Fundamentals of Lubricants and Lubrication

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/55731

1. Introduction

Literature about lubricants is available in all public domains. Readers should search at those platforms in the case of special interests. Citations given here do not represent the full scale but reflect an overview from a today's perspective. [1-7]

Part of this chapter will be the basic chemical structure of lubricants including some property descriptions. Since literature in tribology is innumerous, the reader should check his special area of interest.

Lubricants play a key role in machinery element safety. Their main tasks are

- to keep moving parts apart from each other,
- to take heat out of the contact by their through pass,
- to keep surfaces clean,
- to transport functional additives toward the surface and
- to transfer power in the application (hydraulic, automatic transmission, breaks). [6, 8]

Functionality of lubricants is defined by their chemical structure and their physical properties. Basics of lubrication are covered by organic chemistry to a major and inorganic chemistry to a minor extent. [2, 3]

Lubricants are regulated internationally and locally, e. g. by ASTM (American Standard of Testing Materials) or DIN (Deutsche Industrienorm). Regulation covers the physical, chemical and toxicological description of lubricants including safety guide lines and others. [2, 3]

2. Some basics

The spatial structure of carbon chemistry defines all activities of the lubricants derived from them. The spatial structure of organic carbon chemicals is given by the binding state of carbon. [10]

Three main types are discussed. Two are essential for lubrication: single and double bonds.

2.1. Single bonds: Tetrahedral binding

In the tetrahedral binding state, reflecting the status of single bonds, carbon is placed in the centre of a pyramid with bindings into space from the centre to the corner (Figure 1).

Figure 1. Tetrahedral binding of carbon

Carbon is placed in the centre of the tetrahedral with four attached valences. Within chemical convention in order to abbreviate the structure denotation the atom symbols are neglected.

Carbon may bind to another one by corner to corner. (Figure 2)

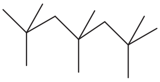


Figure 2. Corner to corner binding state

Corner to corner binding leads to zigzag chains, where the angle of carbon to the hydrogen atoms is 108°. In general the hydrogen is neglected, leading to a skeleton drawing of the structure.

Beyond the fixed angle of 108° and the zigzag shape of such hydrocarbon structures, a high variety of structures arise due to the fact that those bindings may branch or bind to cyclic structures. (Figure 3 and Figure 4)

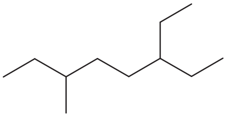


Figure 3. Branched structures by carbon to carbon binding

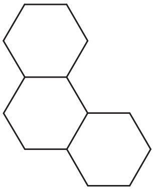


Figure 4. Cyclic Structures by carbon-carbon binding

Single bonds in hydrocarbons are free to rotate (Figure 5). Rotation leads to the situation that hydrogen atoms within the chain get close to each other. As a consequence the energy of the molecule rises.

Figure 5. Energy rise in rotated structures

Similar to internal rotation, molecular energy rises if molecules get under stress by moving them closely together without giving time to relax. (Figure 6)

Figure 6. Excitation by pushing molecules to one another by shear stress

Also the fact of putting or pressing molecules toward a surface may lead to a steep increase in internal molecular energy, sometimes high enough to cut them.

2.2. Double bonds

Carbon may also bind to others by double bonds, such that two of the four bindings attach to the other as double, whereas the remaining bonding stays single. (Figure 7)

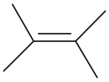


Figure 7. Double bonding

Double bond shows a 120° neighborhood angle to the carbon. This angle is kept constant and will lead toward different structures in the double bond chemistry. (Figure 8)

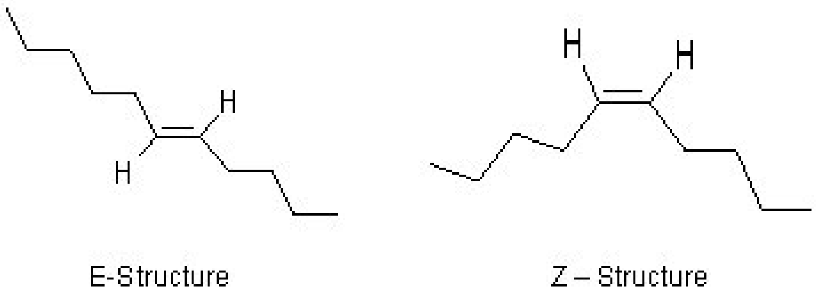


Figure 8. E and Z structures in double bond

Both structures differ in their energy. Double bonds are part of biodegradable additives (native oils) but also additives and thickeners in the case of greases. Z-Structures are dominant in native oils.

2.3. Triple bonds

Triple bonds are seldom found in tribology. They represent a high energy state in molecules with very high reactivity. As such, they are part of catalytic degradation processes in lubricants. Within a triple bond carbons attach to each other by a linear principle (Figure 9):

Figure 9. Triple bond present in a hydrocarbon

3. Base oils in lubrication: General comments about specie and groups

Hydrocarbon Base Oils for Lubrication derive from organic chemistry. Different categories are given by their chemical composition and structure. [2]

Hydrocarbons, e.g. Structures that contain solely Hydrogen and Carbon (H, C)

Ester Oils, e.g. Structures containing Hydrogen, Carbon and Oxygen. Some Esters are derived from other precursors, such as phosphoric acid esters.

Polyglycoles: Structure containing Hydrogen, Carbon and Oxygen but being different in binding state compared to Esters.

Within a general scheme, base oils are identified as Groups.

Group I: Those lubricants are built from saturated hydrocarbons, e.g. hydrocarbons without alkenes (hydrocarbons with double bonds)) (> 90%), obtained by solvent extraction processes and catalytic hydrogenation. Sulfur may part in amount of > 0.03%. Viscosity index (VI) is in between 80 and 120.

Group I+: Oils that are in a VI range of 103-108.

Group II: Hydrogenated (saturated) hydrocarbons (> 90%) and sulfur below 0.03% per weight with viscosity index (VI) of 80 till 120.

Group II+: Oils in the VI range of 113-119.

The base oil within this group is manufactured by hydrocracking, solvent extraction or catalytic dewaxing processes. Those oils are pale or water like colored.

Group III: Oils with a saturation > 90%, sulfur < 0.03% and a viscosity index > 120. Those oils are produced by catalytic procedures with a concurrent rearrangement of the carbon backbone during hydrogenation.

Group III+: Oils providing a VI at least of 140.

Group IV: Poly-α-Olefins with sulfur content approximately 0, viscosity index 140–170, being produced by catalytic polymerization of low molecular weight end terminated olefins.

Group V: All other oils, e.g. esters, polyglycoles, phosphate esters.

North America states Group III, IV and V as synthesized hydrocarbons (SHC) while in Europe Group IV and V is declared as synthetic oil.

4. Saturated natural hydrocarbons

Saturated hydrocarbons are those who do not contain double bonds in their structure. They derive from the tetrahedral binding of carbon (bindings that point into corners of tetrahedron). The simplest structure is given by methane, ethane, propane, butane with carbons attached at the corners of the tetrahedral. These representatives are present in the natural gases, while methane is found in enormous quantities as methane-ice cluster. The gases themselves are not in use as lubricants but are components of fuels. (Figure 10)

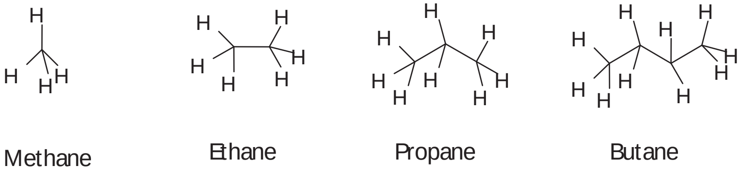


Figure 10. Methane, Ethane, Propane, Butane

Starting from pentane the hydrocarbons get liquid and are the principal components of fuels, solvents, and raw materials for the chemical industry. To facilitate reading and drawing only the carbon backbone is drawn without explicitly showing hydrogen. (Figure 11)

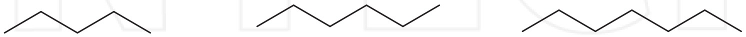


Figure 11. Pentane, Hexane, Heptane

Binding of carbon to carbon may be realized in chains, but also in branched chains and different cycles (Figure 12).

Figure 12. Methylbutane (Isopentane), 2,2-Dimethylpropane (Neopentane), Cyclohexane

Hydrocarbons from C10 on till C14 are in use as solvents for cleaning (C11-C13 isoparaffines) (Figure 13):

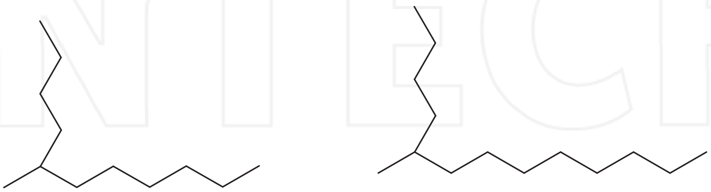


Figure 13. C11-C13 Iso paraffines

From C16 on, hydrocarbons represent typical structures present in lubricants. As the linear hydrocarbons, beginning at C18 are solids, they are common in waxes and thickeners for liquid hydrocarbons. Due to their high solidification point they are a threat if present in Diesel fuels by blocking filters.

Apart from their function as hydrocarbon waxes they are not suitable as lubricants for machine oil circuits.

