Oil dispersancy test for passenger car diesel engines, absolute viscosity increase at 100 °C and 3% soot, piston merits (five elements, average for four pistons).
VW T4	VW PV 1449	Gasoline engine viscosity increase and piston deposit test, oil oxidation, total base number depletion, piston cleanliness.
VW TDI 2	CEC L-78-T-99 (VW PV 1452)	Direct injection, ring sticking (rings 1 and 2), and piston cleanliness test.
VW RNT Wear Test	PV 1473	Pump injection unit diesel engine wear test using radiotracer technique, radionuclide wear test, wear test for low-viscosity oils in PD-Diesel engines with extended drain intervals (250–650 h test duration).
VW FSI Test	VW PV 1481	Engine lubricant performance regarding deposit formation in direct-injection gasoline engines.
VW DPF Test	VW inhouse	Oil ash accumulation in diesel particle filters.
VW Engine Tests (PZD/DL1)	VW inhouse	VW prototype technical-release procedure.
VW Cam and tappet	VW PV 5106	Valve train wear test.
VW/Audi FE	VW PV 1451	Chassis dynamometer test using 1.8l 5V-Turbo 110kW engine.
MWM B	CEC L-12-A-76	Evaluation of piston cleanliness in the MWM KD 12 E diesel test engine.
Sequence II D	ASTM STP B15 M P1	Bearing corrosion.
Sequence III E	ASTM STR 315 M P2	Oxidation, wear, cleanliness.
Sequence VG	ASTM D 6593	Average engine sludge, rocker cover sludge, average piston skirt varnish, average engine varnish, compression ring (hot stuck), oil screen clogging.

Table 8.25 Heavy-duty truck performance tests for four-stroke engines.

Test engine	Test procedure	Test criteria
Caterpillar 1K/1N	Caterpillar inhouse	Piston cleanliness, wear, oil consumption.
Cummins ISB	Cummins inhouse	Valve train wear (cam and tappet) with slider/follower type lifters in a severe environment, sludge.
Mack T 8	ASTM D 4485	Viscosity increase at first, second, and third average, filter plugging (differential pressure), oil consumption.
Mack T 8E	ASTM D 5967	300 h soot handling, viscosity increase at first, second, and third average.
Mack T12	Mack T12 Draft 7	300 h HD EGR engine wear test evaluating diesel engine oils performance characteristics, including lead, corrosion, wear of piston rings and cylinder liners.
	ASTM D 6987	Average engine sludge, average liner wear, average top ring weight loss, end of test lead, delta lead from 250–300 h, oil consumption.
GM 6.2 Liter	GM inhouse	Valve train wear.
Mercedes OM 441 LA	CEC L-52-T-97	Low emission heavy duty diesel (400 h).
Euro II		Average engine sludge, piston cleanliness (no ring sticking), general engine deposits, average wear rating, bore polishing, average cylinder wear, ring sticking second piston rings, specific oil consumption, turbo-charger deposits, boost pressure lost at 400 h.
Mercedes OM 501 LA	CEC L-101-08	The evaluation of engine lubricants using the Mercedes HD engine Euro 5.
Mercedes OM 611 LA	Mercedes inhouse	Currently a Mercedes inhouse test procedure. The evaluation of engine crankcase lubricants with respect to low-temperature lubricant thickening and wear under severe operating conditions, using the DaimlerChrysler OM 611 DE22LA engine. Piston cleanliness (average four pistons), ring sticking, average engine sludge, viscosity increase at 100 °C, oil consumption, bore polishing, timing chain wear elongation, average cylinder wear, average cam wear (inlet and outlet), bearing wear (main and rod bearing), axial and radial piston ring wear (ring 1, 2, and 3).
MAN Meistersinger II	MAN inhouse	Oil performance test using the MAN D2876 LF04 engine (400 h). Engine cleanliness, sludge, piston ring wear, piston ring sticking, bore polishing, cylinder wear, rocker arm wear, tappets, camshaft, rocker arm outlet wear, valve bridges inlet and outlet wear, bearing and oil pump, total engine deposits, used oil analysis, total oil consumption.
SCANIA DSC 1201 FE	Scania inhouse	Fuel economy effect of engine lubricants in HDD engines.
VOLVO Volvo D12D	Volvo inhouse	Engine test, 400 h piston cleanliness test.
VOLVO Volvo D12D FE	Volvo inhouse	Fuel economy effect of engine lubricants in HDD engines.

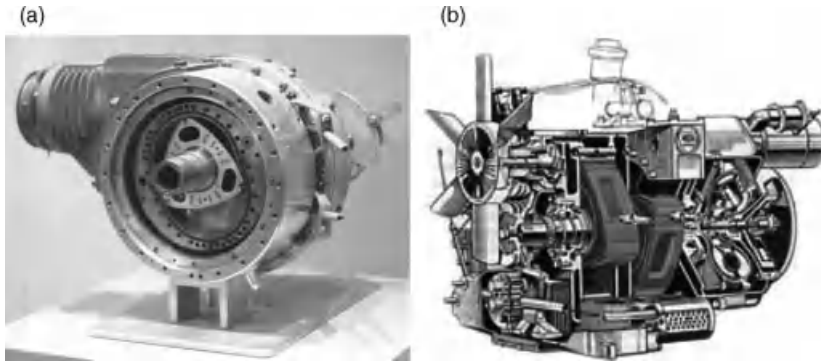


Figure 8.59 Rotary internal combustion engine. (a) The first Wankel engine, DKM 54; (b) Sectional view of the DKM 54 Wankel engine.

Royce Motor Car Division at Crewe, Cheshire, pioneered a two-stage diesel version of the Wankel engine. In Britain, the Norton company developed a Wankel rotary engine for motorcycles, as did Suzuki, who subsequently produced a motorcycle (the RE-5) which was fitted with a Wankel engine. During 1971 and 1972, Arctic Cat produced snowmobiles powered by 303 cV Wankel rotary engines that were manufactured by Sachs in Germany. Overall, however, the car manufacturer Mazda has been the major pioneer in developing rotary engines, having produced the RX-7 – which probably was the most successful rotary-engine-powered car – in 1978. This vehicle had been preceded by a series of rotary-engine cars, trucks and even buses, starting with the 1967 Cosmo Sport. In fact, in 2003, the Mazda RX-8 rotary engine – a naturally aspirated two-rotor engine producing about 250 horsepower – was named International Engine of the Year.

Like a piston engine, the rotary engine uses the pressure created when a combination of air and fuel is burned. In the basic single-rotor Wankel engine, the oval-like epitrochoid-shaped housing surrounds a three-sided rotor; this is similar to a three-pointed curve of constant width (triangle), but with the middle of each side slightly more flattened. Within the triangular rotor is incorporated a central ring gear that is driven around a fixed pinion within an oblong chamber. The rotary motion is transferred to the eccentric shaft (E-shaft), passes through the center of the rotor, and is supported by bearings. As the rotor rotates and orbital revolves, each side of the rotor becomes closer and farther from the wall of the housing, compressing and expanding the combustion chamber, in similar fashion to the strokes of a piston in a reciprocating engine. The power vector of the combustion stage goes through the center of the offset lobe (crank) on the E-shaft, such that the drive shaft rotates once during every power stroke, instead of twice as in the Otto cycle. Usually, the combustion process takes place not in four-strokes but rather in four phases:

First phase – Intake (Figure 8.60a): The intake phase of the cycle starts when the tip of the rotor passes the intake port. At the moment the intake port is exposed to the chamber, the volume of that chamber is close to its minimum. As the rotor moves past the intake port, the volume of the chamber expands, drawing

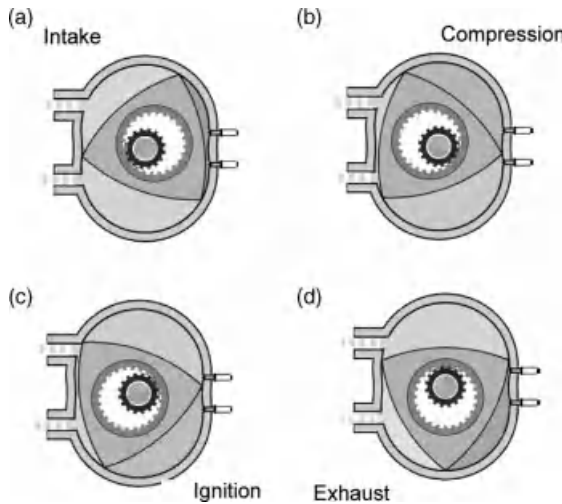


Figure 8.60 The Wankel engine's combustion process. (a) Intake; (b) Compression; (c) Ignition; (d) Exhaust.

the air/fuel mixture into the chamber. When the peak of the rotor passes the intake port, that chamber is sealed off and compression begins.

Second phase – Compression (Figure 8.60b): As the rotor continues its motion around the housing, the volume of the chamber becomes smaller and the air/fuel mixture is compressed. By the time the face of the rotor has moved around to the spark plugs, the volume of the chamber is again close to its minimum. This is when combustion starts.

Third phase – Combustion (Figure 8.60c): The mixture burns here, driving the rotor around. Most rotary engines have two spark plugs; this is because the combustion chamber is long and the flame would spread too slowly if there were only one plug. When the spark plugs ignite the air/fuel mixture, the pressure quickly builds, forcing the rotor to move. The pressure of combustion forces the rotor to move in the direction that causes the chamber to grow in volume. The combustion gases continue to expand, moving the rotor and creating power, until the peak of the rotor passes the exhaust port.

Fourth phase – Exhaust (Figure 8.60d): Once the peak of the rotor has passed the exhaust port, the high-pressure combustion gases are free to flow out with the exhaust. As the rotor continues to move, the chamber begins to contract, forcing the remaining exhaust out of the port. By the time the volume of the chamber is nearing its minimum, the peak of the rotor has passed the intake port, and the whole cycle starts again.

8.5.6.2 Tribology of Rotary Engines

In general, the tribological criteria for the quality and reliability inside rotary engines are comparable to those of reciprocating four-stroke engines (see Section 8.5.5), although all moving parts of rotary engines operate under different kinematic and

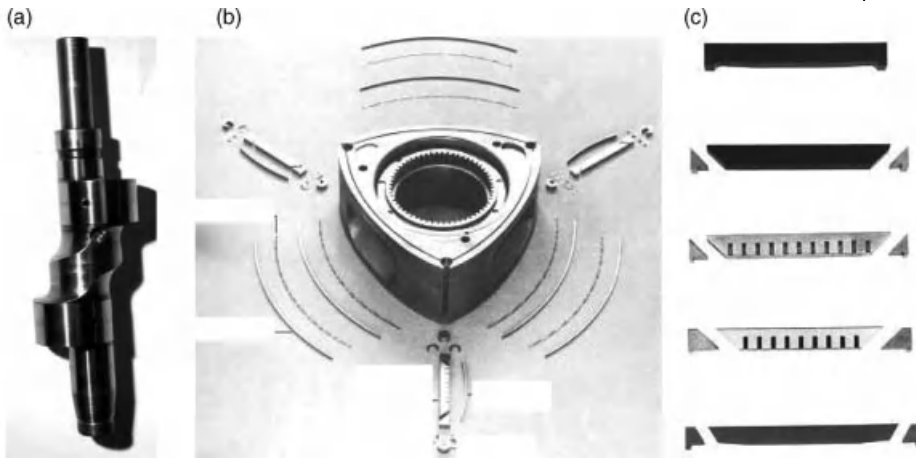


Figure 8.61 Wankel engine's main shaft and sealing. (a) Rotary engine eccentric output shaft or E-shaft (crank); (b) Sealing of a Wankel engine; (c) Seal development within the past.

thermodynamic conditions. In rotary engines, the moving parts spin continuously in one direction, rather than violently changing directions, as do the pistons in reciprocating engines. A four-stroke piston engine has about six to twelve times more moving parts, including pistons, connecting rods, camshafts, valves, valve springs, rockers, timing belt, timing gears and crankshaft, than a rotary engine. Consequently, the rotary engine promises a higher power output with fewer moving parts than piston engines; moreover, their power delivery is smoother, because the rotary engine is internally balanced with spinning counterweights that are phased to cancel out any vibrations. As the rotors spin at one-third the speed of the output shaft (Figure 8.61a), the moving parts of the engine also move more slowly than those of the piston engine, such that there is one combustion stroke for each revolution of the output shaft. A rotary engine has ignition and fuel-delivery systems similar to those of piston engines. The intake and exhaust ports, which are located in the housing, do not carry any valves as the exhaust port connects directly to the exhaust, while the intake port connects directly to the throttle. The rotor has a set of internal gear teeth cut into the center of one side; these teeth mate with a gear that is fixed to the housing. This gear mating determines the path and direction that the rotor takes through the housing. Fixed gears mounted on each side of the housing engage with ring gears attached to the rotor to ensure correct orientation as the rotor moves. Despite these advantages, certain difficulties in technical the design and tribology of rotary engines appear to have prevented their adoption worldwide:

- Heat build-up in rotary engines is more critical than in piston designs, because their “cylinder block” operates at steady state, with intake, compression, combustion, and exhaust occurring at fixed housing locations for all “cylinders.” The combustion area is continually subject to high temperatures and never cooled by an intake stroke. In contrast, reciprocating engines perform these four strokes in

one chamber, so that extremes of freezing intake and flaming exhaust are averaged and shielded by a boundary layer from overheating working parts. Thus, the rotary design leads to very high chamber temperatures of more than 2300 K in the combustion area that reduce the expanding pressure of the burning fuel/vapor mix, restricting available power.

- The long combustion chamber shape in a Wankel lowers the compression ratio when compared to the piston design. Combustion pressures are in the range of 8.5 bar (125 psi) for gasoline and 20 bar (290 psi) for diesel fuel design. This lowers the thermodynamic efficiency and reduces the fuel economy of the rotary engine. In addition, some fuel may be too far from the flame front during combustion and will not be fully burned. Consequently, there may be more carbon monoxide and unburnt hydrocarbons in a Wankel engine exhaust stream, making it more difficult for the rotary engine to meet today's strong emissions regulations.
- A challenge when designing rotary engines arises from the uneven thermal distribution within the housings, which may cause distortion and a loss of compression and sealing. Attempts have been made to normalize the temperature of the housings, thus minimizing the distortion, by using different coolant circulation patterns and housing wall thicknesses.
- Compared to a conventional engine, to seal a Wankel is much more demanding. Sealing of the rotor is shown in Figure 8.61b, where the dynamics of the rotor's eccentric rotation creates centrifugal and Coriolis forces that are relatively high, especially on one face at the corners of the triangular rotor, where it is sealed against the periphery of the housing. As the rotor moves through the housing, the three chambers form three sealed volumes of gas, while the rotor changes size. In turn, this size change produces a pumping action combined with rapidly changing pressure differences between the three chambers and on the seals.
- Thermal distortion may also cause uneven wear between the apex seal and the rotor housing, which is quite evident on higher mileage engines. Therefore, the seals must be made more resistant to heat.
- The shape of the combustion chamber is designed so that the three tips of the rotor will always stay in contact with the wall of the chamber. The apex seal of each face is a metal blade that forms a seal to the outside of the combustion chamber. There are also metal rings on each side of the rotor that seal to the sides of the combustion chamber. Early engine designs had a high incidence of sealing loss, both between the rotor and the housing and also between the various pieces that make up the housing. The development of the apex seals during past years is shown in Figure 8.61c.

8.5.7

Gas Turbines: High-Power Engines

8.5.7.1 Area of Application and Operation of Gas Turbines

Gas turbines are used in a wide array of stationary, marine, and aerospace applications, with land-, sea-, and air-based generating systems producing anywhere from a

few tens of kilowatts to multi-megawatts of power. The drives for natural gas pipeline compressors or land and marine propulsion systems produce thousands of shaft horsepower. Today, most commercial jets are powered by gas turbines, with jet engines being optimized to produce thrust either from the exhaust gases, or from ducted fans connected to the gas turbines. Jet engines that produce thrust primarily from the direct impulse of exhaust gases are often referred to as *turbojets*, whereas those that generate most of their thrust from the action of a ducted fan are termed *turbofans* or *fanjets*. Smaller gas turbines are also used as auxiliary power units, which are designed for auxiliary power of larger machines, such as in aircraft ventilation systems with an appropriate compressor design, as start-up power for larger jet engines, and for electrical and hydraulic power [137].

Simple-cycle gas turbines in the power industry require a smaller capital investment than do either coal or nuclear power plants, and they can be scaled to generate small or large amounts of power. Their main advantage is the ability to be turned on and off within minutes, supplying power during peak demand. Industrial gas turbines range in size from truck-mounted mobile plants to enormous, complex and efficient systems. Gas turbines for electrical power production can be very efficient (up to 60%) when waste heat from the gas turbine is recovered via a heat-recovery steam generator to power a configuration, where the exhaust is used for space or water heating, or to drive a conventional steam turbine in a combined cycle configuration. Gas turbines can also be run in a co-generation absorption chiller for cooling or refrigeration, which may be more than 90% efficient. The power turbines in the largest industrial gas turbines operate at 3000 or 3600 rpm to match the AC power grid frequency and to avoid the need for a reduction gearbox. Gas turbines are also used on helicopters, locomotives (Bombardier's Jet Train), and in tanks. A number of experiments have also been conducted with gas turbine-powered automobiles. In 1950, designers from the British car manufacturer Rover built the first car powered with a gas turbine engine (a two-seater named JET1). The engine was positioned behind the seats, with air intake grilles on either side of the car, and exhaust outlets on the top of the tail. During tests, the car reached top speeds of 140 km h^{-1} (87 mph), at a turbine speed of 50 000 rpm. Although the car could be run on petrol, paraffin or diesel oil, the fuel consumption problems proved to be insurmountable for a production car. Today, gas turbines are often used in many naval vessels, where they are valued for their high power-to-weight ratio, providing the vessel with a high rate of acceleration and an ability to get under way very quickly.

The internal combustion process of the gas turbine engine is extremely simple. The gas turbine is described thermodynamically by the Brayton cycle [138, 139], in which air is compressed isentropically, combustion occurs at constant pressure, and expansion over the turbine occurs isentropically back to the starting pressure. In practice, friction, and turbulence cause non-isentropic compression. For a given overall pressure ratio, the compressor delivery temperature is higher than ideal. Although, in non-isentropic expansion, the turbine temperature fall necessary to drive the compressor is unaffected, the associated pressure ratio is greater, and this reduces the expansion available to provide useful work. Pressure losses in the air intake, combustor and exhaust reduce the expansion available to provide mechanical

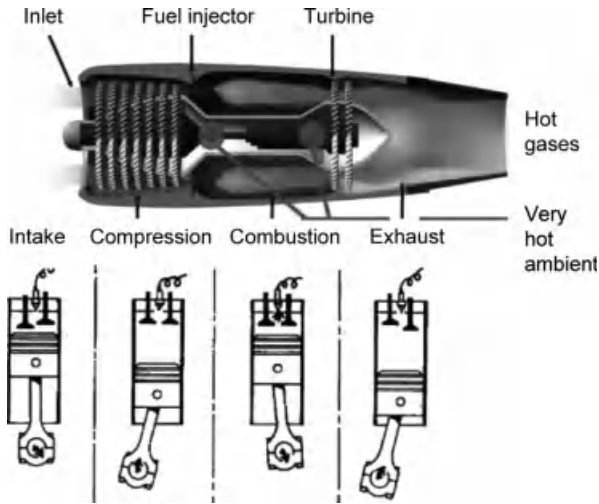


Figure 8.62 Gas turbine combustion process and (lower panels) comparison with a four-stroke reciprocating piston engine combustion process.

work. Gas turbines consist of three parts: (i) the compressor compresses the incoming air to high pressure; (ii) a combustion area burns the fuel and produces high-pressure; and (iii) the high-velocity gas turbine extracts the energy from the high-pressure, high-velocity gas flowing from the combustion chamber. The general layout of an axial-flow gas turbine is shown in Figure 8.62, where the internal combustion process of a gas turbine is compared with the process of a reciprocating piston engine.

The combustion process of a gas turbine usually takes place three phases:

- **Phase 1: Intake and compression.** Air is sucked in from the inlet by the *compressor*, which is basically a cone-shaped cylinder with small fan blades attached in rows. Air at normal pressure is forced through the compression stage, where the pressure rises significantly. In some gas turbine engines, the pressure of the air can rise up to a ratio of 1:40, with potential pressure rises of 1:55 being achievable in future.
- **Phase 2: Combustion area.** The high-pressure air enters the combustion area, where a ring of fuel injectors injects a steady stream of fuel. The fuel is generally kerosene, jet fuel, propane, or natural gas. Within the combustion area, high-pressure hot air is streamed at very high speeds up to 2092 km h^{-1} (1300 mph). The compressed air enters through perforations. In order to keep the flame burning continuously in that environment, a hollow, perforated piece (the so-called “flame holder” or “can”) is used.
- **Phase 3: Turbine and exhaust.** At the end of the gas turbine engine process there is the turbine section. Figure 8.62 shows two sets of turbines which directly drive the compressor, with the turbines, the shaft and the compressor all turning as a single unit. The outcoming gas creates a thrust of very high horsepower.

The main advantages of gas turbine engines are not only their very high power-to-weight ratio, when compared to reciprocating piston engines, but also that they are smaller than most reciprocating engines of the same power rating. Similar to Wankel engines, gas turbines move in only one direction, and usually run very smoothly, without vibrations. Unfortunately, although they are very reliably constructed and of simple design, the cost of a gas turbine engine is much greater than a similar-sized reciprocating engine, mainly due to their tribological requirements (see Section 8.5.7.2).

One major disadvantage of gas turbines is that they use more fuel when idling compared to reciprocating engines, and are also less efficient unless they are in continual operation. These disadvantages explain why high-powered road vehicles, which are smaller, cheaper and follow a less regular pattern of use than jet aviation, ships, helicopters or tanks, do not use gas turbine engines, regardless of the size and power advantages that might be imminently available.

8.5.7.2 Tribology of Gas Turbine Engines

Mechanically, gas turbines can be considerably less complex than internal combustion piston engines. Simple turbines have as the moving part only the shaft/compressor/turbine/alternative-rotor assembly, and a more sophisticated fuel injection system. The gas turbines used in modern jet engines may have multiple shafts (spools), hundreds of turbine blades, movable stator blades, and a vast system of complex piping, combustors and heat exchangers. With most turbines, attempts are also made to recover the exhaust heat which, otherwise, is wasted energy. For this, recuperators pass the exhaust heat to the compressed air, prior to combustion. As with all cyclic heat engines, a higher combustion temperature means a greater efficiency, the limiting factor being the ability of the steel, nickel, ceramic, or other materials that make up the engine to withstand heat and pressure. The obvious target to achieve in the combustion section, and thus to produce the highest thermal efficiency, would be the stoichiometric temperature of the fuel, though this would mean constructing the hot section of the engine from exotic materials capable of coping with high temperatures. Alternatively, there would be a need to increase the cooling of the hot section components, but this would lower the fuel efficiency of the engine. In today's civil aviation high-bypass turbofan engines, the combustion system may be operating at a temperature of 1577 °C (2870 °F). Consequently, many of the systems' components will need to be cooled to protect them from the full heat of the gas flow, and this involves considerable engineering expertise. In other applications, combined cycle designs are employed that pass waste heat to steam turbine systems to provide co-generated power from the waste heat, for hot water production.

The smaller the engine size, the higher will be the shaft rotation rate required to maintain the blade tip speed. In fact, it is the turbine blade tip speed that determines the maximum pressure that can be gained, independent of the size of the engine. Jet engines operate at about 10 000 rpm, and micro-turbines at about 100 000 rpm. The ball bearings, thrust bearings and journal bearings used in these engines form a critical part of their design. Typically, the bearings of a gas turbine generate large amounts of heat, caused by the surface friction of either the rollers or balls in the

bearing and contact with the bearing race. Oil is primarily supplied to the bearings to remove this heat and to provide lubrication, thus reducing the friction as the bearing rotates. For example, the rolling element bearings used in modern gas turbine engines may operate at n - dm values as high as $2.5\text{--}3.0 \times 10^6$, where dm is the bearing bore diameter (in mm), multiplied by n (the shaft speed in rpm). Future directions indicate that operating temperatures will continue to rise, and bearing n - dm values above 4.0×10^6 will be required in the coming decades.

The role of a lubricant in a gas turbine engine is to accomplish the following requirements: (i) to separate the bearing and rotor surfaces in order to prevent material damage; (ii) to remove heat generated in the loaded region; (iii) to offer low shear resistance; and (iv) to wet the surfaces during stops and starts, when the interface or loaded region is minimally lubricated. Depending on the film thickness between the two surfaces, the lubrication regime can be identified as an extended “Stribeck graph,” which includes nonlubricated, liquid, and powder-lubricated conditions with dry, boundary, mixed, hydrodynamic, and limiting shear stress regimes. In hydrodynamic fluid film bearings, the most important property in fulfilling the above functions is that of lubricant viscosity. The level of generated hydrodynamic pressures – and hence the load capacity, as well as performance characteristics such as temperature, flow and power loss – all depend very heavily on the lubricant viscosity.

Gas turbine technology has steadily advanced since its inception, and continues to evolve, with research projects actively producing ever-smaller gas turbines. Today, computer-aided design (specifically, finite element analysis along with material advances) has allowed higher compression ratios and temperatures, more efficient combustion, a better cooling of the engine parts, and reduced emissions. On the emissions side, the challenge in technology is actually to develop a catalytic combustor that, when running correctly, will achieve single-digit NO_x emissions to cope with today’s regulations. In general, present-day areas under development, as identified by the industry for new and existing systems, include the following tribological problem areas:

- High-temperature liquid lubricants such as polyphenylethers and perfluoralkylethers
- Hybrid ceramic/steel bearing materials
- Solid-film lubricant coatings
- Advanced alternative lubrication systems such as vapor-phase or powder lubricants
- Magnetic and auxiliary bearings
- High-performance gas bearings capable of operating at temperatures up to 815°C (1500°F)
- Corrosion of bearing materials due to oil breakdown
- Lubricant limitations in life and temperature capability
- Contamination of the lubricant and the bearings
- Breakdown in elastomeric seals and components
- Reliability and service life of the bearing, lubricant, and lubrication systems

- Lubricant bulk and spot temperature limitations
- Seal wear
- High thrust loads and the impact on bearing and lubricant life.

8.5.8

Future Trends

New generations of internal combustion engines using optimized technologies continue to advance the concept of tailor-made solutions. Indeed, a continuing optimization of the combustion process to increase the efficiency of gasoline engines has led to the development of direct injection gasoline engines (GDI engines) which may offer fuel savings of about 20%. On the diesel side, direct injection with unit pumps or common rail technology using pressures of up to 3000 bar (43 500 psi) have become the norm. These designs, which originated in truck engines, offer power increases of up to 50% at almost constant fuel consumption. Concern for the environment which, in most cases is supported by legislation, is the largest single market driver impacting on the future performance requirements of new and sophisticated tribological solutions. In order to meet these requirements of European Union legislation, vehicle manufacturers must develop new engine designs that, in turn, will create a demand for new interacting lubricants and surface performance. Changes in ICE technology over the past decade are the result of distinct factors, each of which addresses an environmental concern:

- fuel economy
- extended drain and biofuel compatibility
- emissions
- weight reduction.

This convergence of trends is resulting in a continuing demand for new materials, surface treatment technologies, coatings, and oil additives for enhanced lubricant formulations, in an attempt to meet most of these requirements. The trends and concerns of meaningful influence for tribology are noted with respect to the development of new ICEs and driveline components, in the following sections. Moreover, in order to support and to overcome these issues, it is necessary today to employ the best available tribological knowledge, which presents a major challenge to tribologists and chemists alike.

8.5.8.1 Fuel Economy

During the past five years of global warming, there has been a very strong demand for vehicles to reduce the emission of “greenhouse gases” or carbon dioxide (CO₂), as well as to reduce fossil fuel consumption and the costs of using a vehicle. Today, vehicle manufacturers are working intensely to increase fuel efficiency by using less fuel in order to meet a combination of environmental and cost requirements. As a result of strict limits to fuel consumption in the USA (CAFE; Californian Act for Fuel Emissions) and the proven fuel economy effect of low-viscosity engine oils and

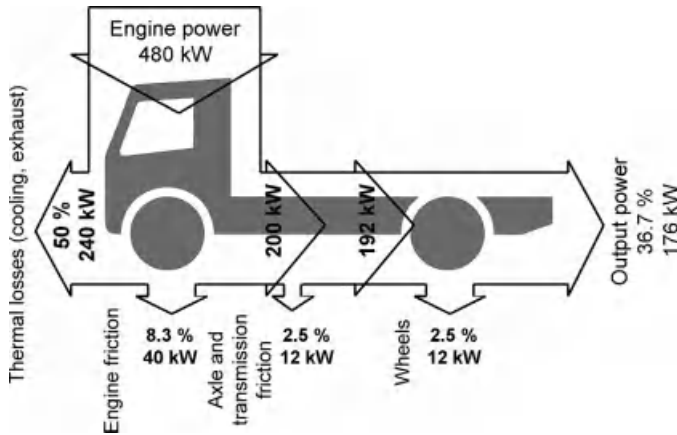


Figure 8.63 Typical values for total energy losses in a heavy-duty vehicle.

driveline fluids, this issue is now attracting attention in Europe and Asia Pacific [154]. As a rule of thumb, achievable fuel savings in the internal combustion engine and in driveline aggregates overall can reach two-digit numbers (see Figures 8.45 and 8.46 and Section 8.5.5). Although engine oils and driveline fluids cannot totally eliminate frictional losses, they may help to minimize friction inside the engines and transmissions. An example of the total thermal losses in a commercial vehicle is shown schematically in Figure 8.63. The potential for a further reduction of friction losses in the engine, transmission and axle account for about 13%, but this may be further reduced by, for example, the development of new engine oils and driveline fluids targeting this fuel economy issue.

8.5.8.2 Extended Drain and Biofuel Compatibility

The development of average oil-drain intervals for new passenger cars and for heavy-duty diesel vehicles is shown graphically in Figure 8.64. Based on the manufacturer's specifications from 1993, the average oil-drain intervals for passenger cars (PCMO) are currently 30 000 km (18 650 miles) for gasoline engines, and up to a maximum of 60 000 km (37 300 miles) for diesel engines. Compared to car engine oils, today's heavy-duty diesel oils (HDDOs) achieve average drain intervals ranging from 120 000 km (74 500 miles) to 150 000 km (93 200 miles). Because of the ever-increasing number of trucks on the roads, this is a useful contribution to improving environmental compatibility. During the past four years, however, the extent of oil-drain intervals has stagnated, due mainly to the increased demands for lower-ash, -phosphorus and -sulfur contents of the oil, to meet new low-emission targets. At the same time, the average operating conditions of engines has been somewhat aggravated. The move to increase oil-drain intervals has primarily been to reduce the amount of used oil that requires disposal, and also to reduce the cost of vehicle ownership. In order to enable extended oil-drain intervals for all of the engine's lubricating contacts, it is essential to provide not only an increased resistance to thermal and oxidative degradation, but also lower rates of oil consumption.