Suitable lubricants are derived from C16–C70 hydrocarbons with branched chains. Branching leads to low pour points (the point where the lubricant starts to get solid). Machine oils with low pour point, suitable for low temperature applications are branched in their carbon chain. (Figure 14)

Figure 14. Representatives of saturated hydrocarbons as typical lubricants

In general, the viscosity of a lubricant - as a measure for the ability to move across - increases with the molecular weight, e.g. the number of carbon atoms attached. Viscosity is measured by different techniques. Basically the lubricant is pushed or moved in between plates or by moving it in the gravity field. International convention states 16 classes of viscosity as an ISO Standard (ISO VG classes): ISO VG 5, 7, 10, 15, 22, 32, 46, 68, 100, 150, 220, 320, 460, 680, 1000 and 1500. Low numbers indicate low viscosity, higher numbers high viscosity. Since viscosity is strictly related to temperature, the ISO VG classification refers to 40°C as a standard temperature. The nature of measuring the viscosity leads to the physical value of an area per time: mm^2/s. Hence, ISO VG 68 for example denotes a viscosity of the lubricant, measured at 40°C within 68 mm^2/s within a range of roughly 10% below and 10% beyond the given 68mm^2/s.

Low molecular weight, branched hydrocarbons are often used in *pneumatic spraying*, due to their viscosity range, starting at 2 (water-like), 5, 10 and 15.

Low viscous hydrocarbons from ISO VG 10, 15, 22, 32, 46, 68 and 100 are in use as *hydraulic oils.* Common hydraulic oil viscosity is around ISO VG 32, 46 and 68.

Hydrocarbons with higher viscosities are part of *machine oils*, carrying out the ordinary lubrication functions. Machine oil viscosities are in the range of ISO VG 68, 100, 150, 220, 320, 460. The number of carbons is in the range of 30–80 in the chain.

Some applications in heavy duty processes demand viscosities even higher in the range of ISO VG 680, 1000 and 1500.

4.1. Cyclic hydrocarbons (Naphtenes)

Naphtenic hydrocarbons are derived from hydrocarbon cycles with more or less long chains attached to the cycle. Due to their high branching they are very common in low temperature applications (below -30°C) for hydraulics; low temperature greases. (Figure 15)

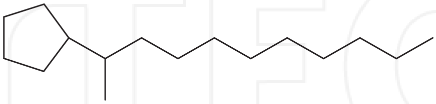
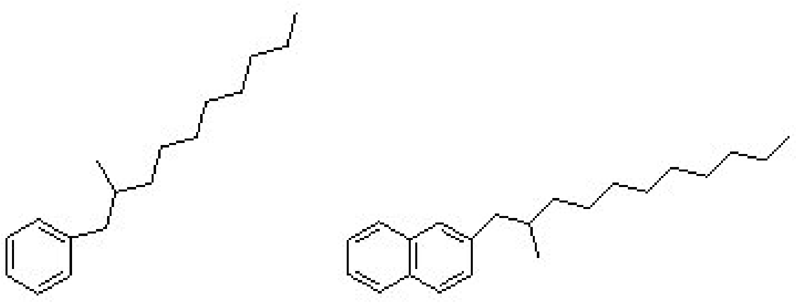


Figure 15. Principal Structure of Napthenic Hydrocarbons

4.2. Aromatic hydrocarbons (Alkyl aromats)

Aromatic Hydrocarbons (Alkyl Aromats) derive from the six-membered benzene ring system, attached by hydrocarbon chains. Aromatic hydrocarbons are in use for low temperature applications.

Alkyl Naphthalenes are a modern group of aromatic hydrocarbons. They may act as solvent improvers for synthetic oils, facilitators in generating greases, low temperature applications and much more (Figure 16):



Alkyl Aromat

Alkyl Napthalene

Figure 16. Alkyl Aromats and Naphtalenes

Aromats and aromat-containing hydrocarbons are very vulnerable toward oxygen. Oxidation of aromats starts at the attached hydrocarbon chain, proximate to the aromat nucleus by a radical attack. This position is always very sensitive in similar structure, due to the fact, that the intermediate carbon radical is stabilized by the aromat and thus starts to stay persistent. As a fact, aromats may strongly boost oxidation of hydrocarbons if present in the mixture due to the mentioned persistency of the reactive intermediates. (Figure 17)

Aromats and naphtenics (containing unsaturated hydrocarbons and aromats) should be stabilized against oxidation.

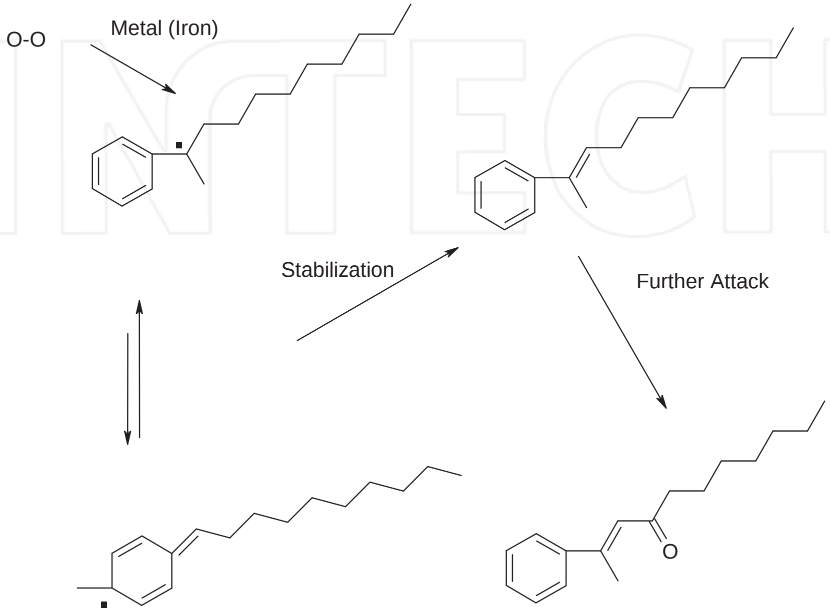


Figure 17. Oxygen attack in the oxidation mechanism of Alkylaromats

5. Synthetic hydrocarbons

5.1. Poly-α-Olefins (PAO)

PAO is dominating all synthetic hydrocarbons by amount of production and worldwide turnover. Syntheses start from Dec-1-ene, a linear C10 hydrocarbon with a double bond at the beginning of the molecule. Polymerization and hydrogenation leads to PAO, as a highly branched and fully saturated hydrocarbon (Figure 18). [2, 4]

Modern PAO may also start from a variety of hydrocarbons (C8-C12) by the same processes. PAO are the most prominent worldwide used hydrocarbons and found in all important applications, e.g. gear oils, circuit oil, hydraulic oil, base stock for automotive applications and others. [2, 3, 6, 7]

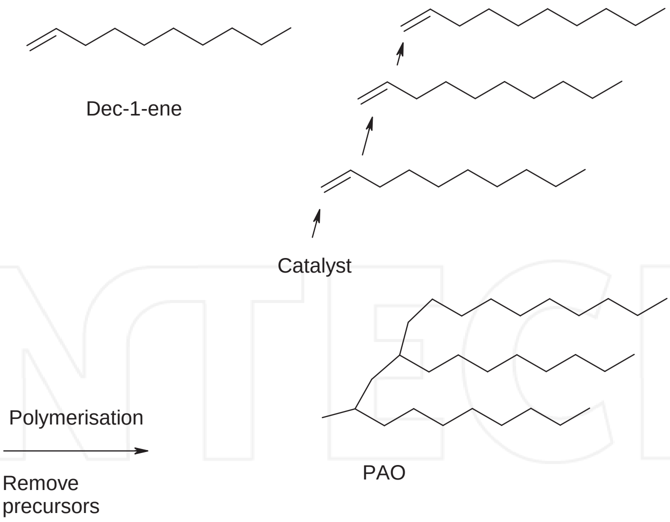


Figure 18. Principle of PAO formation

The extraordinary importance of PAO is due to its applicability at very low temperatures (pour points below –30°C) and, in the case of suitable antioxidant prevention also at higher temperatures (> 120°C). While PAO is, by its structure, very common in low temperature applications, it is very poor in the contact with metal surfaces beyond 120°C if not properly additivated by antioxidants.

Principal antioxidants for PAO are Phenyl-α-Naphtylamine (PAN) and octyldiphenylamines (see antioxidants (AO)).

5.2. Polyisobutenes (PIB)

PIB are a sub class of polymerized olefins. They are widely used to boost low viscous oils to higher ISO VG grades or as functional additives to improve the viscosity index (VI): the attitude of the lubricant to lower its viscosity strongly by temperature is reduced by addition of PIB. Synthesis is carried out starting from isobutene by catalytic oxidation processes (Figure 19):

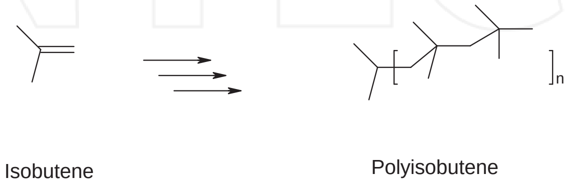


Figure 19. PIB formation by catalytic polymerization of Isobutene

Sulfurization with activated sulfur precursors lead toward sulfurized isobutenes (SIB) widely used as extreme pressure (see also section about EP/AW additives).