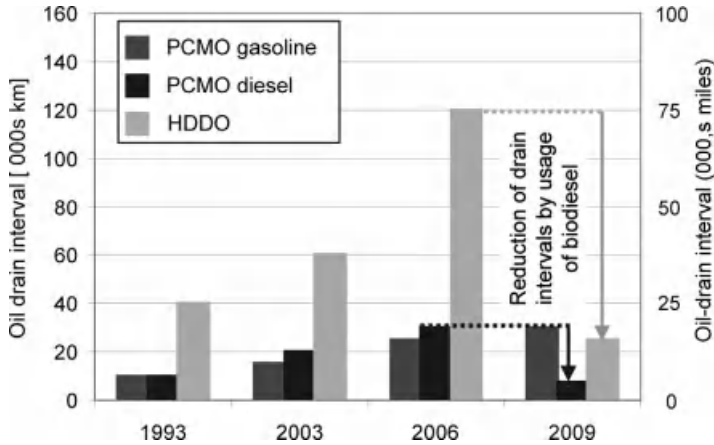


Figure 8.64 Comparison of average oil-drain intervals for passenger car motor oils (PCMOs) and for heavy-duty diesel oils (HDDOs), and the reduction of service intervals when using alternative biofuels.

Currently, there is much global interest in the use of alternative fuels, due to the desire for energy independence, the high cost of petroleum-derived fuels, and environmental concerns such as greenhouse gas emissions (CO_2). Of particular interest here is the use of biodiesel (esters of vegetable oil), which can be produced on a worldwide basis, and is increasingly used in passenger cars as well as heavy-duty vehicles equipped with diesel engines. Unfortunately, the evaluation of biofuels, and especially of biodiesel, will impact on the fuel dilution of crankcase oil, an effect which has been identified as a primary performance issue [155].

While biofuel use will continue to increase worldwide in the near future, engine builders and fuel system suppliers currently are restricting the use of biofuel during warranty periods, due to operational concerns. From a tribological point of view, biofuel's properties render it more likely to enter and remain in the crankcase, leading to a dilution of the lubricating oil; moreover, the subsequent oxidation of biofuel in the crankcase oil will create increased deposits and lead to corrosion. Hence, equipment operators are being encouraged to conduct used oil analyses, as well as to reduce the oil-drain intervals to compensate for the increased severity due to biofuel use (see Figure 8.64). The appropriate use of performance additives, in conjunction with engine oil-formulating technologies, can be used to offset some of the impact of biofuel use. Despite these issues, biofuel is today the fastest-growing alternative fuel worldwide. Clearly, during the next decade, the biofuel issue may become a major challenge for tribologists and chemists if they are to maintain the working life service intervals of the ICE [156, 157].

8.5.8.3 Emissions

One crucial factor which is influencing changes in engine lubricant requirements is the continuing move to reduce potentially harmful vehicle exhaust emissions. Currently, European Union legislation defines the maximum permissible emissions

of a range of substances. Whilst the current legislation is known as Euro 4 and Euro 5, a new set of standards (Euro 6 and higher) will become mandatory from 2010 for heavy diesel trucks, passenger cars (under 2.5 tonnes) and light commercial vehicles (under 3.5 tonnes). However, various EU member states are introducing national legislation to encourage the early adoption of the new standards. The dramatic reduction in permissible emissions for Euro 5 and 6 is resulting in vehicle manufacturers developing new engine and after-treatment systems that are, in turn, bringing new performance demands for combustion engines. Today, some vehicle manufacturers are setting significantly lower sulfated ash, phosphorus and sulfur levels compared to incumbent engine lubricants. As sulfated ash, phosphorus and sulfur represent some of the most fundamental “building blocks” of engine lubricant formulations, extended drain intervals and fuel economy are driving the levels of sulfated ash, phosphorus and sulfur higher, while emission trends are driving the levels down for after-treatment compatibility. These reductions will result in the development of new technologies for the lubricating contacts, where European listing requirements may also further restrict the types of materials, coatings, base oils and additives with which tribologists and chemists will be allowed to work in the near future.

8.5.8.4 Weight Reduction

One way to address fuel economy would be to reduce vehicle weights. Thus, if aluminum components were to be used in an engine or in an automotive wearing surface, it would become important to identify a design such that aluminum oxide (which can form on an aluminum surface) would not be rubbed off and allowed to enter the lubricant (this is important because aluminum oxide is abrasive and can act as a severe polishing agent, thus increasing the wear rate). Those lubricant additives that are optimal for use with an iron surface do not necessarily provide the same wear and scuffing protection for an aluminum surface. Hence, aluminum engine blocks with cast iron cylinder bores must be designed such that differences in the rate and magnitude of thermal expansion of these metals does not cause unacceptable gaps to open between the contacting surfaces.

8.6

Tribology of Hydraulic Pump and Circuit Design

8.6.1

Hydraulic Fundamentals

The word “hydraulics” originates from the Greek *hydraulikos*, which in turn originates from *hydraulos*, meaning a water organ, which in turn comes from *hydor* (Greek = water) and *aulos* (Greek = pipe). Today, the term hydraulics refers to the applied science and engineering that deals with the mechanical properties of liquids. In fluid power, hydraulics is used for the generation, control, and transmission of power by the use of pressurized liquids [158]. The principle of the hydrostatic displacement machine is based on Pascal’s law from the seventeenth century, which states that, “. . . a change in

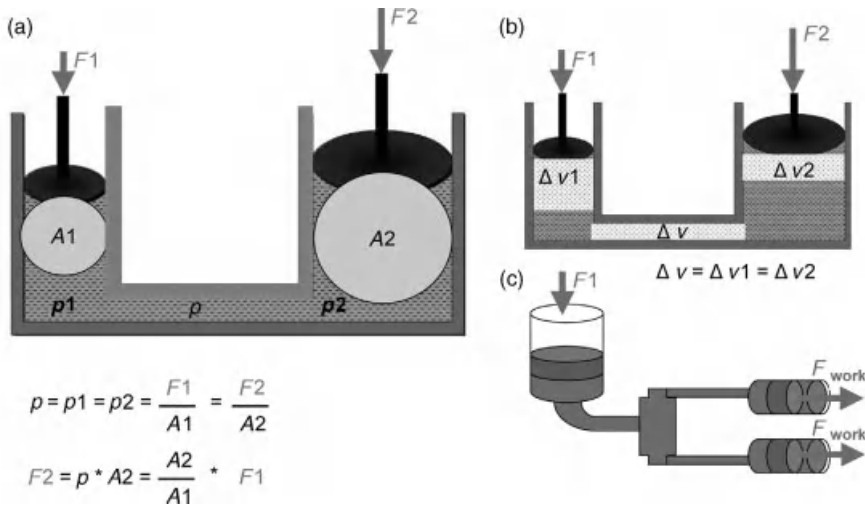


Figure 8.65 Hydraulic fundamentals. (a) Force multiplication; (b) Constant-volume displacement and constant pressure within the fluid; (c) Fork of a main pipe.

the pressure of an enclosed incompressible fluid is conveyed undiminished to every part of the fluid and to the surfaces of its container.” This law assumes an incompressible fluid and a nonviscous flow. As illustrated in Figure 8.65a, force multiplication is made fairly easy by changing the size of one piston and cylinder relative to another [159]. Figure 8.65b reveals, how the applied force (F_1 , input) and the reactive force (F_2 , output) generate a constant pressure increase ($p = p_1 = p_2$) within the hydraulic fluid. The force multiplication now takes place, due to the different diameters of the pistons and cylinders (geometry). The displaced volume of the hydraulic fluid (Δv) at the piston and cylinder 1 (v_1 , input) relative to the piston and cylinder 2 (v_2 , output) is always kept constant, assuming incompressibility and a nonviscous flow ($\Delta v = v_1 = v_2$). All connected pipes can be of any length and shape, allowing them to be routed through or around various obstacles. The main pipe can also fork, so that more than one “slave” cylinder may operate off of one “master” cylinder (as illustrated in Figure 8.65c). The hydraulic transfer of power is characterized by the simplicity of its elements, durability and longevity, high performance, and economy [160]. Compared to gears and transmissions, the hydraulic system has the highest power-to-weight ratio. The variety of hydraulic field-applications is mainly determined by the required components and by the hydraulic fluids that are allowed to be used (e.g., water-containing or non-water-containing fluids).

Hydraulics at work follow the general laws of a hydraulic system [158–161], which are:

- Fluids under pressure transmit energy for work
- Hydraulic pumps create “flow” – not pressure
- Resistance to the flow creates “pressure”
- Flow determines actuator speed (linear and/or rotational speed)

- Pressure determines actuator force
- Fluid under pressure “always” takes the path of least resistance
- Fluid movement is from an area of “high-pressure” to an area of “low-pressure”
- Fluid movement always generates “heat” (frictional losses or dissipation).

8.6.2

Area of Hydraulic Application and Operation

Hydraulic systems and fluids are crucial components of a healthy operation. Today, construction equipment, injection-molding machines, steel mills, excavators, forestry equipment, as well as many other types of industrial and off-road operations, rely on hydraulic systems and fluids to keep the machinery running. The purposes of the tribological contacts and fluids in such systems include helping to reduce pump wear, protection against cavitation, and keeping hydraulic systems free from yellow metal corrosion. The hydraulic fluid must enable a smooth functioning of the components (actuator and valves), extend the life of the components and fluids, and also must provide a long service life under severe wet and dry operating conditions. Continuing progress in the development of hydraulic systems has led to extended maintenance intervals, increased equipment uptime, and reduced overall maintenance costs, all of which improve production efficiency [162]. The demand for antiwear hydraulic components for use in mobile equipment utilizing high-performance hydraulic pumps is increasing rapidly, and equipment breakdowns are costly. Hydraulic equipment failure can be reduced by using components and fluids that provide good antiwear protection in hydraulic pumps [163].

8.6.3

Hydraulic System Components and Loop Circuits

A fundamental hydraulic system consists of the following components [164]:

- Hydraulic pumps (various different designs)
- Rotary and linear actuators (hydraulic motors and cylinders)
- Flow-control (by pumps, flow dividers, or valves)
- Pressure control (relief valves)
- Accumulators
- Tubes, pipes, and hoses
- Seals, fittings, and connections (gaskets and elastomers)
- Filters (main filter and bypass filter)
- Heat exchanger (cooling systems using air, water and/or coolant)
- Reservoir (fluid tanks).

One hydraulic system can consist of three different loop circuit designs:

- Open-loop circuit
- Closed-loop circuit
- Half-closed-loop circuit.

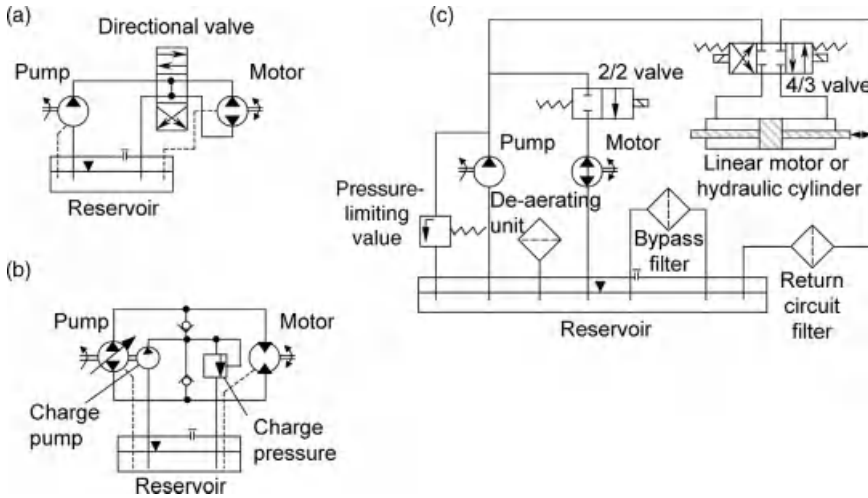


Figure 8.66 Hydraulic loop circuit designs. (a) Open-loop circuit; (b) Closed-loop circuit; (c) Field-related open-loop circuit design working with one rotary and one linear actuator controlled by valves.

An *open-loop circuit* design is shown in Figure 8.66a [161]. The pump-inlet and motor-return versus the directional valve are connected to the reservoir (here, the term “loop” applies to feedback). This is by far the most popular design and, in contrast to the reversible hydraulic motor, the pump’s ports are not the same size; rather, the inlet port is always larger than the outlet port. The advantage of the open-loop design is that only a single pump can be used to operate several different actuator functions simultaneously. However, the main disadvantage is that a relatively large reservoir size is always required; as a rule of thumb, the reservoir is sized to hold at least three times the volume of fluid that can be supplied by the pump in 1 minute.

An example of a *closed-loop circuit* design is shown in Figure 8.66b [161], where the closed circuit eliminates the need for a large storage reservoir. In this design, an adjustable reversible pump drives a non-adjustable reversible hydraulic motor. The closed-loop design is mostly used in conjunction with a supercharger circuit, working efficiently with a smaller fluid reservoir, filters and heat exchanger, to recharge the fluid losses that derive from the unavoidable leakage flow within the closed loop. The main advantages of the closed-loop circuit are that high-horsepower systems are compact, efficient, and require less hydraulic fluid storage. In the closed loop, the pump is responsible for the whole system, as it controls the direction, acceleration, speed and torque of the hydraulic motor. In a closed loop, there is also no need for pressure and flow-control systems.

A *half-closed-loop circuit* design is similar to a closed circuit, but the pump can suck from two different reservoirs. This approach must be used when the pump uploads or unloads fluid to the cylinder actuators, which often have differential areas with different fluid volume requests. If needed, the pump must suddenly generate a larger flow to the actuating cylinder at its right-hand port than is being returned from its left-

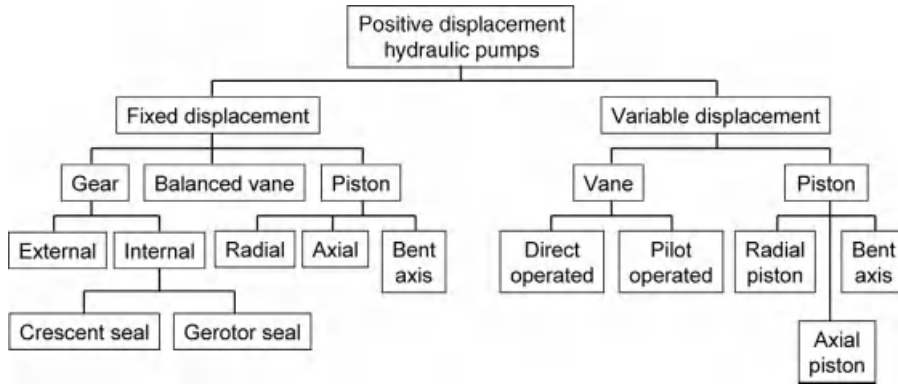


Figure 8.67 The variety of hydraulic pump design.

hand port. Usually, a hydraulic system operates with more than one pump, actuators and valves. A schematic of a more field-related but simple hydraulic open-loop circuit design working with one rotary and one linear actuator controlled by valves, is shown in Figure 8.66c [159].

8.6.4

Tribology of Hydraulic Pumps and Performance Tests

Hydraulic pumps are used in hydraulic systems to transfer energy. Either electricity or mechanical energy can be transformed into hydraulic energy by hydrostatic machines, such as positive-displacement pumps (see Figure 8.67) [161]. The most important types of pump are external and internal gear, rotary vane, and axial and radial piston pumps. External gear pumps are used for flow rates of 0.4 to 1200 ml per revolution and pressures of 160–250 bar (2400–3600 psi), and internal gear pumps for up to 350 bar (5100 psi) [165–168]. Although rotary vane pumps can generally create pressures up to 160 bar (2400 psi), new developments have enabled the use of pressures ranging between 210 and 290 bar (3050 and 4200 psi), with flow rates of between 30 and 800 ml per revolution.

Radial piston pumps cover the range up to 700 bar (10 150 psi), but this pump type is normally used for pressures of about 480 bar (7000 psi). Axial piston pumps are divided into swash-plate and bent-axis designs [168, 169], and can create pressures of up to 450 bar (6500 psi), and higher. The flow rates will vary greatly, depending on pump dimensions; the ranges of typical pump performance parameters, collected from different manufacturers, are listed in Table 8.26.

Hydraulic pumps, actuators, and valves are mostly subjected to proper hydraulic stress and heat. However, besides maximum pressure, there is also a temperature limitation imposed by the tribological contacts and the hydraulic fluid. The main functions of the hydraulic fluids and coatings are to protect, for example, to prevent all components against wear and corrosion and also to reduce friction, thus reducing the accumulation of deposits and providing a better overall efficiency. An analysis of the

Table 8.26 Typical hydraulic pump performance parameters.

Hydraulic pump type	Flow rate	Maximum pressure [bar (psi)]	Maximum speed (rpm)	Total efficiency (%)
External gear	Fixed	250 (3600)	500–5000	85–90
Internal gear	Fixed	350 (5100)	900–1800	90
Vane	Fixed	160–290 (2400–4200)	900–3000	86
	Variable	70–160 (1000–2300)	750–2000	85
Radial piston	Fixed	700 (10 000)	1000–3400	90
Axial piston (bent-axis)	Fixed	350–450 (5100–6500)	950–3200	92
	Variable	400 (5800)	500–4100	92
Axial piston (swash-plate)	Variable	320–450 (4600–6500)	500–4300	91

latest research on pump test machines has revealed that the selection of a correct hydraulic fluid can lead to significant improvements in overall efficiency [170]. The selection of an appropriate high-VI, highly shear-stable fluid can improve pump efficiency when compared to a conventional monograde fluid of the same ISO VG grade [171]. Hydraulic equipment failure can be reduced by using fluids that provide good antiwear protection in hydraulic pumps. In particular, the increased use of ashless (metal-free) additives can help to minimize disposal and effluent-treatment costs, while the technology also supports a trend towards limiting heavy-metal contamination of the environment. Finally, the identification of criteria defining an optimized hydraulic fluid, by using test rigs and other procedures, enables the equipment operator to easily improve the performance of the system, and also to reduce both wear and fuel consumption. Effective tests can be conducted with modern vane, piston, and hybrid pumps (see Sections 8.6.4.1–8.6.4.4).

8.6.4.1 Gear Pumps

Generally, gear pumps are the most common type of pump for hydraulic power applications, because they are the most robust and rugged form of fluid power pump. The rigid design of the gears and housing allows for very high pressures, as well as an ability to pump highly viscous fluids. The simplicity, reliability, and very high power ratings of gear pumps represent major field-related advantages, when they are used for hydraulic service. Many gear-type pumps are available, including helical and herringbone gear sets (instead of spur gears), lobe-shaped rotors (similar to Roots Blowers, which are commonly used as superchargers), and mechanical designs that allow the stacking of pumps [158, 161].

As the gears rotate they separate on the intake side of the pump, creating a void and suction which is filled by fluid. The fluid is carried by the gears to the discharge side of the pump, where meshing of the gears displaces the fluid. Industry standards exist for gear pump mounting flanges, drive shaft sizes and splines, and ports. The suction port will usually be larger than the pressure port in order to reduce the possibility of

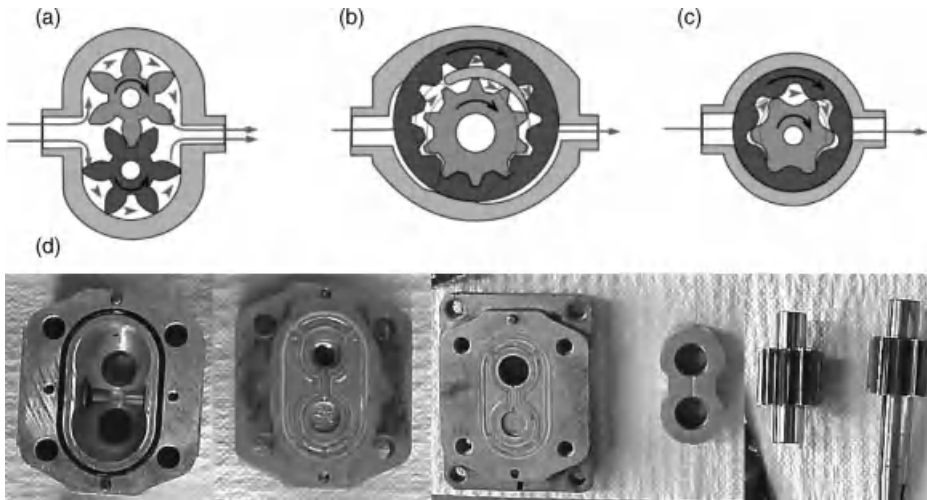


Figure 8.68 Gear pump design. (a) External gear pump for hydraulic power applications; (b) Internal gear (crescent) pump for high-viscosity fluids; (c) Internal gear (gerotor) pump for automotive oil pumps; (d) The parts of an external gear pump.

cavitation. Gear pumps always consist of two gears – a drive and a driven gear – with the number of teeth, the pitch circle diameter, and the width of the gears being the dominant parameters that control the displacement. The housing and a side plate enclose the gears. Fluid leakage in this type of pump occurs between the tips of the gears and across the side plate. The mechanical clearances are small (on the order of microns); such tight clearances, along with the speed of rotation, effectively prevent the fluid from leaking backwards. Notably, the suction and pressure ports must be interfaced where the gears mesh.

The most common variations of gear pump types are shown in Figure 8.68; the external gear pump (Figure 8.68a) is the most prevalent in industrial applications. Internal gear pumps perform better at lower speeds and with higher-viscosity fluids than do external gear pumps. Automotive oil pumps are usually internal gear designs.

The two different types of internal gear pump are the “crescent” seal type (Figure 8.68b) and “gerotor” seal type (Figure 8.68c) (see Section 8.5.5.9). The crescent seal internal gear pump consists of a small internal gear and a larger ring gear; the small internal gear, which is driven by the prime mover, will mesh with the ring gear and turn it in the same direction. Sealing of the high-pressure chamber from the pump’s inlet is achieved by positioning a crescent seal between the upper teeth of the internal small gear and the upper teeth of the ring gear. In the gerotor gear pump, the inner element has one tooth less than the outer element. The internal gear is driven by the prime mover, and this in turn causes the outer element to be driven in the same direction. Although all gear pump designs operate with constant displacement, their displacement cannot normally be varied.

Wear of the tooth flanks and bearings represent the most common types of gear pump failure. Wear leads to increased leakage flow, and ultimately to pump damage,

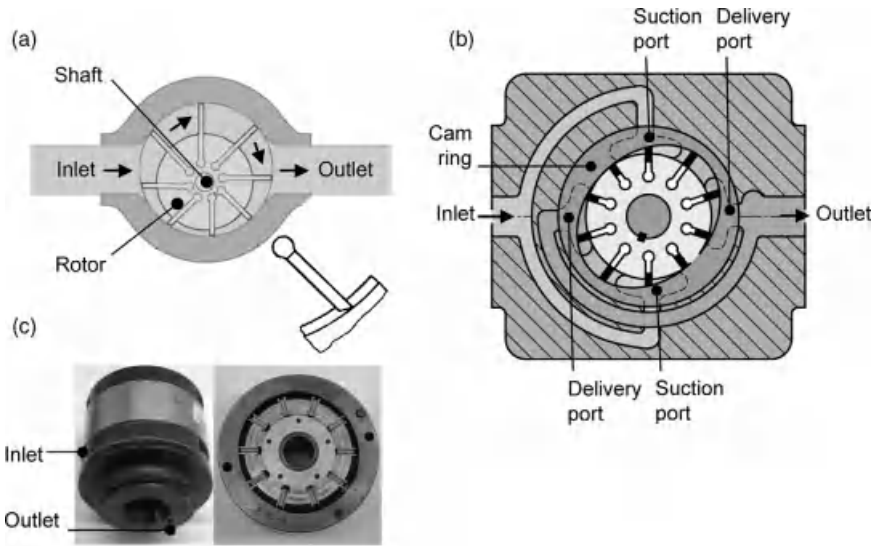


Figure 8.69 Vane pump design. (a) Unbalanced design; (b) Modern balanced design; (c) Industrial standard vane pump with fixed displacement.

although scuffing and fatigue are also possible types of failure. In most cases, the tribological mechanical–dynamical performance testing of the gear pump types can be carried out using the test methods described in Section 8.4.4.

8.6.4.2 Vane Pumps

The vane pump is a very common type of pump; a schematic of many variations is shown in Figure 8.69. Vane pumps are high-pressure hydraulic pumps mainly for automotive uses that include supercharging and automatic transmission. Power steering units also often rely on a vane pump to obtain the pressure needed for the power cylinder, and may also be used as vacuum pumps to provide braking assistance (through a braking booster) in diesel-engined vehicles. Pumps for mid-range pressures include applications such as pumping for fountain soft drink dispensers and espresso coffee machines. In some types of vane pump, the center of the vane body can be changed to obtain a simple adjustable pump that is capable of providing a generally constant pressure or constant power. The displacement is increased until the required pressure or power is reached, and subsequently the displacement or swept volume is decreased until an equilibrium is achieved. Vane pumps operating with a fixed or simple adjustable displacement have efficiencies comparable to those of gear pumps. Generally, vane pumps based on variable displacement can be used for pressures up to 160 bar (2350 psi); however, new developments based on a fixed displacement design can create pressures of up to 290 bar (4200 psi) (see Table 8.26).

Vane pumps can be designed in either balanced or unbalanced configuration designs. The unbalanced design has only one inlet and outlet port, whereas in the balanced design there are opposing pairs of internal inlet and outlet ports that

distribute the thrust force evenly around the shaft. All modern vane pumps are of the balanced design [158, 161].

The vane pump relies on several sliding vanes that ride on a cam ring, to increase and decrease the volume of the pumping chambers within the pump (see Figure 8.69b). The sides of the vanes and rotor are sealed by side bushings, while the housing may be eccentric with the center of the rotor, or its shape may be oval. When the rotor spins, centrifugal force pushes the vanes out to touch the casing, where they trap and propel the fluid, although on occasion springs may also be used to push the vanes outward. In another design, pressurized pins urge the vanes outward. During rotation, as the space or chamber enclosed by the vanes, rotor, and housing is increased, a vacuum is created such that mostly atmospheric pressure forces the fluid into this space, on the inlet side of the pump. Subsequently, as the space or volume enclosed decreases, the liquid is forced out through the discharge ports. If fluid leakage occurs between the high- and low-pressure sides of the vanes and across the side bushings, this results in a decreased volumetric efficiency and hence a reduced flow output. The unbalanced design of pump suffers from a shortened bearing life due to the unbalanced thrust force within the pump (see Figure 8.69a). Although, in general, vane pump leakage flow is quite small, it can be increased significantly by wear. In the past, test pumps have been carefully selected and test methods created to prevent early pump breakdown due to various applications [165].

Standardized Vane Pump Test Rigs and Test Standards Since the mid-1960s, tests using vane pumps have represented the most important wear tests for both water-containing (classified as HFA, HFC, HFD) and non-water-containing hydraulic fluids (classified as H, HL, HLP) [172]. The most important tests for the qualification of hydraulic fluids are conducted in Vickers vane pumps. Some standardized procedures exist for the determination of antiwear properties using an electric motor-driven Vickers V-104-C or V-105-C-10 hydraulic pump (see Table 8.27) [173], using test cartridges manufactured by Conestoga. The antiwear performance is determined by

Table 8.27 Vane pump performance test rigs and test standards.

Technical data	Vickers V-104-C (V-105-C-10)	Eaton Vickers 35VQ25A	Denison T6CM (HF0, HF2)
Test duration	100 h or 150 h	50 h	100 h
Test temperature	71–90 °C (160–194 °F) at $13 \text{ mm}^2 \text{ s}^{-1}$	93.3 °C (200 °F)	71 °C (160 °F) for 60 h 99 °C (210 °F) for 40 h
Maximum pressure	250 bar (3625 psi)	210 bar (3000 psi)	180 bar (2500 psi)
Pump speed	1500 rpm	2400 rpm	2400 rpm
Flow rate	221 min^{-1} (5.8 US gal. min^{-1})	14401 min^{-1} (38.0 US gal. min^{-1})	2651 min^{-1} (70.0 US gal. min^{-1})
Fluid volume	701 (18.5 US gal.)	1971 (52 US gal.)	1891 (50 US gal.)

measuring the weight loss of the pump vanes and cam rings after hours of continuous operation, followed by a visual inspection for scoring and scuffing [174]. Modern pumps operate at up to twice their nominal pressure. For example, the Baton Vickers 35VQ25A pump test (form M-2952-S, revised 8/88) requires a 50 h operation period at maximum rated pressure and speed. For this vane pump, which can be driven by either an electric motor or a diesel engine, the associated flow-control, reservoir and heat-exchanger equipment combine to provide substantial flexibility under a variety of operating conditions, while the pump must pass three out of the five procedures. The same test is also required for the Caterpillar TO-4 specification [174]. For the T6CM pump (TP-30 283), the Denison test targets evaluate hydraulic fluids in vane pumps at both high pressure and high temperature, with and without the presence of water, by running an intermittent pressure cycle (see Table 8.29). The test objective is to check the evolution of viscosity, filterability, thermal stability, anticorrosion fluid capability, and pump wear, with time, and with or without the addition of water. The first test phase is run dry, after which 1% distilled water is added and the test is re-run with the same fluid as in the first phase [174]. The Denison T6CM vane pump, as used for approval tests, is shown in Figure 8.69c.