6. Ester oils

6.1. General

Esters are in general reaction products between alcohols and acids. Their formation is also possible by means of other techniques, e.g. specific oxidation reactions, rearrangements in organic molecules or different reactions. [10]

Carboxylic Acid esters are created by the reaction of alcohols and carboxylic acids [A] and their derivatives, by trans–esterification (B), or catalytic reactions, e.g. epoxides with carbon dioxide (C) (Figure 20). [10]

6.2. Esters in lubrication technology

Despite their high variety in structure esters are used in different categories: [1, 2, 4]

6.3. Mono-esters

Mono-Esters derive from a monocarboxylic acid (Carboxylic Acid that contains only one acidic centre) and monofunctional alcohols (Alcohole with only one OH group). [10]

Esters derived from this structure are seldom used as pure lubricants, more as solvents or dispersants. For example alcohol ethoxylates, formed by addition of alcohols to epoxides may be esterified by a monocarboxylic acid leading toward a dispersant or self-emulsifying solvent. (Figure 21)

6.4. Di-esters

Di-Esters are synthesized by use of dicarboxylic acids, mainly adipaic or sebacaic acid and two molecules of an alcohole. 2-Ethylhexylalcohole (Iso Octanole), leading to Di-isooctyladipate (DOA) or Di-isooctylsebacate (DOS, DEHS = Di-ethylhexylsebacate). (Figure 22)

They constitute an important group of oils, with either the function of base oil by themselves but also as adjuvant to mineral oil or PAO formulations.

For Di-Esters the reaction of alcohols (A) with two hydroxyl groups and a monofunctional carboxylic acid (B, B') is also applicable. (Figure 23)

For technical purposes the reaction product of Neo Pentylgylcole (3.3 Dimethyl-propane-1.4-diol) with oleic acid is important in lubrication technologies for use as a friction reducer and in minimal lubrication systems. (Figure 24)

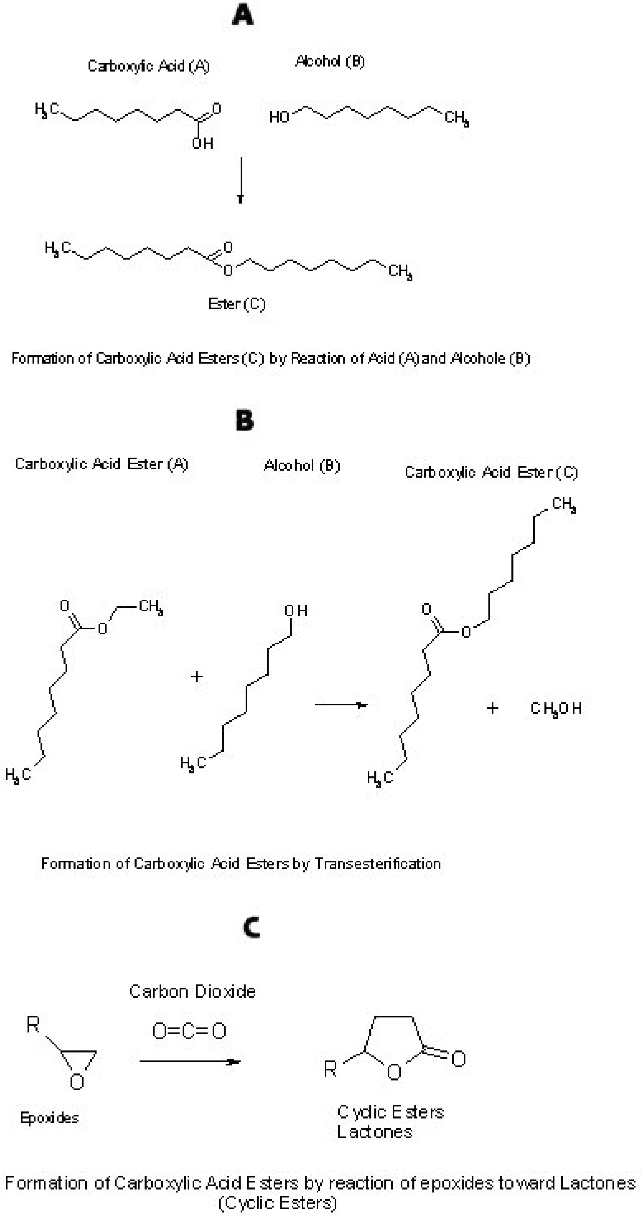


Figure 20. Examples for creation of esters. (A) Reaction of Carboxylic Acids with Alcohols, (B) Transesterfication, (C) Reaction of Expoxide to cyclic Esters.

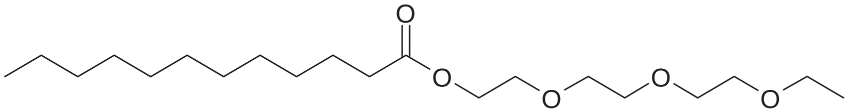


Figure 21. Mono Ester Formation with the specialty of esterified alcohole ethoxilates

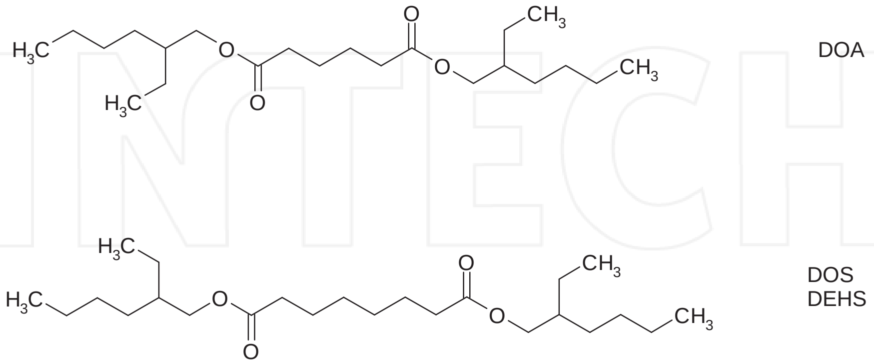


Figure 22. DOA and DOS

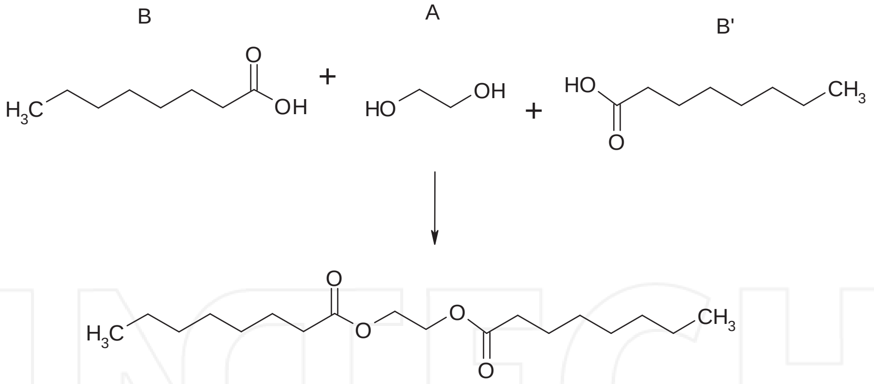


Figure 23. Formation of Di-Esters by Di-Alcoholes (A) reacted with Monocarboxylic Acids (B, B')

6.5. Tri-esters

Tri-Esters are mainly created by the reaction of trivalent alcohols with monocarboxylic acids. They are mainly represented by to major groups:

6.5.1. Glycerol esters

Esters derived from glycerol as a trivalent alcohole leads to tri-Esters. (Figure 25)

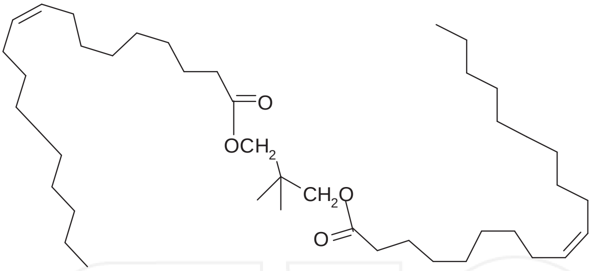


Figure 24. Neopentylgylcoledioleate (NPG-Dioleate)

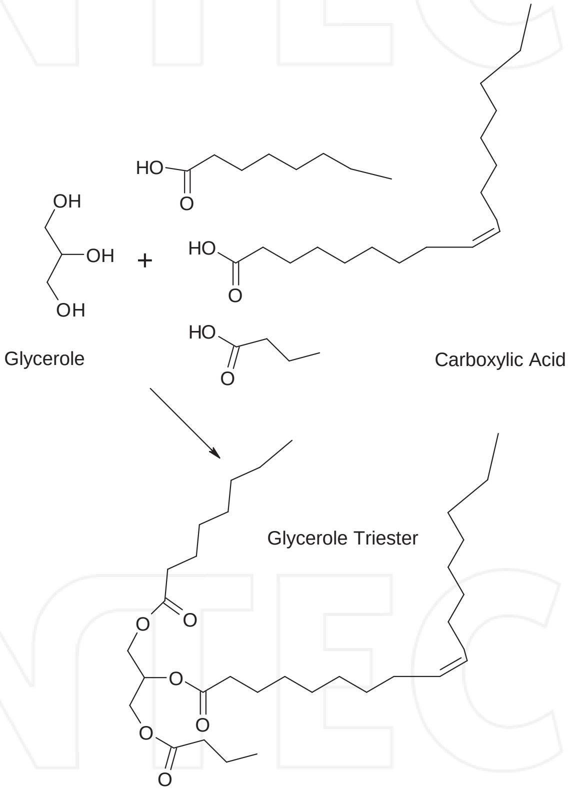


Figure 25. Esterification of Glycerole to tri-Esters

Glycerol Tri-Esters represent the huge group of natural oils. Sunflower, rapseed oil are prominent representatives. A mixture of short chain carboxylic acids with unsaturated long chain acids is used.