8.6.4.3 Piston Pumps

In general, the piston pump design operates at the highest pressure of all different pump types normally found in hydraulic applications (see Table 8.26). The piston pump is manufactured in either axial or radial configuration, with both configurations allowing also either a fixed or variable displacement. The radial piston pump (Figure 8.70a) features a circular arrangement of hydraulic pistons, and valves which

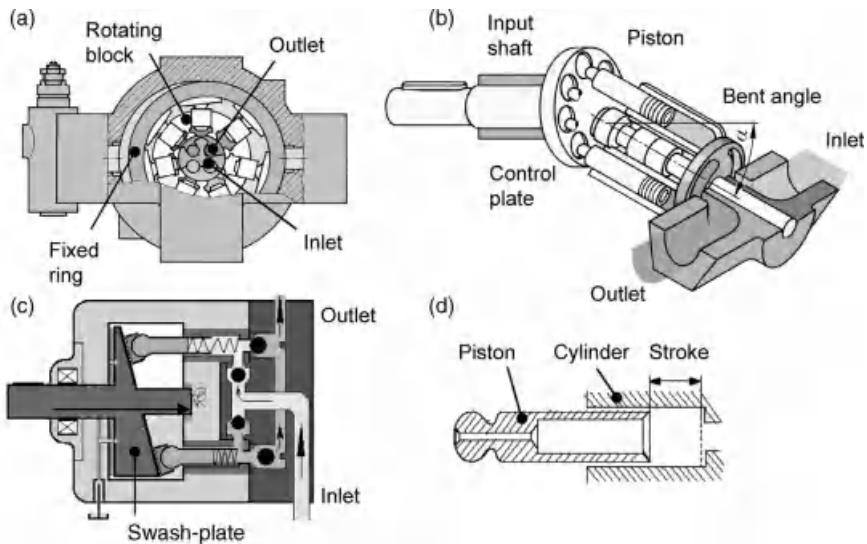


Figure 8.70 Piston pump design. (a) Radial piston pump; (b) Axial piston pump (bent-angle design); (c) Axial piston pump (swash-plate design); (d) Axial piston contact.

allow pressures of up to 700 bar (10 000 psi) to be built [167]. Radial piston pumps can produce a very smooth flow under extreme pressure and, in general, are variable-displacement pumps. In variable models, the flow rate changes when the shaft holding the rotating pistons or the casing is moved, respectively. The output flow can also be varied by changing the rotational speed. The valve area near the axis is easier to seal with minimal frictional losses than in the case of axial pumps, where the valves are further away from the axis. The cylinder case can also rotate, which may help to reduce frictional losses [161, 164, 166]. Typical applications for radial piston pumps include cylinder jacking, crimping, and holding pressure on hydraulic presses. When used for extremely high-pressure applications, the displacements of radial piston pumps are normally limited to relatively small volumes and rotation speeds, since even with an overall efficiency of $>90\%$ at pressures of about 700 bar (10 000 psi), such a pump would require a very high input power rate (see Table 8.26).

Nowadays, axial piston design configurations predominate among hydraulic systems, and may be categorized into two different groups, namely those with a bent-axis design (see Figure 8.70b) and those with a swash-plate design (see Figure 8.70c). Axial piston pumps may be operated as either open- or closed-loop circuit pumps, and can also be used with other components in a system to transfer and control hydraulic power [158, 161, 162]. In particular, they provide an infinitely variable flow rate between zero and maximum. Moreover, the pumps are compact, high power-density units which use the axial piston concept in conjunction with a tiltable swash-plate to vary the displacement of the pump. Depending on the speed of the engine and the swivel angle, the pump can deliver a high flow, while the torque of the drive shaft results from the pressure difference between the tank and the load [169].

From a tribological standpoint, axial piston pumps have become the most challenging pump design. Hydraulic test pumps for performance testing are normally of a bent-axis design [159, 162], and often used in mobile hydraulic applications, such as excavators and forest machines. The pistons of a pump of the bent-axis design are connected with spherical joints to the drive shaft, and are forced axially in the rotating piston drum. The toggling of each piston must be allowed; otherwise, the system would become kinematically blocked, because the angle of the drum forms an ellipse on the flange of the drive shaft [169]. The stroke of the pistons depends on the swivel angle between the drive shaft and drum. The “kidney-shaped” opening of the control plate (which does not rotate) connects the piston, by high pressure, to the power supply and the low-pressure tank. The control plate with its spherical bearing is moved by a bolt, which also has a spherical bearing so that the stroke from the piston depends directly on the swivel angle. The bearing of the pistons minimizes friction between the pistons and drum, such that the forces between them become very small. As a result of this construction, these types of pump have very good efficiency coefficients at low rotational speed. A more complex construction, when a double bearing becomes necessary on the connecting rods, has proved to be detrimental. A cyclic change during one rotation, or a variation of the driving speed, can result in torsion oscillations caused by the complex construction of a double bearing. The consequences of this could be wear and damage of the

connecting rods and gear wheels or, at worst, broken pistons. It is for this reason that an axial piston pump normally has an odd number of pistons, arranged in a circular array within a housing [166].

Standardized Axial Piston Pump Test Rigs and Test Standards Hydraulic pump performance is evaluated in the Denison P46 piston pump test rig (see Table 8.28). The aim of the tests is to determine the effects of hydraulic fluid on flow, deposits and wear in a Denison 46 series piston pump. The main equipment used in the procedure are a Cummins L-10 diesel engine equipped with a speed-increasing gearbox coupled to a 46 series pump, a 46 series motor, and 21 Denison charge pump. Each test is run at 2400 rpm for 60 h at 71 °C (160 °F), and subsequently for 40 h at 99 °C (210 °F). After 60 h, the pump is dismantled and inspected for evidence of distress, and the pump hardware examined microscopically with three-dimensional stereo-zooming that enables up to 160-fold magnification. A real-time color video display facilitates simultaneous viewing of the microscopic phenomena [174]. Although Denison P46 testing is now obsolete, it is still available in many laboratories worldwide.

The Sundstrand series 22 axial flow pump, driven by a six-cylinder diesel engine, is a highly specialized system that can be used to determine the ability of hydraulic fluids to maintain a rated flow at high pressure in the presence of water (see Table 8.28). Hydraulic pump efficiency can be degraded by a small amount of water in the hydraulic fluid, if the water causes any dynamic corrosion of yellow metals in the pump. In this procedure, which has become known as the Sundstrand dynamic corrosion test, the Sundstrand pump is run at high pressure at an outlet temperature of 82 °C (180 °F) for 225 h, with water being added after the first 25 h. Evaluations using this technique have included John Deere fluids, ASTM multipurpose power transmission fluids, and a variety of hydraulic fluids. The performance of Orenstein and Koppel (O&K) hydraulic fluid is evaluated in the O&K test rig using an A2F010 “Brueninghaus Hydromatik” (Bosch Rexroth) piston pump with a bent-axis design (see Table 8.28). This procedure covers hydraulic pump performance at high pressure

Table 8.28 Axial piston pump performance test rigs and test standards.

Technical data	Denison P46 (HF1)	Sundstrand series 22	O&K Bosch Rexroth A2F010 test pump
Test duration	100 h	225 h	5000 h
Test temperature	71 °C (160 °F) for 60 h 99 °C (210 °F) for 40 h	82 °C (180 °F)	80 °C (176 °F)
Maximum pressure	350 bar (5000 psi)	350 bar (5000 psi)	350 bar (5000 psi)
Pump speed	2400 rpm	3100 rpm	1460 rpm
Flow rate	96.5 l min ⁻¹ (25.5 US gal. min ⁻¹)	94.6 l min ⁻¹ (25 US gal. min ⁻¹)	11.0 l min ⁻¹ (2.9 US gal. min ⁻¹)
Fluid volume	50 l (13 US gal.)	45 l (12 US gal.)	20 l (5.3 US gal.)

and at high temperature, without the presence of water, by running intermittent pressure cycle. This endurance test evaluates all the hydraulic equipment utilized, including the fluid. The minimum duration is 5000 h, with pump wear being kept under surveillance by precise measurement of leakage flow after each 500 h period.

8.6.4.4 Hybrid Pumps

Parker Hannifin (formerly Denison Hydraulics) is a leading industrial pump manufacturer, and services highly engineered hydraulic fluid power systems and components. Parker maintains sales and manufacturing operations worldwide, serving a broad array of original equipment manufacturers, hydraulics distributors and end-users. They can be regarded as having been a leading company in the area of tribological pump test and hybrid pump test developments during the past few decades. In 2005, Denison reviewed the test procedure for evaluating the effect of hydraulic fluid on flow, pressure loss, filterability, and wear using a hybrid T6H20C style piston and vane pump run at close to rated conditions (TP-30 533) (see Table 8.29). These tests comprise a break-in phase, a dry fluid-testing phase (no

Table 8.29 Pump performance tests rigs and test standards.

Test method	Test machine	Application
ASTM D 2882	Vickers vane pump	Test method for indicating the wear characteristics of petroleum and non-petroleum hydraulic fluids in a constant volume vane pump [18–21]
ASTM D 7043		35VQ25A pump test eaton vickers 35VQ25A pump test [18–21]
IP 281/77		Determination of anti-wear properties of hydraulic fluids – vane-pump method [175, 176]
DIN 51 389		Mechanical testing of hydraulic fluids in the vane pump [22–24]
DIN 51 389, Part 1		General working principles
DIN 51 389, Part 2		Procedure A for non-water-containing hydraulic fluids
DIN 51 389, Part 3		Procedure B for water-containing, flame-resistant hydraulic fluids
Denison specification TP-30 283	Denison vane pump (HF0, HF2)	Denison T6CM hydraulic vane pump test
Denison specification TP-30 560	Denison piston pump (HF0, HF1)	Denison P46 hydraulic piston pump test
O&K specification	O&K Hydraulic test stand	Determination of the wear behavior and oil aging of hydraulic oils in an axial piston pump
Denison specification TP-30 533	Denison hybrid pump (HF0, HF1, HF2)	Denison T6H20C vane and piston pump test [177]

water added), and a wet fluid-testing phase (water added). The dry and wet phases, which are each slightly longer than 300 h, take the form of cyclic tests in which the outlet pressures for both pumps are changed every 2 s, with the same test pump being used for both wet and dry phases. The test targets are to evaluate hydraulic pump and fluid performance on vane pumps at 250 bar (3600 psi), and on piston pumps at 280 bar (4000 psi), 1700 rpm, high temperature, with and without the presence of water. The pressure cycles are intermittent. As in the older Denison procedures (which are compared in Table 8.29), the evolution of viscosity, filterability, thermal stability, shear stability, anticorrosion fluid capability and pump wear, with or without the addition of water, are checked as time passes. This test enables a reliable evaluation to be made of the suitability of fluids for use in hydraulic pumps in severe duty applications. Further development steps have enabled improvements of the performance and characteristics of both the pumps and the fluids.

Test phase 1 requires the use of a fluid of the quality of NAS 1638 class 8 maximum, thus providing a measurand for oil cleanliness and particle content.

Phase 2 tests the same fluid as in phase 1, but with 1% of distilled water added for between 307 and 308 h. The water concentration must be maintained between 0.8 and 1.2% throughout this phase, but some water must eventually be added at the minimum circuit pressure. These water additions must all be recorded. During this phase, a maximum of 2 l of distilled water will be added at the pump suction level (30 ml min^{-1} for a total of 1 h), and the pump will be run at a minimum circuit pressure of between 7 bar (100 psi) and 10 bar (143 psi). Water decantation, when unexpected, may occur after a prolonged stop. The minimum fixed acceptable time is either 1 h or, if a detergent fluid is being tested, the time will be a function of the fluid quality. If the vane cartridge is damaged or destroyed, it can be removed. The test is continued only for HF-1 evaluation; however, if the piston-rotating group is damaged or destroyed, then the barrel, pistons, wear plate and port plate must be removed, and the test then continued for HF-2 evaluation. If a fluid is HF-0-approved, it is suitable for both piston pumps and vane pumps; otherwise, approval is HF-1 or HF-2 only [177].

8.6.5

Tribology of Valves

Hydraulic systems are divided into three different operating valve types, where each design has a unique mission in operation [160, 164]:

- Flow-control valves
- Pressure-control valves
- Directional-control valves.

Flow-control valves are commonly used to control the rod velocity of linear actuators, or the rotary speed of hydraulic motors. Flow-control with valves can be accomplished by using:

- uncompensated flow-control needle valves;

- compensated flow-control needle valves; or
- flow dividers.

Flow-control valves may vary from a simple orifice to simply restrict the flow, to a complex pressure-compensated flow-control valve and on to flow dividers. Pressure control in hydraulic systems may also be accomplished by using: [164]

- pressure-relief valves;
- pressure-reducing valves; or
- counterbalance valves.

Finally, directional flow in hydraulic systems can be accomplished by using:

- check valves; or
- directional control valves.

From the tribological point of view, the hydraulic requirements of these different valves can be considered as relatively equivalent. Valves have preset switching points; for example, proportional and servo valves are electro-hydraulic, with their movement being proportional to the electrical input signal. As noted above, the main differences between these valves are their mechanical design, their static and dynamic properties, and their cost. It is predominantly the nature of the hydraulic fluid itself, and its level of cleanliness, that controls valve operation and tribological performance. Typically, a hydraulic fluid within a valve should dissipate heat, reduce wear, minimize friction, and avoid corrosion. Of equal importance is that no deposits should be formed within the narrow tolerances found in valves. Each hydraulic system will include particulate contamination that has been entrained in the circulating fluid, the contaminants having entered the system not only from reservoir breathers and seals, but also as a result of the wear of internal surfaces. Whilst these contaminant particles can enter the clearance space of each valve, more specifically they can also enter the hydraulic pump [178]. Extended fluid drain intervals and high thermal loads (e.g., caused by solenoid magnets) must not lead to deposits in, nor the gumming of, flow valves [159, 168]. Finally, the hydraulic fluid must be compatible with all other materials used (including all coatings and paint finishes [159]) to construct the fluid tanks, filter systems, pressure tanks, fittings, and also connections such as gaskets and elastomers [179, 180].

8.6.6

Tribology of Seals, Gaskets, and Elastomers

When a hydraulic system is in operation, every seal or elastomer in that system is either fully or partially exposed to the hydraulic fluid. Hence, interaction between the seal material and the hydraulic medium is unavoidable. The hydraulic medium can influence the sealing material, insofar as it may cause shrinkage or swelling that, in turn, will not only affect the volume of the seal but also alter its mechanical properties such as hardness, elasticity, tensile strength, and elongation [159].

Elastomeric seals are influenced chemically by temperature, oxygen, water, additives, and the oxidation byproducts of the hydraulic fluid. It is, therefore, vital that the seals and the hydraulic fluid are chemically compatible. A seal will be mechanically stressed by the pressure and pulsation of the fluid; dynamically stressed seals such as piston and rod seals are also subject to sliding friction [181, 182]. Both, physical and chemical factors will impact directly on the mechanical wear of a seal. For example, swelling will cause the seal material to soften leading to a higher friction and thus greater wear and power consumption. Normally, it is accepted that seals can swell within defined limits in order to avoid leakage; however, ideally, a hydraulic fluid should have no effect on the seal materials and elastomers, whilst at the same time protecting them from wear, dissipating heat, reducing friction, and avoiding the accumulation of deposits in crevices. Normally, seal manufacturers test the compatibility of their products with different hydraulic fluids, and report their findings in compatibility lists. Lubricant manufacturers are primarily concerned with the performance of seals when in contact with hydraulic fluids (as detailed in DIN 51 524 [183]), and the effect of mineral oil-based fluids on SRE NBR 1 (a seal material as detailed in DIN 53 521 and DIN 53 502). These standards establish thresholds for both volume and hardness changes to seal materials. Fundamental and comparison tests are performed with reference fluids which are specified and classified according to an ASTM standard. Typically, ASTM Fluid 2 and Fluid 3 – and their successor products, IRM2 and IRM3 – are used for testing purposes [184].