As a fact of the presence of short chain carboxylic acids those esters are nutrients, biological degradable and widely used as natural, biodegradable oils.

As a special glycerol ester, important for lubrication, ricinoleic acid esters have to be mentioned.

Within this group ricinoleic acid represents the group of 12-hydroxy substituted C18 carboxylic acids.

Hence, alkaline cleavage of ricinoleic acid glycerol esters lead to 12-Hydroxi-oleic acid on the one hand and to sebacaic acid on the other hand by degradation of the double bond.

Catalytic hydrogenation of 12-Hydroxioleic acid results in the formation of 12-Hydroxistearic acid, which is important for modern grease concepts. Sebacaic Acid on the other hand is a raw material for DOS (see above) but also for the production of complex greases. (Figure 26) [1, 2, 4]

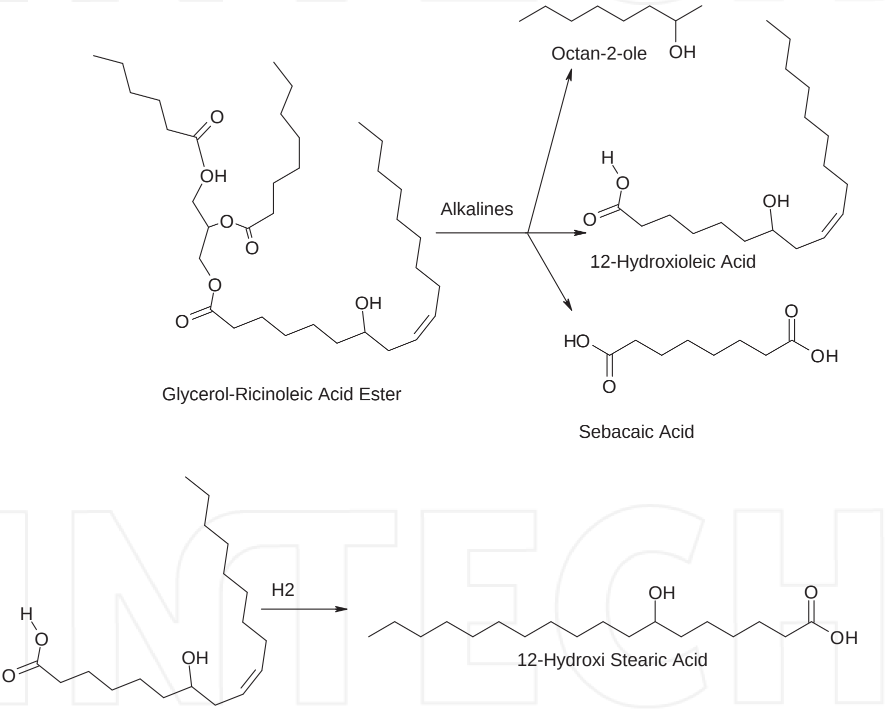


Figure 26. Cleavage of Glycerol – Ricinioleic Acid and hydrogenation to 12-Hydroxistearic Acid, Sebacaic Acid and Octan-2-ole [10].

Glycerole Esters with long chain carboxylic acids only, e.g. Glycerole Tristearate, are no longer nutrients and sparingly biodegradable. They are used as emulsifiers, consistency givers.

Glycerole Trioleate is a powerful friction reducer in tribological applications.

6.5.2. Triesters, derived from alcohols else than glycerole

6.5.2.1. Trimethylolpropane esters (TMP-esters)

TMP-Esters are created out of Trimethylolpropane (TMP) by reaction with short chain carboxylic acids, e.g. the range from C6 to C10. (Figure 27)

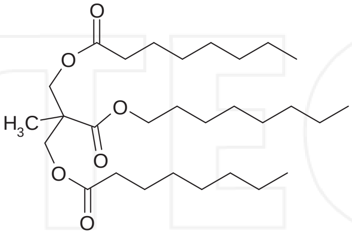


Figure 27. TMP Esters

TMP Trioleate is created by reaction of TMP with oleic acid or by trans-esterification.and commonly used as lubricant in minimal lubrication.

6.5.2.2. Trimellitic esters (TM-esters)

Apart from the described structures where trivalent alcohols get reacted with monocarboxylic acids, trimellitic Esters (TM-Esters) are products from Trimellitic Acid Anhydride with Mono alcohols. (Figure 28)

Due to the aromatic core those esters are high in thermal stability and widely used in high temperature applications.

6.6. Tetra esters (Pentaerythrolesters, PE-esters)

Pentaerythrole acts as a four-valent alcohole which may be esterified by four carboxylic acids. (Figure 29)

Carboxylic acids are in the range from C6 to C10.

Dipentaerythrol Esters (Di PE Esters) are formed starting from Dipentaerythrole as a six- valent alcohole reacted by six monocarboxylic acids in a Carbon Chain length from 6 to 10. (Figure 30)

6.7. Polyesters

In the past 20 years new groups of esters have been created by reaction of polycarboxylic polymers with alcohols. Those are reaction products of maleic acid anhydride (MSA) by Ene-Reaction with PAO precursors, leading to the PAO-backbone MSA addition product that might be esterified by butanole, leading to carboxylic complex esters (Figure 31).

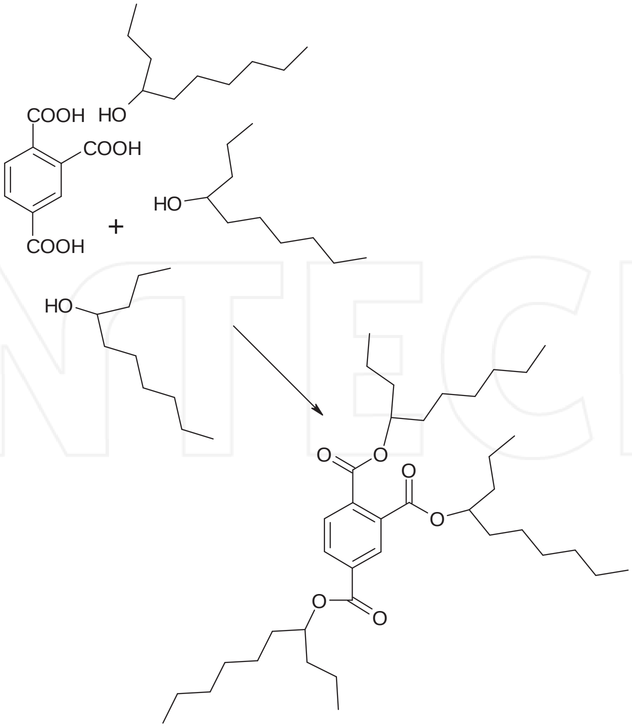


Figure 28. TM Esters by reaction of trimellitic acid with branched alcohole

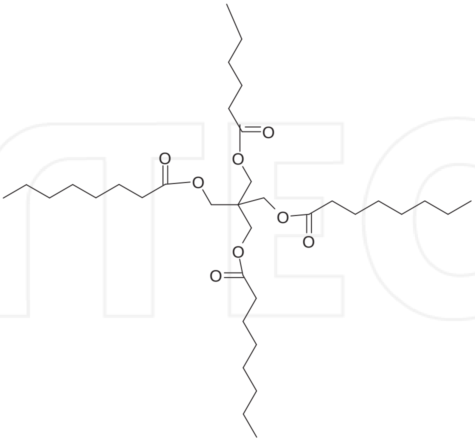


Figure 29. PE Esters

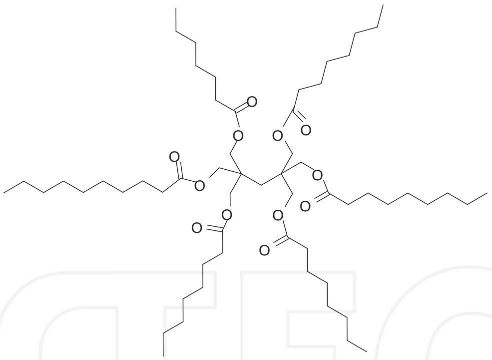


Figure 30. Di PE Esters

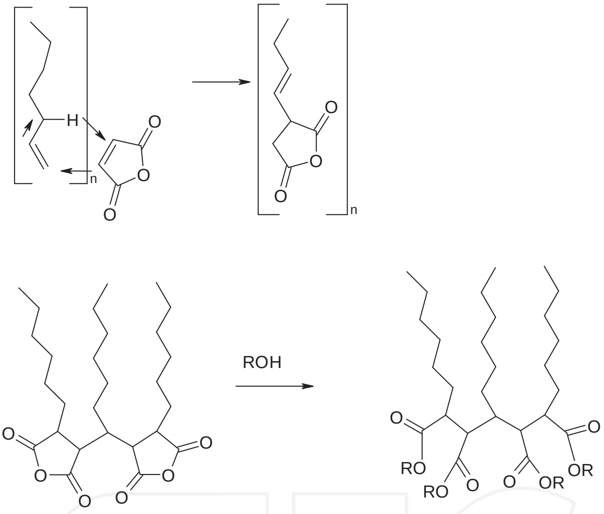


Figure 31. Complex Ester Formation by Ene-Reaction Sequences

Complex Esters from those structures are widely used to improve the additive solubility and performance. Their structure with shielding the carboxylic groups causes less aggressiveness toward sealings.