Basically, a seal must not shrink when in contact with a hydraulic fluid, because of the danger of leakage, although slight swelling is permissible. The seal must not harden, but a slight softening is allowed. The duration of compatibility tests on seals with hydraulic media is seven days at 100 °C (212 °F) [183], although rapidly biodegradable hydraulic fluids based on vegetable oils, esters, and polyglycols are tested for longer periods to obtain more practically relevant results. The behavior of rapidly biodegradable hydraulic fluids, in contact with standard reference elastomers (SREs), is tested for 1000 h at temperatures ranging from 80 to 100 °C (176–212 °F), as laid down in CETOP R81H, ISO 6072 [184]. The seal materials listed in this test include HNBR, FPM, AC6, NBR1 and AU grades (see Tables 8.30 and 8.31). Currently, the properties tested include hardness changes, volume changes, tensile strength, and elongation breakage-point. According to this test, the tensile strength and elongation breakage-point must not exceed 30% in the presence of rapidly biodegradable hydraulic fluids [185–187]. The general compatibility of elastomers with different field-relevant hydraulic base oils are listed in Table 8.30, and also compared in Refs [181, 182, 187].

In principle, the saying “like dissolves like” applies, but to illustrate this suggestion, non polar elastomers such as ethylene propylene diene monomer (EPDM) rubber are swelled to the point of dissolution in non polar hydrocarbons contained in mineral oil-based hydraulic fluids. Conversely, polar fluids such as HEPGs (synthetic hydraulic fluids based on polyglycols) function perfectly with these non polar elastomer rubbers (as shown in Table 8.30). Elastomer tests with fire-resistant hydraulic fluids are described in the 7th Luxembourg Report [188]. As food-grade lubricants are based on white oils and PAOs, they are used in the DIN 51 524 and ISO

Table 8.30 Compatibility of elastomers with hydraulic fluids.

	NBR	HNBR	AU	FPM	EPDM mineral oil-free
	Average temperature range of the elastomers in °C (permanent operating range)				
	–30/(–40)/ + 100	–20(–30)/ + 140	–30/ + 80(+ 100)	–20/ + 200 ^{b)}	–50/ + 150 ^{b)}
HL/HLP/HLPD mineral oils	+	+	+	+	–
HFD	–	–	–	+ ^{a)}	+ ^{a)}
HFC	+	+	+ ^{a)}	–	+ ^{a)}
HFB	+	+	–	+	–
HFA	+	+	+ ^{a)}	+	–
HETG	+	+	+	+	–
HEES	+ ^{a)}	+ ^{a)}	+ ^{a)}	+	–
HEPG	+ ^{a)}	+	–	+	+

a) Check the application in case of dynamic stress of elastomer material.

b) Maximum ambient temperature.

6743 part 4 elastomer test procedures (see Ref. [183]). General seal compatibility statements must consider the different manufacturing processes and the different compositions of elastomers in practice. For example, nitrile butadiene rubber (NBR) materials can contain different amounts of acrylic nitrile, and this must be borne in mind when testing and evaluating elastomers and fluid performance. The new ISO working paper “Hydraulic fluid power-compatibility between fluids and standard elastomeric materials” (ISO TC 131/SC7N343), lists methods which describe the influence of fluids on standard elastomeric materials [184].

Table 8.31 Symbol according to DIN ISO 1629 respectively ASTM D 1418.

Symbol according DIN/ISO/ASTM	Chemical name	Trade name
NBR	Acrylonitrile-butadiene-caoutchouc	Perbunan, Nipol, Europrene
HNBR	Hydro-treated acrylonitrile-butadiene-caoutchouc	Zetpol, Theiban
AU	Polyurethane-caoutchouc (Polyesterurethane-caoutchouc)	Desmopan/Urepan
FPM	Fluoro-caoutchouc (FKM)	Viton, Fluorel, Tecnoflon
EPDM	Ethylene-propylenediene-caoutchouc	Vistalon, Buna BPG, Keltan
SBR	Styrene-butadiene-caoutchouc	Buna SB
CR	Chlorobutadiene-caoutchouc	Neoprene/Chloroprene
PTFE	Polytetrafluoroethylene	Hostafon/Teflon

8.6.7

Fuel Efficiency and Emissions Reductions**8.6.7.1 Trends and Key Factors**

Today, certain key factors are continuing to drive the present hydraulic-equipment businesses, including the environment, energy, functions, and costs. On the environmental front (and especially in mobile equipment), tighter exhaust-emission regulations represent an ongoing concern for equipment manufacturers and users. *Machine noise* is also coming under regulatory scrutiny. Currently, with fuel costs increasing to new record highs, energy savings has become a crucial argument for machine manufacturers [189]. There is also an increasing demand for automated repetitive functions that will improve operating efficiencies, enhance productivities, and reduce operator fatigue. All of these proposals are putting pressure on the suppliers of hydraulic systems to drive down their component costs, to improve reliability, and to make the equipment more maintenance friendly [190]. Tribological contacts with respect to the hydraulic fluids may play a major role in this challenging context.

8.6.7.2 The Role of Hydraulic Fluids for Energy Efficiency

Hydraulic fluids are multipurpose functional fluids, which simultaneously serve to transmit power and to lubricate and cool tribological contacts. However, the function of power transmission alters the role that viscosity plays in total system efficiency in an important way [191]. *Mechanical efficiency* relates to the frictional losses within a hydraulic component, and the amount of energy required to generate fluid flow. *Volumetric efficiency* relates to the flow losses within a hydraulic component, and the degree to which internal leakage occurs. Both of these properties are, to a large degree, viscosity-dependent [192]. As can be seen in Figure 8.71, mechanical efficiency varies inversely with fluid viscosity, but volumetric efficiency on the other hand increases with fluid viscosity. For hydraulic systems, the optimal overall efficiency (η_{Overall}) corresponds to the maximum product of mechanical efficiency

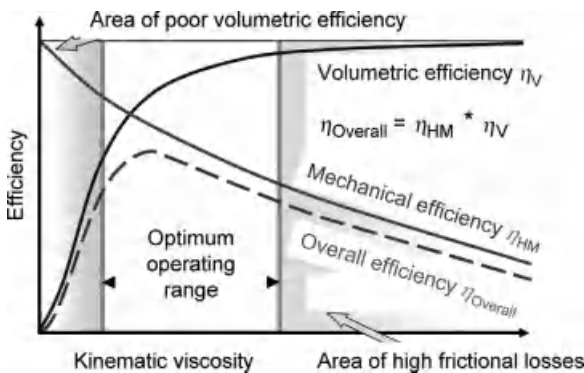


Figure 8.71 Characteristic hydraulic pump efficiency curves.

(η_{HM}) and volumetric efficiency (η_V) [193]. The maximum efficiency of a hydraulic fluid will increase the overall system efficiency through viscosity modification. Hence, by using measured flow rates with different test fluids, and a value of nominal flow rate of a given test pump installed on a pump test rig, the volumetric efficiency can be calculated as a function of actual flow rate (Q_a) and nominal flow rate (Q_n) of the test pump. The overall efficiency is also equal to the ratio of the hydraulic power produced by the pump (P_{aH}), and by the actual mechanical power provided to the pump (P_{aM}) (Eq. (8.1)). Here, P_{aH} is equal to the product of the actual flow rate of the pump (Q_a) and the pressure drop across the pump (ΔP) (Eq. (8.2)) [194]:

$$\eta_{\text{Overall}} = \eta_V \cdot \eta_{HM} = \frac{Q_a}{Q_n} \cdot \frac{P_{aH}}{P_{aM}} = \frac{\Delta P \cdot Q_a}{600} \cdot \frac{600}{\Delta P \cdot Q_n} \cdot \frac{P_{aH}}{P_{aM}} = \frac{P_{aH}}{P_{aM}} \quad (8.1)$$

$$P_{aH} = \frac{\Delta P \cdot Q_a}{600} \quad (8.2)$$

When comparing the volumetric and the frictional losses occurring in a pump, or the influence of different hydraulic fluids working in the pump, the overall efficiency is the best parameter to consider [195].

8.6.7.3 Hydraulic Pump Efficiency Test Rigs and Test Methods

Many universal hydraulic test rigs have been developed for testing hydraulic fluids, or for investigating the interaction of hydraulic hardware with the fluid. In the main, these test rigs have very flexible capabilities, for example variable drive speed and drive units up to 400 kW, and enable the online measurement of particles (debris), fluid density, and pump-driving input and output torque with state-of-the-art computer data monitoring and control systems. These universal hydraulic test machines are configured so that virtually any type of hydraulic pump can be installed to evaluate hydraulic fluid or equipment performance, under a multitude of test conditions. The rigs are mainly used to investigate the effect of hydraulic fluid viscosity on the pumping efficiency of gear, vane, piston, double-piston and hybrid pumps [196]. Hydraulic fluids must sustain their minimum viscosity under load and shear. These rigs are particularly important for investigating the modern phenomenon of temporary shear-loss, especially when testing high-VI fluids [197].

Gear Pump Efficiency Test: The Bosch Pump The first experiments to measure pump efficiency were run in gear pumps. The earliest and most fundamental of these studies were conducted in a pump loop with a small Bosch gear pump running at constant nominal pressure of 150 bar (2200 psi), 1500 rpm and fluids at 80 °C (176 °F) oil inlet temperature [193]. The test procedure, which was according to DIN 51 382, became known as the shear test for hydraulic fluids and engine oils in a Bosch Diesel injection nozzle (see also Table 8.6). In this case, the injection nozzle pressure is built up using a gear pump. In general, for arbitrary gear pumps, it is possible to plot their flow rate as a function of kinematic viscosity at a constant gear pump pressure (usually the nominal pressure). When the kinematic viscosity of the hydraulic fluid at the gear pump's oil inlet is known, it is possible to calculate the volumetric efficiency

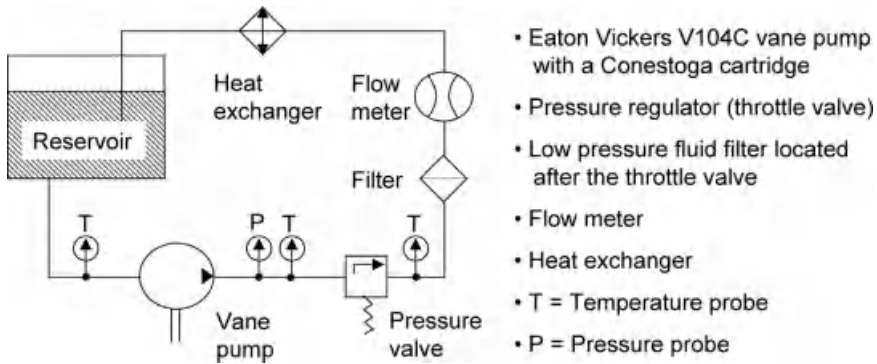


Figure 8.72 Schematic of the vane pump circuit to determine pump efficiency in dependence of hydraulic fluids in a medium-pressure loop.

for different operating conditions [193, 197]; the results obtained have revealed a good correlation for an ISO VG 46 hydraulic fluid. Moreover, a simple volumetric efficiency equation can be applied as a regression curve of the test results.

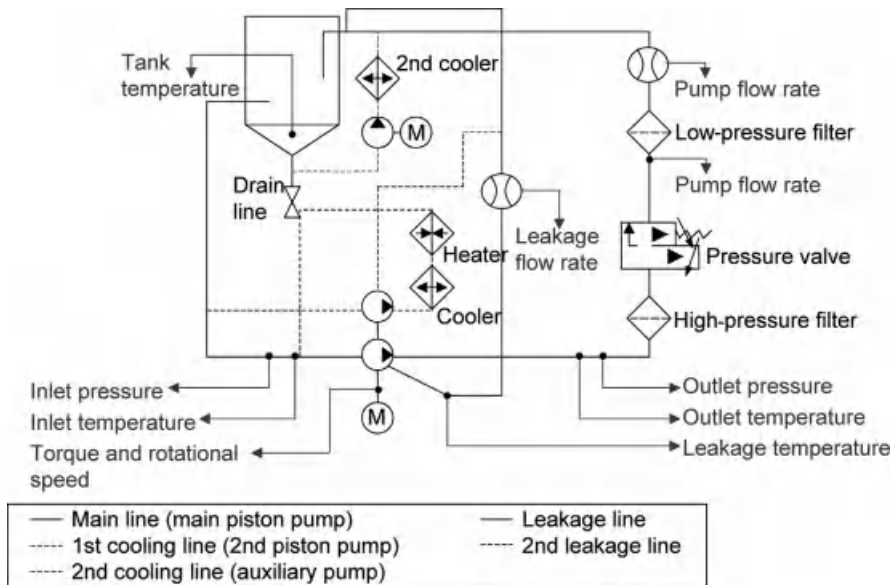
Vane Pump Efficiency Test: The Eaton Vickers V104C For this test pump in an open-loop circuit, Figure 8.72 shows (schematically) the set-up used to measure the vane pump efficiency in a medium-pressure loop. The test rig uses an Eaton Vickers V104C vane pump equipped with a Conestoga cartridge. The maximum pressure of the pump is 140 bar (205 psi), and the pump is driven by a 15 kW electric motor at 1165 rpm. With the cartridge selected, according to the pump manufacturer's data sheet the vane pump has a nominal flow rate of 301 min^{-1} (7.9 US gal. min^{-1}). Further technical data are provided in Table 8.32. The pressure, temperature, flow rate and input power at the pump shaft are recorded during the test. After thoroughly flushing the circuit and installing a new filter, the reservoir is filled with 18.91 (5.0 US gal.) of test fluid. All tests are started with the fluid and circuit at room temperature, at which point the discharge pressure is increased to 140 bar (2000 psi) until the desired fluid temperature is attained. The pressure is then either maintained at 140 bar (2000 psi), or reduced to 70 bar (1000 psi), while the temperature is controlled by using the heat exchanger. The data are collected for a period of 30–60 min, during which time data relating to the pump flow rate, the power consumed by the electric motor, the torque at the driving shaft, and the temperatures are collected at 1 s intervals and averaged once per minute. Each candidate hydraulic fluid is tested with the pump inlet temperature ranging between 30 and 90 °C (86–194 °F) at 70 bar (1000 psi), and at 40–80 °C (104–176 °F) at 140 bar (2000 psi).

Vane Pump Efficiency Test: The Parker–Denison T6CM The pump circuit (as shown schematically in Figure 8.73) provides an example of the test set-up that was used to measure vane pump efficiency in a high-pressure loop. In this hydraulic circuit, a Parker–Denison T6CM vane pump designed for mobile equipment was used; this

Table 8.32 Vane pump loops to determine efficiency of different hydraulic fluids.

Application	Medium-pressure loop	High-pressure loop	High-pressure loop
Vane pump type	Eaton Vickers V104C	Parker Denison T6CM	Komatsu HPV35 + 35
Input power	15 kW	22 kW	22 kW
Test duration	60 h	60 h	60 h
Maximum test temperature	90 °C (194 °F)	90 °C (194 °F)	105 °C (221 °F)
Maximum pressure	140 bar (205 psi)	250 bar (3600 psi)	350 bar (5080 psi)
Pump speed	1165 rpm	1500 rpm	1700 rpm
Nominal flow rate	301 min ⁻¹ (7.9 US gal. min ⁻¹)	321 min ⁻¹ (8.5 US gal. min ⁻¹)	301 min ⁻¹ (7.9 US gal. min ⁻¹)
Fluid volume	18.91 (5 US gal.)	641 (16.9 US gal.)	641 (16.9 US gal.)

pump can operate at up to 250 bar (3600 psi) on a continuous basis, and is driven by a 22 kW electric motor at 1500 rpm. With the cartridge selected, the vane pump has a nominal flow rate of 321 min⁻¹ (8.5 US gal. min⁻¹), according to the pump manufacturer's data sheet. Further technical data are provided in Table 8.32. The other elements of the circuit include a reservoir, two filters (high- and low-pressure), a flow meter, a pressure valve, a heat exchanger, and different sensors to measure the operating conditions (temperatures, pressures, torque, rotational speed). After thoroughly flushing the circuit and installing a new filter, the reservoir is filled with 64 l

**Figure 8.73** Schematic of the vane pump circuit to determine pump efficiency in dependence of hydraulic fluids in a high-pressure loop.