7. Structure activity relationship in esters

Esters are prominent representatives of lubricants where the chemical structure promptly leads to a specific tribological activity. However, if a tribological acitivity is demanded, the specific construction of esters may offer the solution.

7.1. Polar acitivity

Esters are polar by their nature due to the central element where a carboxylic acid tail binds toward an alcohol. Polarity gives some advantage but also disadvantage in the case esters are used. In general, esters enhance the solubility of functional additives and keep them away from fall-out. Esters also enhance the cleaning of metal surfaces in operation, preventing a formulation by creation of sludge. Esters are, as a fact of their polarity, aggressive toward sealings with a general tendency to shrink them. Plastics and elastomers under bending are susceptible toward stress corrosion cracking if attacked by esters. Hence, stress-corrosion cracking has to be considered explicitly in the case if esters are used. Since hydrocarbons, like PAO have a tendency to swell elastomers, the addition of esters may counteract such that the effect is neutralized. As a fact synthetic oils based on PAO are additivated by addition of 10 or 20 % esters per weight to create this effect.

7.2. Low temperature (Pour point) properties

Di-Esters, e.g. DOA, DOS are very useful in temperature ranges that undergo -40°C. This effect might be explained by the lack of hydroxyl groups that might associate at low temperature via hydrogen bridging, but also as a consequence of the crystallization hindrance due to the spatial structure of esters which does not allow a dense crystal packing. In contrast, esters may be designed such that their low temperature properties are lost, just by changing their structure. Also, if the number of polar groups increase the tendency to molecular association increases, and hence the pour point rises.

7.3. High temperature properties

High temperature applications in the use of esters are achieved by

- Sterical hindrance of the ß-Position in the Alcohol
- Use of Aromatic Nuclei in the Ester structure

As a specialty esters may rearrange within their structure via a preferred six-membered cyclic intermediate that creates an alkene on one side and a carboxylic acid on the other side (Figure 32).

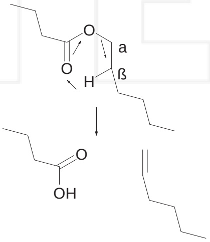


Figure 32. Decomposition of esters via cyclic rearrangement

Degradation of esters via such mechanisms takes place at ambient temperatures, e.g. by copper activation even at 70°C. The formation of carboxylic acids and alkenes may lead to corrosion and unfavorable deposits on metals. In the case of blocking the ß-position, as in the NPG and TMP esters, the cyclic rearrangement is blocked and the ester does not undergo the thermal degradation. Such oils are commonly used as turbine oils.

7.4. Side reactions

7.4.1. Hydrolysis

Ester Oils generally hydrolyze by interaction with water. The hydrolytic process is somehow the reverse reaction how esters form. The attack of water is enhanced if alkalinity is present but also acids may catalyze the hydrolysis. Common understanding states the attack of so called nucleophiles, like water at the carbonyl C-atom, followed by rearrangement sequences, leading to carboxylic acid and alcohols. (Figure 33)

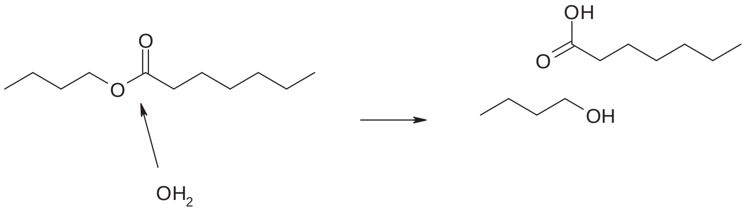


Figure 33. water-based cleavage of Esters toward carboxylic acids and alcohols.

Catalytic hydrolysis of ester oils also take place at metal surfaces, e.g. under tribological conditions. Formation of carboxylic acids may lead to corrosion as a consequence.

7.4.2. Biodegradation

Esters may decline under the interaction of bacteria and combust. Biodegradation is observed in the case of vegetable oils, e.g. glycerol esters, seldom on technical esters. In principal biodegradation cleaves esters, like water does to carboxylic acids. Biodegradation as a complex process does not stop there but lead to further products. Esters may oxidize as described in mineral oils and PAO at the organic tail. As a specialty they may undergo hydroxylation at a side position followed by trans-esterification to lactones. The lactone sequence is described already in the mineral oil section. Lactones are observed if esters, but also PAO are decomposed on iron at higher temperature. Infrared Spectra show absorption at 1800 -1760 cm^{-1} caused by lactone formation (see also chapter of antioxidants). (Figure 34)

7.5. Other esters

Esters may be created, as already mentioned by reaction of acids, in a different way as carboxylic ones. Prominent representatives are esters derived from phosphoric acid. Phos-

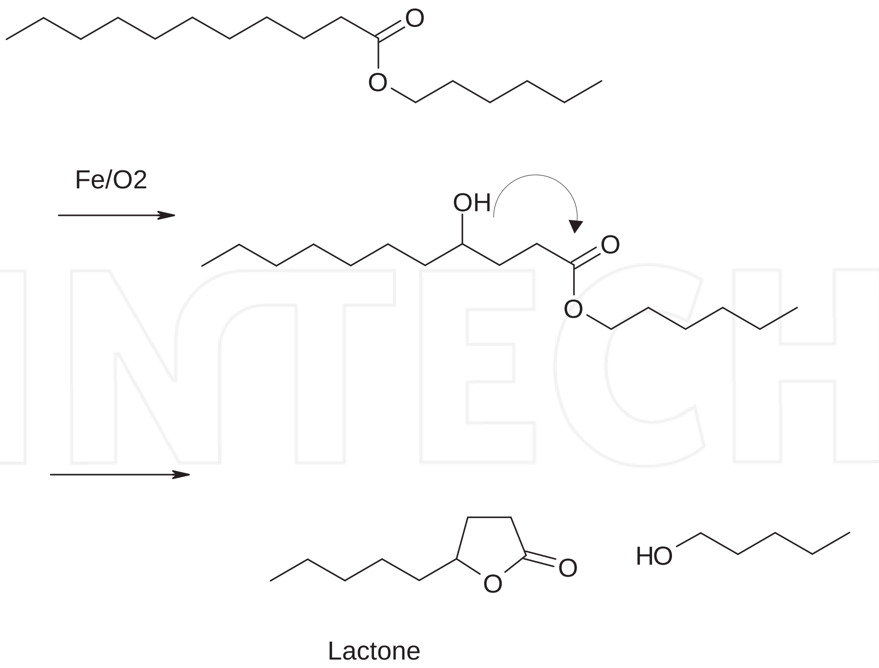


Figure 34. Lactone formation by side-chain oxidation of esters

phorous offers two main oxidation states (+III and +V) from which acids are derived. Depending on the oxidation state and the alcohols, phosphoric esters are different in use. Also phosphorous overtakes the role of anti-wear activity in such substances. [9]

A common representative is Trilaurylphosphite (Figure 35).

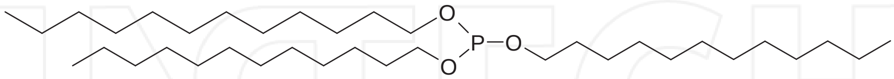


Figure 35. Trilaurylphosphite as a representative of Phosphinic Acid Esters

7.5.1. Phosphoric acid esters

Phosphorus in the oxidation state (+V) creates a plenty of variant Acids, such as Orthophosphoric Acid, Diphosphoric Acid, Triphosphoric Acids switching into each other. (Figure 36)

Phosphoric Acids are created by reaction of either phosphoric acid anhydride with alcohols or phosphoric acid derivatives, e.g. $POCl_3$ (Phosphorous-Oxi-Chloride) with alcohols. Aliphatic alcohols are in use, but also Phenols [10].

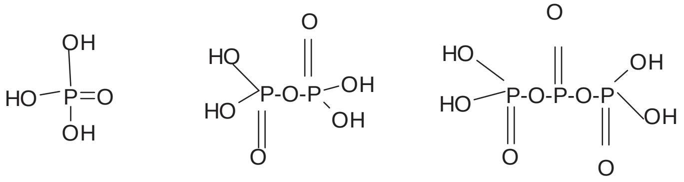


Figure 36. Representation of Phosphoric Acid Ester

7.5.1. Formation of phosphoric acid ester

Reaction of aliphatic alcohols, e.g. hexanole, with phosphorous pentoxide leads to hexylphosphate. In general some acidity remains due to insufficient esterifications. As a consequence those esters are often neutralized with amines to give amine phosphates. [10] (Figure 37)

Amine phosphates are widely used as anti-wear and anti-corrosion additives in all kinds of applications. Phosphoric Acid Esters derived from Phenoles are shown below. (Figure 38).