(16.9 US gal.) of test fluid. All tests are started with the fluid and circuit at room temperature. The discharge pressure is increased until a desired pump inlet temperature is reached, and the heat exchanger then activated to maintain this temperature. The pump performance is measured at six different steps of pressure during a 5-min period, at 15, 50, 100, 150, 200, and 250 bar (215, 725, 1450, 2175, 2900, 3625 psi). During that test period, the pump flow rate, power consumed by the electric drive motor, torque meter at the driving shaft and temperatures are collected at 1 s intervals and averaged once per minute. Each candidate hydraulic fluid is tested with the pump inlet temperature ranging between 30 and 90 °C (86 and 194 °F).

Dual-Piston Pump Type Komatsu HPV 35 + 35 The dual-piston pump selected for another study was an axial variable dual-piston pump series HPV35 + 35, as used in Komatsu mobile hydraulic equipment (e.g., excavators) [198]. The pump circuit is shown schematically in Figure 8.73. Only one of the two dual pumps was used, while the other pump was run idle. The pump, which can operate at up to 350 bar (5080 psi) nominal pressure, is driven by a 22 kW electric motor at 1700 rpm. Further technical data are listed in Table 8.32. The other elements of the circuit included a reservoir, two filters (high- and low-pressure), two flow meters (to measure the actual flow and the leakage), a pressure valve, a heat exchanger, and different sensors to measure the operating conditions (temperatures, pressures, torque, rotational speed). All tests are started with the fluid and circuit at room temperature. The discharge pressure is increased until a desired pump inlet temperature is reached, after which the heat exchanger is activated to maintain this temperature. The pump performance was measured at six different steps of pressure during a 5-min period, at 30, 70, 140, 210, 280 and 350 bar (435, 1015, 2030, 3045, 4060, 5080 psi). During the test period, the pump flow rate, power consumed by the electric drive motor, torque meter at the driving shaft and temperatures are collected at 1 s intervals and averaged once per minute. Each candidate hydraulic fluid is tested with the pump inlet temperature ranging between 30 and 105 °C (86 and 221 °F).

8.6.7.4 Test Results of Pump Efficiency Tests and Field Test Verification

An optimum efficient hydraulic fluid should bring about significant environmental benefits, by reducing the amount of fuel needed to produce a desired level of work. This fluid will also contribute to improve the energy efficiency of the equipment by maintaining a high efficiency under both high- and low-temperature conditions. It should also help lower the cost of ownership by providing proper pump lubrication under high-temperature conditions, and limiting the temperature increase in the circuit that promotes oxidation, oil leakage, and elastomer hardening. In order to compare the pump performance of different hydraulic fluids used in today's mobile equipment, a host of efficiency tests in gear, vane, and piston pumps are required for verification purposes. Finally, field tests must be conducted to verify the expected gains in system efficiency.

Using Viscosity-Modified Hydraulic Fluids to Target Maximum Efficiency When selecting hydraulic fluids, the additive type of viscosity modification (commonly

Table 8.33 Characteristics of viscosity-modified model fluids (ISO VG 46).

Model Fluid	Fluid grade	kV@ 40 °C	VI	kV@ 40 °C ^{a)}	VI	Δ kV@ 40 °C (%)	kV@ 40 °C ^{b)}	VI	Δ kV@ 40 °C (%)
Reference	Monograde	46.00	100	46.00	100	0.0	46.00	100	0
MSSF	Multigrade	46.00	150	40.27	129	12.5	32.21	121	30
HSSF	Multigrade	46.00	150	42.84	140	6.9	40.02	137	13

a) After sonic shear test according to ASTM D 5621.

b) After taper roller shear test according to CEC L-45-T-98.

known as a “thickening effect”) must be considered carefully [195–197]. An example of the effects of viscosity at high and low temperatures on the total system efficiency, by comparing two different viscosity-modified hydraulic fluids to a nonmodified low-reference fluid, is shown in Figure 8.69. Since all three fluids have the same viscosity at 40 °C (104 °F), all three model fluids may be classified as ISO VG 46 (additional fluid data are listed in Table 8.33). The overall efficiency (total efficiency) at 40 °C (104 °F) would be expected to be equivalent for all fluids in a pump test comparison. At lower temperatures, however, the lower kinematic viscosity of the two fluids (MSSF = medium shear-stable fluid and HSSF = high shear-stable fluid) leads to an increase in the total efficiency due to a rise in mechanical efficiency, because the MSSF and HSSF both lead to reductions in churning energy effects (see Figure 8.74). At higher temperatures, the two fluids will differ in their shear stability because they are formulated with different viscosity-modifying additives (i.e., VIIs; viscosity index improvers) in the same base oil. Consequently, both fluids will show an increased overall efficiency due to an increased volumetric efficiency at these temperatures. However, the gain of HSSF compared to MSSF at 100 °C (212 °F) is more than 10% higher, due to the presence of a very shear-stable VII rather than only a medium shear-

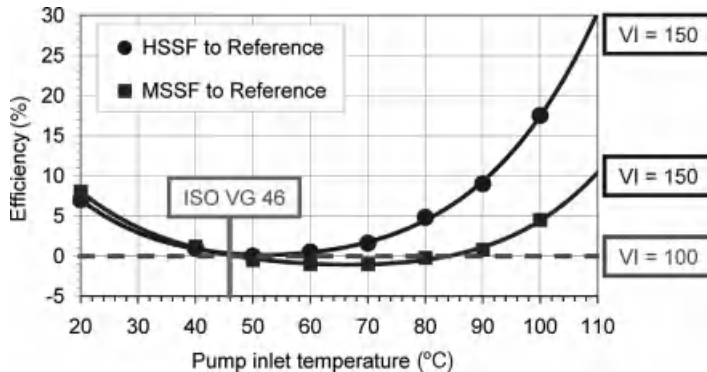


Figure 8.74 Denison T6CM B06 vane pump efficiency. Comparison of two multigrade ISO VG 46 model fluids with two different shear-stable additives. Measured overall pump

efficiency gain relative to an ISO VG 46 monograde reference fluid as a function of temperature at 250 bar (2625 psi).

Table 8.34 Characteristics of hydraulic efficiency test fluids.

Fluid code	Reference ^{a)}	HF1	HF2
Fluid grade	Monograde	Monograde	Multigrade
SAE grade	SAE 10W	—	—
ISO grade	—	VG 46	VG 46
NFPA grade ^{b)}	L46-46	L46-46	L32-100
KV @40 °C (mm ² s ⁻¹)	38.38	45.1	49.94
KV @100 °C (mm ² s ⁻¹)	6.10	6.71	10.14
Viscosity index	104	101	196

a) Reference fluid (SAE 10W engine oil) recommended by equipment maker.

b) NFPA grade according to Ref. [199].

stable VII (see Figure 8.74). In this case, the difference in shear stability of the fluids was determined using a Sonic (ASTM D 5621) and a taper roller shear test after a 20 h test period at 65 °C (149 °F), according to CEC L-45-T-98 (cf. Table 8.1).

When considering these most important fluid-related shear effects, two new and very shear-stable formulated hydraulic fluids with ISO viscosity grade VG 46 and different VIs have been tested and compared in different hydraulic circuits, and with different pump types (as noted in Section 8.7.4.3). The characteristics of the three fresh test fluids are listed in Table 8.34. With regards to a final field test verification, the selected fluids are compared towards a commonly used reference fluid, namely a SAE 10W monograde mineral (engine) oil, as recommended by the field test equipment maker (Caterpillar). The aim here was to show that the differences in operating efficiency observed in hydraulic pump loops with different fluids could also be observed in actual field service [189].

Gear Pump (Bosch Pump) The Bosch gear pump test results (as plotted in Figure 8.75) shown the measured curves of volumetric (Figure 8.75a) and mechanical efficiency (Figure 8.75b) for the three test fluids, according to the fluid data given in Table 8.34 as a function of pump inlet temperature at 150 bar (2175 psi). Since mechanical efficiency is approximately independent from the fluid viscosity, the influence of viscosity on overall efficiency derives only from the volumetric efficiency. Therefore, the relative differences in overall efficiency between the test fluids are essentially the same as those observed for the volumetric efficiency. The measured overall efficiency as a function of the pump inlet temperature is shown in Figure 8.75c. By using the data from this graph, it is possible to estimate the improvement in overall efficiency relative to the reference fluid (SAE 10W) at 150 bar (2175 psi) as a function of the pump inlet temperature (as seen in Figure 8.75d) [200].

Vane Pump (Eaton Vickers V104C; Medium-Pressure Loop) The Eaton Vickers V104C test results (as plotted in Figure 8.76) shown the measured curves of volumetric (Figure 8.76a) and mechanical efficiency (Figure 8.76b) for the three test fluids according to Table 8.34, as a function of pump inlet temperature at 140 bar (2300 psi).

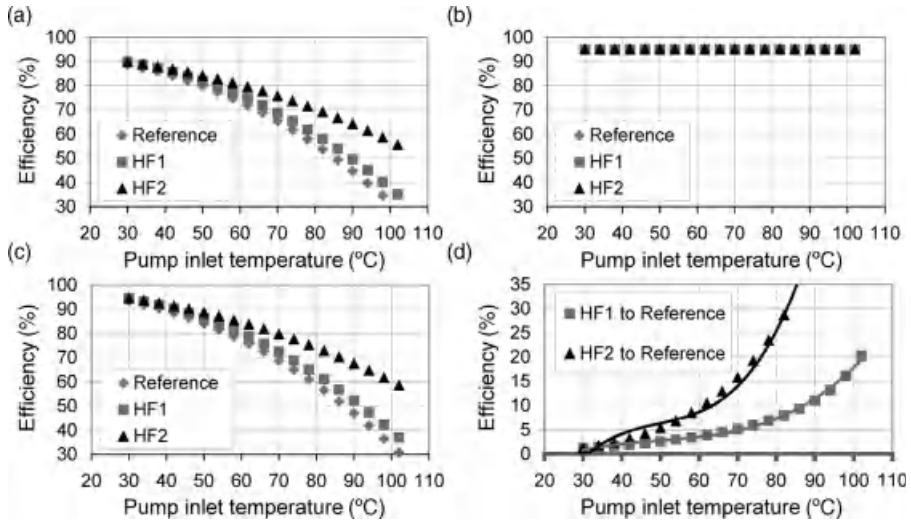


Figure 8.75 Gear pump flow rate as function of pump inlet temperature at a nominal pressure of 150 bar (2175 psi). (a) Volumetric efficiency; (b) Mechanical efficiency; (c) Overall efficiency; (d) Percentage improvement in overall efficiency relative to a recommended reference fluid.

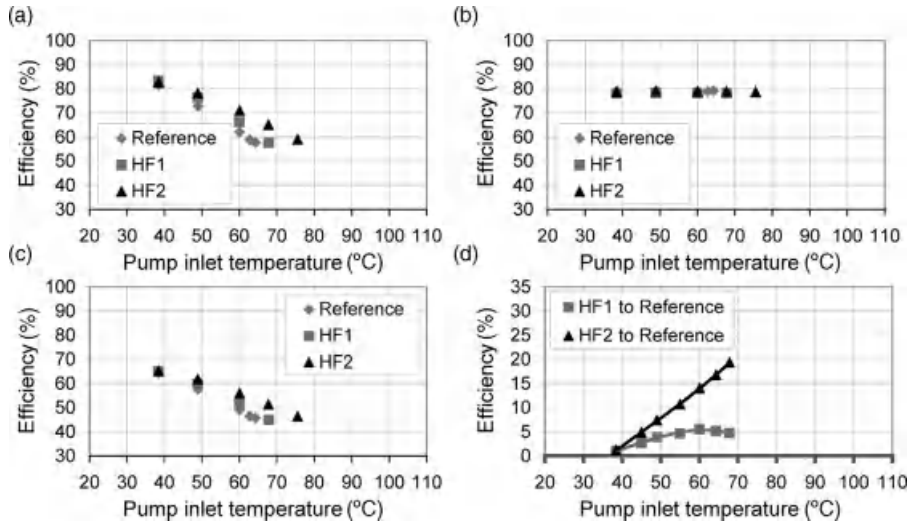


Figure 8.76 Vane pump Vickers V104C flow rate as a function of pump inlet temperature at a nominal pressure of 140 bar (2300 psi). (a) Volumetric efficiency; (b) Mechanical efficiency;

(c) Overall efficiency; (d) Percentage improvement in overall efficiency relative to a recommended reference fluid.

As mechanical efficiency is approximately independent of the fluid viscosity, the influence of viscosity on overall efficiency derives only from the volumetric efficiency. Therefore, the relative differences in overall efficiency between the test fluids are essentially the same as those observed for the volumetric efficiency. The measured overall efficiency as a function of the pump inlet temperature is shown in Figure 8.76c [201]. By using the data from this graph, it is possible to estimate the improvement in overall efficiency relative to the reference fluid (SAE 10W) at 140 bar (2300 psi) as a function of the pump inlet temperature (see Figure 8.76d).

Vane Pump (Denison T6CM B06; High-Pressure Loop) The three hydraulic fluids described in Table 8.34 have also been tested in the Denison T6CM B06 vane pump circuit. The three curves representing the volumetric, mechanical, and overall efficiency, as measured for the three test fluids as a function of the pump inlet temperature in the high-pressure pump loop operating at 250 bar (3625 psi), are shown in Figure 8.77a, b, and c, respectively. These test results correlate well with those from the medium-pressure loop, and have the same raking of efficiency. It should be noted that, between 30–40 °C (86–104 °F), the overall efficiency is essentially the same for the three fluids. However, above 60 °C (140 °F), a significant improvement could be observed. For example, at 80 °C (176 °F), an overall efficiency of 65% was recorded for the fluid HF2, compared to only 55% for the reference fluid (SAE 10W) (see Figure 8.77c) [197]. The test fluid HF1 (ISO VG 46 monograde fluid) gave an intermediate overall efficiency equal to 57%. The graph in Figure 8.77 can also be used to determine the fluid temperature-related gain in overall efficiency

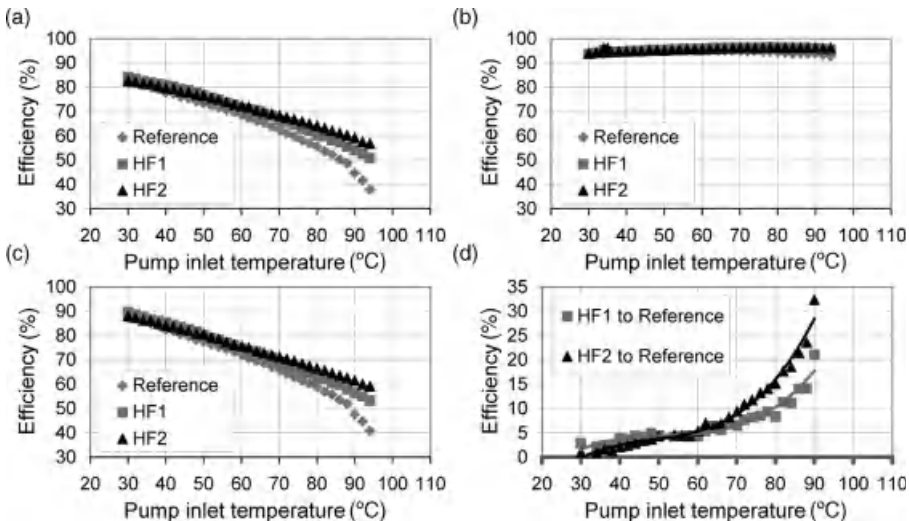


Figure 8.77 Vane pump Denison T6CM B06 flow rate as a function of pump inlet temperature at a nominal pressure of 250 bar (2625 psi). (a) Volumetric efficiency; (b)

Mechanical efficiency; (c) Overall efficiency; (d) Percentage improvement in overall efficiency relative to a recommended reference fluid.

relative to the reference fluid (SAE 10W), as recommended by the equipment maker (Figure 8.77d).