In a different reaction Scheme Phosphoroxichloride reacts with alcohols. Those reactions are convenient to come to aryl phosphoric acid esters. Arylphosphates are somehow used to come to non-flammable high temperature lubricants at temperatures beyond 200°C.

Apart from the use as base oil phosphoric esters like Tricresylphosphates, based on the reaction from Phosphorous Oxichloride with Cresol (Methylphenols) are common additives for lubricants in bearing industry.

Whilst TCP with the methyl group in the para-position is seen as hazardous, TCP isomers in the ortho is registered to be highly toxic. Also mixtures of TCP isomers, due to the content of the highly toxic ortho isomer are registered as highly toxic. TCP, despite its superior behavior as AW additive for bearing lubrication is restricted for use (Figure 39).

Use of Thiophosphorylchloride as precursor, the reaction with Phenole leads to EP/AW additives like Triphenylphosphorothionate (TPPT) and its derivatives. (Figure 40)

TPPT is widely used as non metal EP Additive as a substitute for Zn and Molybdenum Dithiophosphates. Due to its thermal stability, TPPT undergoes reactions at higher temperatures (>100°C). As to the fact that TPPT is ashless and starts to react at higher temperatures, it is a preferred additive in high temperature lubrication in combination with sterically hindered esters and PAO. In contrast to TCP, TPPT is not registered to be toxic, even more, the use of TPPT is allowed at level of 0.5% per weight for incidental food contact.

8. Polyglycoles (PG)

8.1. General

Synthesis of Polyglycoles starts from Epoxides, obtained by catalytic oxidation of Alkenes from Petrol- or hydrocarbon chemistry. Polymerization catalysed either by acids or alkaline result

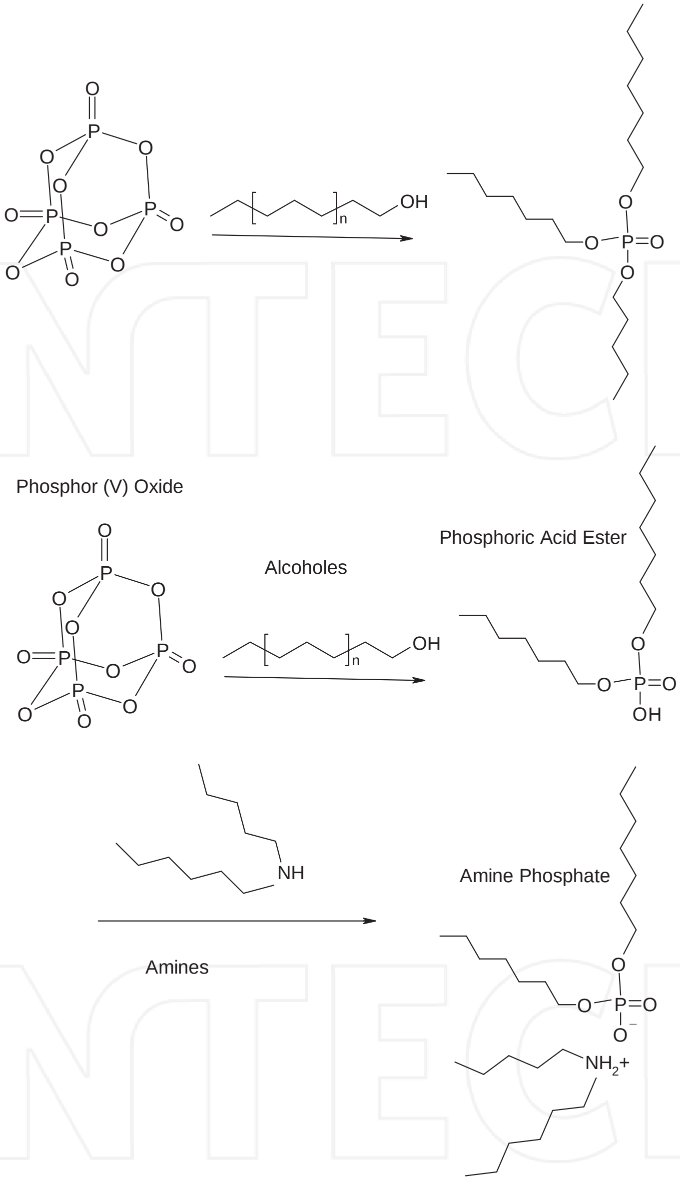


Figure 37. Phosphate Esters and Amine phosphates

in the formation of polyglycoles. In the case of alkaline catalyst, e.g. alkoxides on half of the PG contains a hydroxyl group while the end is capped by an ether function. (Figure 41) [1, 2, 7, 10]

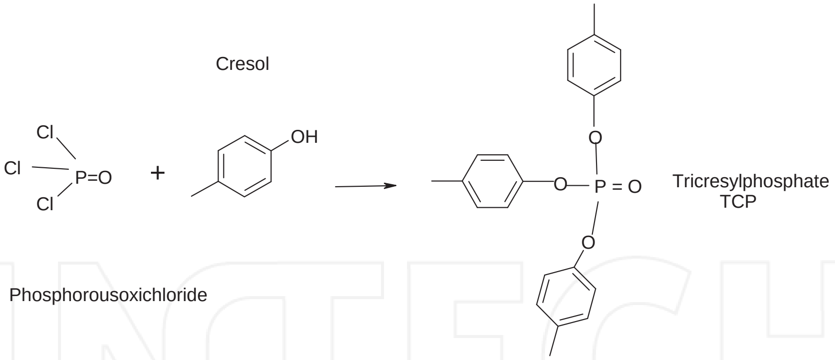


Figure 38. Arylphosphates derived from Phosphor Oxide Chloride Reactions

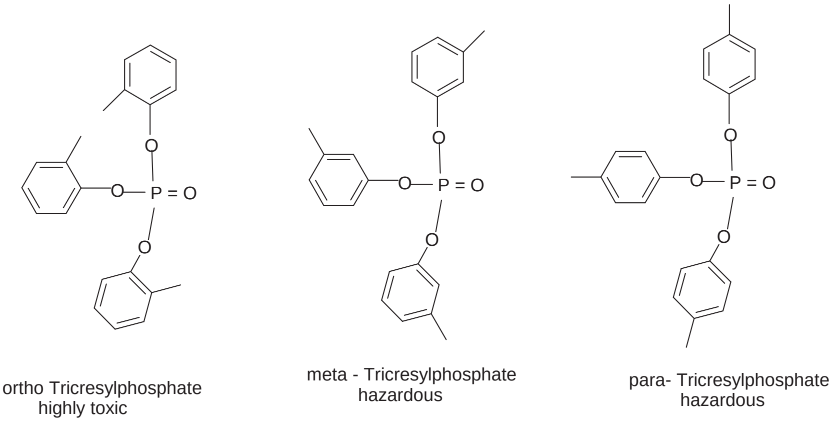


Figure 39. TCP and some isomers

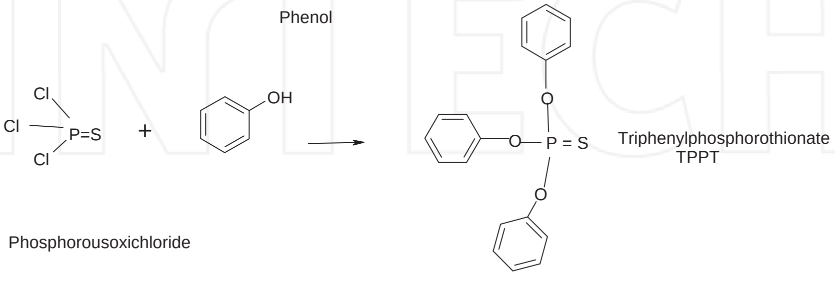


Figure 40. Synthesis of TPPT

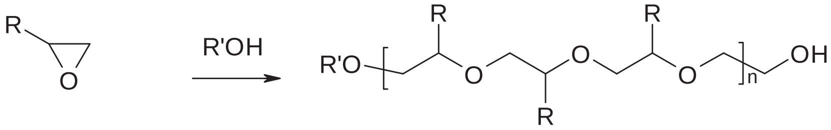


Figure 41. General Formation of Polyglycoles by alkaline catalytic polymerization of Alkene Epoxides

The choice of either different alkenes (Group R) or alkoxides (R′) leads toward a huge variety of PG, all of them with different chemical and physical properties.

Polyglycoles			**PEG**	**PPG-PEG**	**PPG**	**PBG**
Description	Ethyleneoxide Polymer			Mixed Polymers Ethylene/Propylene Oxide	Proyleneoxide Polymers	Butyleneoxide Polymers
Chemical Data						
Physical Data	Density	approx.	1	0.95-0.98	0.95-0.98	0.95-0.98
	Flashpoint	approx.				
	Pourpoint	approx.				
	Water miscible(%)		100	partially		
	Hydrocarbons		non miscible	partially	partially	partially
	Ester Oils		partially- full	partially-full	partially-full	partially-full
	Other PG	PPG	partially- full	partially-full	partially-full	partially-full
		PBG	partially- full	partially-full	partially-full	partially-full
Tribological Data	Viscosity, 40°C	Range	32 - 46	32- 100	32- 100	32- 100
	VT Coefficient	Range	180-..>200	180-..>200	180-..>200	180-..>200
	VP Coefficient	Range				
Others	Seals	NBR	compatible			
		ABS	compatible			
	Paintings		not compatible			

Table 1. PG and their data and applicability

Technically only a couple of variances are produced in a larger scale, such as:

- *Polyethylenglycoles (PEG)* where Ethylene Oxide is the starter
- *Polypropyleneglycoles (PPG)* where Propylene Oxide is the starter
- *Polyethylene- Polypropylene Oxide Mixtures* started from mixtures or Ethylene and Propylene Oxide

Table 1 offers an overview across the most common PG their data and applicability.

Single addition of long chain alcohols lead to the formation of fatty alcohol ethoxilates, for use as non-ionic detergants and dispersants in lubricant formulations, as silicone free defoaming and emulsifiers for lubricant formulae.

In general PG are not thermally stable by themselves and tend to decompose by emission of volatile degradation products, e.g. low boiling compounds, such as aldehydes, ketones, acids and others. Due to this behavior PG are used in high temperature applications where the formation of polymers and lacquers due to heat induced degradation of lubricants is not convenient, for example high temperature chain lubrication.

Presence of alkalines, such as overbased sulphonates, widely used in motor oils, as corrosion inhibitor lead to multiple cross-reactions with the decomposition products of PG (aldol reactions): Results of the aldole reaction are tars, sludge and slurries in the system. In consequence corrosion resistance of PG should always be carried out by acidic corrosion inhibitors, such as succinic-esters, Zinc-Naphtenates or Phosphoric partial esters. (Figure 42)

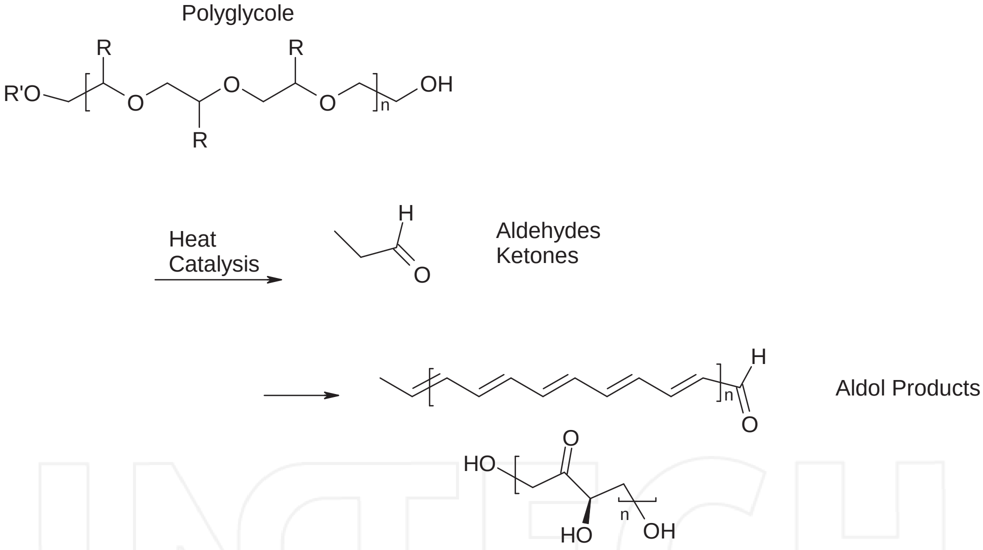


Figure 42. Aldole sludge formation in PG by use of alkaline

It has to be considered that PG are poorly soluble even amongst themselves and should be carefully checked. In general their solubility in mineral oils is poor, better in esters (depending on the structure). However, PG needs to be stabilized by antioxidants in order to prevent the early thermal degradation. By doing so, the application of PG are enhanced significantly, such, that even applications temperatures > 160°C are approached.

Convenient stabilizers are Phenyl-α-Naphtylamine, Phenothiazines or Alkyldiphenylamines. The amount should be adapted to the application.

In general PG offer very high viscosity indices, mainly above 160 (compared to mineraloils at ranges from 20 (alkylnaphtalenes), napthenics (70), paraffine base solvates (110), Poly-α-Olefines (140).

This high VI allows reducing the calculated viscosity in a given tribological application down to one or two levels. For example, if in a given application ISO VG 320 (320 mm^2/s, at 40°C) is calculated for a mineral oil with a VI of 100, this viscosity maybe reduced by use of a PG down to 220 mm^2/s or even 150 mm^2/s. Pour points are low in the case of PG, very often in the range of -30.. – 40 °C even. Reaching the Pour point, PG tend to form highly viscous liquid, however, crystallization-inhibited. As a fact of this huge increase, PG is not for use even at temperatures above the pour point. Realistically PG is not suitable in the vicinity of their pour point. Therefore they are not very good low temperature base oils compared, for instance, with esters or PAO fluids. Due to their chemical structure PG are somehow strong solvents, e.g. paintings. In the case PG is used, the system has to be checked whether the paintings of the tank, the machine housing or others are affected. Dissolved painting from the tank may cause severe problems in the oil circuit by blocking filters. Additive response, known from standard applications, may change seriously by use of PG due to their different solvent capability. Extreme Pressure Additives have to be checked in their performance if used in PG. Normally anti-wear and anti-friction additives may be decreased in their content.

As a fact of the presence of epoxides in PG and due to their cancerogenic potential, the use of PG formulations drops down.

8.2. Polyethylene Glycols (PEG)

Polyethylene Glycols are made from ethylene oxide by polymerization (Figure 43).

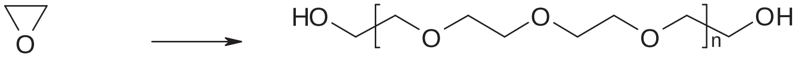


Figure 43. PEG formation and structure

PEG, apart from its wide use in cosmetic industry is completely water miscible. Due to its water miscibility PEG is only or sparingly soluble in hydrocarbons. Compatibility of the PEG with a given fluid has to be checked before use. PEG, as facts of its water miscibility will uptake water without separation. In case of the use of PEG in applications within water environment the water ingress should be checked carefully. Effects of water ingress are increasing threat of corrosion and thinning due to the mixture.

8.2.1. Use of PEG

Water miscibility is of use in non-flammable hydraulics in coal mining industries, but also in applications of pharmacy and food processing. In general PEG is allowed within the FDA regulation to be safe for incidental food contact. Due to the positive effect of sliding especially in worm gears PEG is somehow recommended for use in such applications. [2, 6, 7, 9]

8.3. Polypropylene Glycoles (PPG)

Polypropylene Glycols are made from Proplyene Oxide by polymerization by use of butoxides leading to a half ether structure (Figure 44):

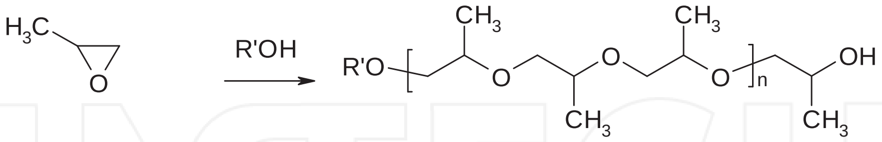


Figure 44. PPG Structure

Due to the additional methyl group in the structure water miscibility drops down (contrast to PEG) while the oil miscibility promotes. Also by choosing longer alkyl chain butoxides, PPG structures may be obtained with enhanced oil solubility.

While PEG is highly dissolved in water, PPG forms droplets immersed in the water. Due to this fact water separation out of PPG is difficult to achieve.

The partial solubility and immersion of PPG in water causes a very high fish toxicity. PPG should never be used in the case of its break out-in free lands or water

8.3.1. Use of PPG

PPG is commonly used as high temperature circuit oil, e.g. calandars, compressors, high temperature chain lubrication. All over PPG has to be stabilized by acid corrosion inhibitors, e.g. phosphoric partial esters and antioxidants like Phenyl-α-Naphtylamine [2] [3] [5] [8].

8.4. Polybutylene Glycoles (PBG)

PBG are seldom in use and made consequentially from Butylene Oxide polymerization by use of alkoxides, leading to half esters (Figure 45)

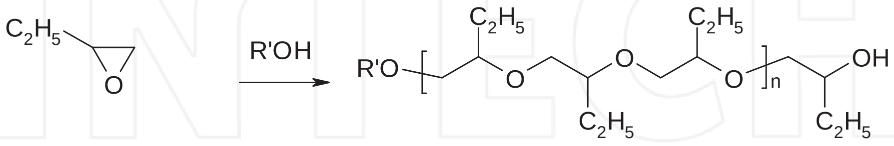


Figure 45. PBG Structure

8.4.1. Use of PBG

PBG is useful for enhancing the solubility of additives, boosting the viscosity index of mineral oil variants.

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8.5. Alcohole Ethoxilates

Alcohole Ethoxilates are formed by a cross reaction of epoxides with alcohols. (Figure 46)

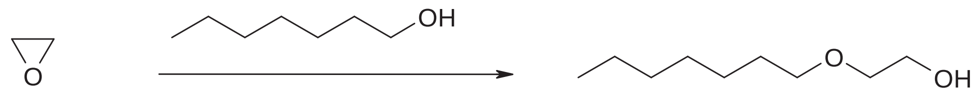


Figure 46. Alcohole Ethoxilates

The use of long chain alcohols leads to alcohole ethoxilates being used as non-ionic surfactants, emulsifiers and dispersants in multiple applications, e.g. hydraulic oils with dispersant capability, cutting fluids, and dispersants for applications where sludge is expected.