Dual-Piston Pump Test (Komatsu HPV 35 + 35) The efficiency curves at 350 bar (5080 psi) discharge pressure of the three tested fluids listed in Table 8.34, as measured in a Komatsu HPV35 + 35 dual-piston pump according to the test procedure described in Section 8.6.7.3, are shown in Figure 8.78. During the test run it was observed that, for the low discharge pressures from 30 to 140 bar (435 to 2030 psi), no significant differences could be recognized in overall efficiency between all the three fluids. However, for higher discharge pressures, the volumetric efficiency (Figure 8.78a) and mechanical efficiency (Figure 8.78b), and also the overall efficiency (Figure 8.78c) of the reference fluid (SAE 10W), is always lower than the efficiency for the two other fluids [198]. As noted above, this is due to the different fluid formulations. This graph can also be used to determine the fluid temperature-related gain in overall efficiency relative to the reference fluid (SAE 10W) as recommended by the equipment maker (see Figure 8.78d).

Field Tests and Test Equipment Laboratory studies completed with gear pumps and with both medium- and high-pressure vane and piston pumps, showed that the pump circuit efficiency depends on the discharge pressure and on oil viscosity. To verify these findings in actual service, field tests are requested by most equipment makers and applicers (OEMs). In order to verify the pump test data, a field test with two of the three fluids was also conducted in a medium-sized excavator running under moderate operating temperatures.

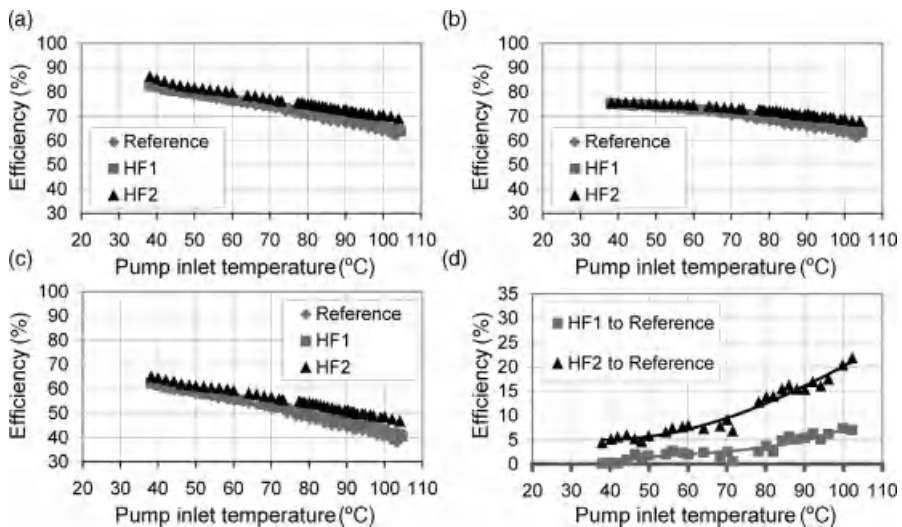


Figure 8.78 Axial variable piston pump flow rate as a function of pump inlet temperature at a nominal pressure of 350 bar (5080 psi).

(a) Volumetric efficiency; (b) Mechanical

efficiency; (c) Overall efficiency; (d) Percentage improvement in overall efficiency relative to a recommended reference fluid.

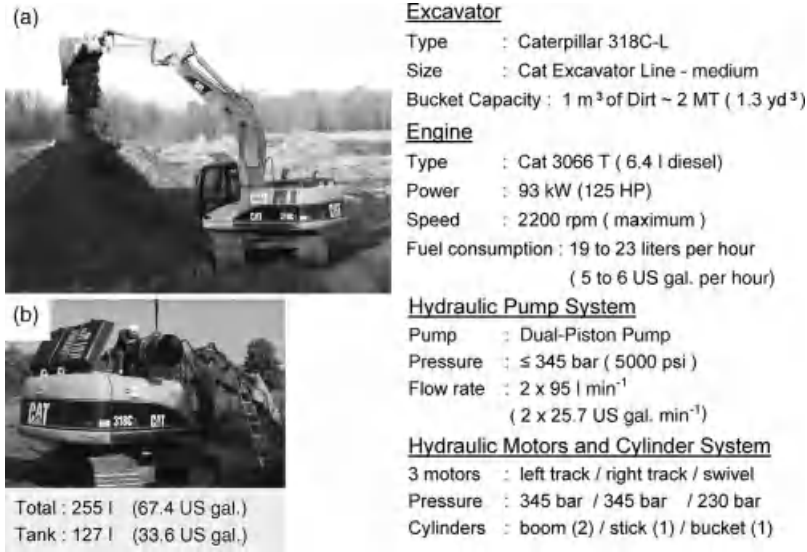


Figure 8.79 Field test equipment and technical data. (a) Technical data of engine and hydraulic equipment; (b) Fluid volume.

In this case, a medium-sized excavator, the Caterpillar 318C-L (Figure 8.79) was used to evaluate the effect of lubricants on hydraulic equipment performance. The excavator, which has a 1 m³ bucket (corresponding to a capacity of 2 metric tons) is powered by a Caterpillar 3066T diesel engine (6.4 liters) producing 93 kW (125 HP) at 2200 rpm. The engine has a typical fuel consumption of 19–23 l h⁻¹ (5–6 US gal. h⁻¹). The equipment has a dual-piston pump feeding three piston motors that operate the tracks and swivel, plus boom, stick, and bucket cylinders. The two pumps can work at a maximum pressure of 345 bar (5000 psi), with each pump having a nominal flow rate of 95 l min⁻¹ (25.7 US gal. min⁻¹), yielding a total flow of 190 l min⁻¹ (49 US gal. min⁻¹). The hydraulic circuit contains 255 liters (67.4 US gal.) of fluid, and the hydraulic fluid reservoir has a capacity of 127 liters (33.6 US gal.). Pressure transducers were installed to monitor pump pressures, while thermocouples were placed at the stick, boom, and hydraulic reservoir locations.

Test Fluids and Test Procedure Two hydraulic fluids (coded Reference and HF2 in Table 8.34) were evaluated in the excavator. The complete test program, which consisted of a test protocol and a work profile, is shown in Figure 8.80. One single work cycle consisted of the steps shown in Figure 8.81, and was conducted under mild climatic conditions, with the ambient temperature ranging between 7 and 18 °C (45–65 °F). The equipment was operated with the engine running at 90% and 100% throttle.

Field Test Results: Energy and Cost Savings The fuel consumption for the two test fluids and the two throttle settings are detailed in Table 8.35. Although the fuel

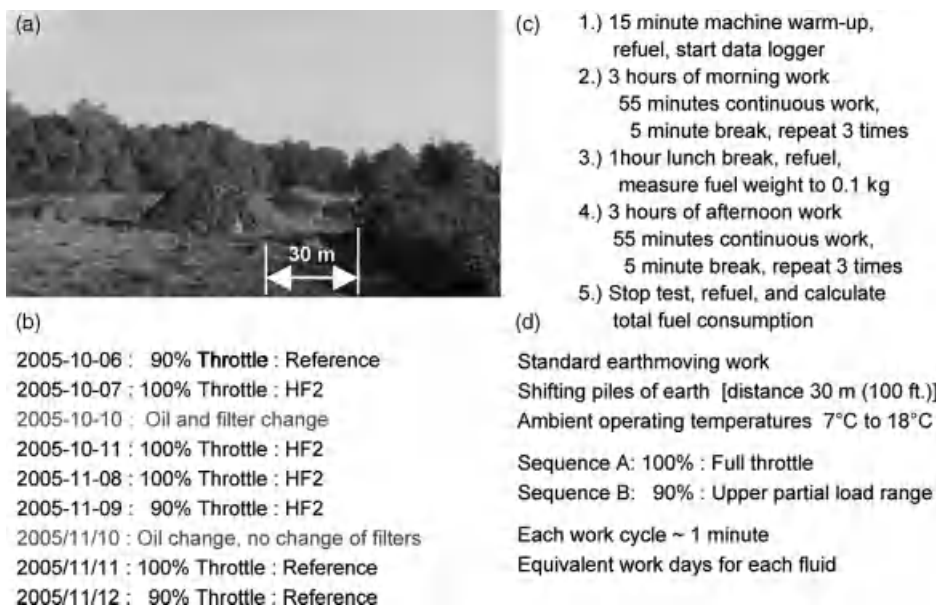


Figure 8.80 Field test conduction. (a) The field test area; (b) Field test program and test fluids; (c) Test protocol; (d) Work profile.

consumption was increased when going from 90% to 100% throttle settings, the results in Table 8.35 showed that the equipment consumed significantly less fuel per hour with fluid HF2 (High Efficiency Hydraulic Fluid 2), irrespective of the throttle setting. When the number of work cycles per hour was recorded (average values are shown in Table 8.36), more cycles per hour were completed with fluid HF2, irrespective of the throttle setting. A combination of the fuel consumption per hour and the number of cycles per hour yielded the average fuel consumption per work cycle; the results for the two fluids at the two throttle settings are listed in Table 8.37. The productivity improvements achieved when using fluid HF2 were 26.3% at 90% throttle, and 18.4% at 100% throttle.

In addition, a cost–benefit analysis was performed to compare the value of HF2 to the OEM-recommended reference fluid (SAE 10W). A 4000 h drain interval was assumed, with a value of US\$ 9.00 per gallon assigned to the SAE 10W fluid, and US\$13.50 per gallon to HF2 (i.e., a 50% premium). The cost of diesel fuel at the time of the analysis was US\$ 3.15 per gallon. From a conservative aspect, a fuel economy improvement at full throttle of 18.4% was used instead of the 26.3% improvement seen at 90% throttle. No value was assigned to the approximately 6% additional work that the excavator could perform when using HF2. The estimated energy and cost savings are shown in Table 8.38.

Final Conclusions Viscosity is a critical property of all lubricants. Whilst equipment will operate within a wide range of lubricant viscosities, there are optimal points where such viscosity will contribute to the correct lubrication, without being



Figure 8.81 The work cycle used in this test lasted about 1 min. (a) Take a full scoop; (b) Rotate 90–180° and travel 30 m (100 ft); (c) Dump load and rotate 90–180°; (d) Empty return of 30 m and start with next cycle.

Table 8.35 Fuel consumption per hour.

Throttle (%)	Fluid	Fuel consumption per hour (kg)	Improvement (%)
100	Reference	19.50	—
100	HF2	16.80	13.8
90	Reference	15.20	—
90	HF2	13.89	8.6

Table 8.36 Work cycles completed per hour.

Throttle (%)	Fluid	No. of cycles	Improvement (%)
100	Reference	53.5	—
100	HF2	56.6	5.8
90	Reference	40.0	—
90	HF2	49.7	24.3

Table 8.37 Fuel consumed per work cycle.

Throttle (%)	Fluid	Fuel consumption per cycle (kg)	Improvement (%)
100	Reference	0.364	—
100	HF2	0.297	18.4
90	Reference	0.380	—
90	HF2	0.280	26.3

detrimental to overall efficiency. As viscosity is a function of temperature, and equipment can be operated over a range of temperatures during typical duty cycles, the design of a lubricant's viscosity profile over temperature represents an important aspect of lubricant design when system efficiency is considered. The most obvious role of lubricants in improving efficiency is to reduce frictional losses in the system. Lubricants reduce friction between surface contacts and, typically, a minimum viscosity is necessary for a lubricant to perform this function. However, as lubricant flow itself is a source of mechanical drag in a system, the viscosity must be high enough to provide the correct lubrication, yet low enough for the lubricant to be delivered efficiently. These are the typical design criteria for automotive lubricants such as engine oils and transmission fluids, and in this case the system efficiency can be improved by lowering the viscosity of the fluid in operation. However, these viscosity-related effects must not only be consistent over the range of operating temperatures for the equipment, but they must also be resistant to the effects of shear. Hence, shear-stable VIIs have been designed to maximize mechanical efficiency for these applications [202]. In other applications, such as hydraulics, volumetric losses may be larger than mechanical losses. In this case, lubricant additives can improve the system efficiency by increasing the viscosity at operating temperatures, so that the

Table 8.38 Potential energy and cost saving using high-efficiency hydraulic fluid (HF2).

Units	Reference	HF2	Benefit
Hours of work per drain	4000	4000	
Hydraulic fluid volume [l (US gal.)]	255 (67.4)	255 (67.4)	
Hydraulic fluid price (US\$ per gal.)	9.00	13.50	
Hydraulic fluid cost (US\$)	606.60	909.90	−303.30
Work cycles at 100% throttle	214 000	226 400	12 400
Fuel consumed (US gal.)	24 459	21 114	3346
Fuel price (US\$ per gal.)	3.15	3.15	
Fuel cost total (US\$)	77 047	66 508	10 539
Overall costs savings total (US\$)	77 654	67 418	10 236

working output of hydraulic pumps and motors is maximized. But, this must be balanced by a lower viscosity at lower, start-up temperatures, so that equipment can be started without unnecessary energy use, and without sustaining damage. The performance requirement must be resistant to the high levels of mechanical shear found in hydraulic systems. When considered as design elements of a system, lubricants represent a significant factor in the efficiency, fuel economy and emissions of automotive and industrial equipment.

8.7

Interpretation and Precision of Tribological Mechanical–Dynamic Testing

Most results from tribological mechanical–dynamic tests must be interpreted, and cannot often be regarded as absolute values. For this reason, reference tests based on reference materials and reference lubricants have particular significance in tribology. The precision of all test methods is, usually, substantially affected by the manufactured tolerances achieved by the test machines and test pieces, by the measurement and control systems used, by mechanical elasticities, and by other factors which depend on the operating conditions and on ambient conditions. The precision of a test method is evaluated from data on the repeatability and reproducibility of the test results and, in Germany for example, the demands made on these data are standardized in accordance with DIN 51 848 [203]. The repeatability of a test result is applicable for one observer and one test machine on which it was performed. The reproducibility of a test result is extremely important in relation to compliance with the test standards and specifications of a test result. High repeatability is a basic prerequisite for satisfactory reproducibility of a test result. In addition, the comparison of existing test conditions with “real” conditions is of particular importance when assessing the relevance of results obtained in tribological performance tests. This requires adjustment of the test conditions to the field-related specific loads, sliding speeds, ambient temperatures, and materials used in real applications. Only when all of these requirements are taken into account can a suitable test method be selected. Then, with help from tribological mechanical–dynamic performance testing, the effect of the tribological contacts and lubricants in application can be predicted.

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