Due to their non ionic nature alcohole ethoxilates are widely compatible in lubricant formulations.

9. Siloxanes

Siloxanes (Silicone Oils) are common lubricants in multiple applications, such as food and pharmacy, but also in applications where special low friction properties are demanded [2, 3, 8]

In general silicones are the result of alkylchlorosilane hydrolyses [10] (Figure 47).

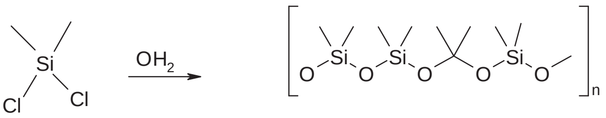


Figure 47. Scheme of Silicone Oil formation

Side groups are methyl, but also phenyl groups leading to polydimethylsiloxanes or polyarylsiloxanes. Mixtures of methyl and arylsiloxanes are in use with different spreading between in the side chain (Figure 48).

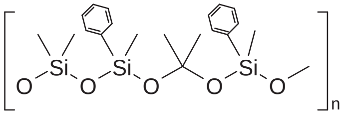


Figure 48. Polymethyl-Aryl Siloxanes

Siloxanes with different structures are not generally miscible amongst each other. Miscibility has to be checked carefully. As mentioned, siloxanes are widely used in lubrication technology due their exceptional properties concerning low friction capability, high temperature stability and low toxicity in various applications. Prominent applications are starter components in cars, valves in food industry, slow speed bearings and high temperature applications where arylsiloxanes are in use. Siloxanes creep widely across surfaces and may cause problems in coatings, lacquering and paintings.

10. Polyfluorinated Polyether (PFPE) base oil

PFPE Base Oil is created by polymerization of Perfluoroepoxids. Structure of PFPE is similar to polyglycoles but with overall substitution of hydrogen by fluorine [2] [3] (Figure 49)

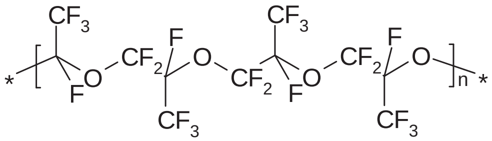


Figure 49. PFPE Base Oil

Due to the effective shielding of the C-O-C backbone in the structure of PFPE by the trifluoromethyl side chain group PFPE are completely insoluble in water, inert toward alkaline and acids and even oxygen.

PFPE Base oil is used for high temperature purposes and in the presence of aggressive media, mentioned above in junction with PTFE thickener. (Figure 50)

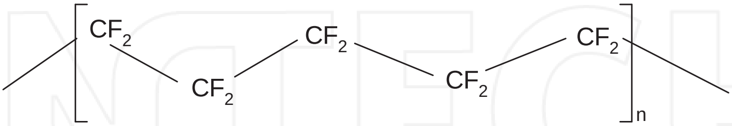


Figure 50. PTFE as thickener for PFPE

PFPE sparingly adheres to metal surfaces due to droplet formation. The low adhesion causes creeping across surfaces and mal-lubrication if the surfaces are not cleaned thoroughly. Creeping and low adhesion may cause low friction in certain applications. PFPE is insoluble in most of the common base oils. Use of PFPE hence is restricted to the fluorine group of base oil.

Inertness of PFPE and PTFE make greases suitable for incidental food contact lubrication.

High temperature combustion of PFPE may cause the emission of hydrogen fluoride and fluoro phosgene which makes PFPE formulations somehow corrosive, especially on steel alloy compositions. Due to this fact, the high temperature corrosiveness should be carefully taken into account in the case of PFPE use.

11. Additives

Additives in lubricants enhance base oil functionalities. Additive technology is in broad scale based on organic chemistry syntheses. From their origin they are found by chance, less than by a real scientific approach. Nevertheless, literature about their reactions is innumerous from the very beginning. [2, 3, 9]

Modern additive technology commenced in the early 20th century and has progressed continuously due to advanced organic chemistry syntheses. Upcoming modern spectrometry has been used to clarify their structures and their reaction at different metal sites. [2, 3, 9]

Beyond the basic and industrial reaction mechanism studies, mixtures of additives have been studied extensively by industry and science over the years. Such studies reveal the mechanisms of compatibility and incompatibility of additives acting together at a given application. [9]

For example a functional mismatch is caused by diverse demanding addressed to additives, e.g.: additives acting against corrosion may interfere with additives that have to prevent metal surfaces against fretting or welding.

Modern additive technology is inevitable to reach the “for-life” goal of modern technologies. As “for-life” might be understood in a different manner by users, additive packages are developed during the decades adapted to a given customer demanding. For example, the demanding to get automatic transmission gear oil performances is achieved by additive packages that may not fit for wind turbine or paper mill applications. Hence, additives and their mixtures have to be selected carefully for each purpose. [2, 3, 8, 9]

In general there are no rules up to now to predict additive performances at a given technical application. As a consequence formulations have to be tested in forecast extensively to assure its functionality. Such testing is addressed by international and national regulations.

Additives may cover a distinct structure-property relationship. Since there are no scientific rules declaring on how a chemical structure of an additive causes a function all variations in additives have to be validated by tests.

Additive technologies have been revised many times during their history, either due to a change in demanding or due to their toxicity. Toxicity is a severe problem in additive technology, since no one knows their real long term biological and ecological effects. [9]

Since the validation of those different chemical additive structures causes tremendous costs, it is a fact, that additive free technologies or additive technologies with marginal content level are favored as future solutions.

The following chapter addresses additive technologies concerning extreme pressure, anti-wear functions and also corrosion-protecting and antioxidants.

11.1. Extreme Pressure (EP) and Anti-Wear (AW) additives

11.1.1. General

Extreme Pressure (EP) and Anti-Wear(AW) Additives are functional chemicals in lubricants with the task to separate metal surfaces in the case of heavy loading and to improve their resistance toward wear in the case of oil film break in the contact [9].

Machinery elements that start to run or stop due to emergency show pronounced loading due to a lack of lubrication, e.g. the oil does not separate the metal surfaces and the protection of the oil film drops down. At that point EP and AW additives are supposed to jump into the arena by causing reaction layers preventing the metal from direct rupture or welding.

Their chemical structures are found by chance. For example observations during drilling and maching show that tools perform better if lubrication is carried out by use of sulfurized oils derived from vegetables, mixed and heated with sulfur.

Later on intense research the nature and reaction started including modern surface spectrometry techniques. The transformation of EP/AW additives as a function of the nature of the surfaces, their loading, contact geometry, temperature and their structure shows a clear picture of structure-activity relationship. Also additives perform as a function of their chemical structure, but also as a function of their solubility in base oil and as a function of other additives being present. In that sense, it is shown that additives either may prolong service life but are also capable to shrink life.

11.1.2. Sulfur additives

Sulfur acts as a powerful extreme pressure additive. The high reactivity, especially toward copper makes it unlike to use sulfur as element in tribology.

Sulfur embedded in organic framework acts as a powerful Extreme Pressure additive. Choosing appropriate organic structures the activity toward copper drops down. However, using sulfurized additives copper deactivation should be present anyhow.

Sulfur is added either by reaction of reactive organic precursors like alkenes and their derivatives by heating up with the element, or by polymerization sequences with activated sulfur precursors such as di-sulfur dichloride. Doing so, all kinds of unsaturated specie gives reaction products leading to sulfurized specie. Prominent representatives are reaction products of Isobutene with Disulfur Dichloride, or reaction products with terpenes (Figure 51) but also unsaturated carboxylic acid esters, like rapseed oil:

Sulfurized Additives (S-Additives) are often used together with phosphoric acid esters, since the synergistic between those additives are known from the past. Doing so, gear oils may contain S-Additives with amine phosphate esters. Also extreme pressure additives containing

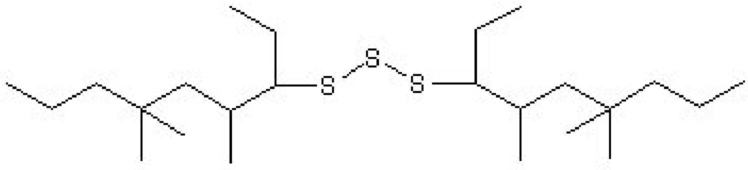


Figure 51. Didodecyltrisulfide as polysulfide representative

Dialkyl-Thiophosphoricacidesters are prominent representatives in sulfur additive chemistry. (Figure 52).

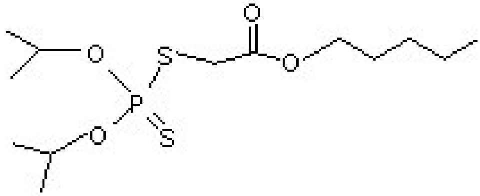


Figure 52. Thiophosphoric Acid Ester

11.1.3. Dithiophosphates

Zinc- and Molybdenum dithio phosphates (ZndtP- ModtP)

Zincdithiophosphate (ZndtP) represent a prominent group of EP/AW additives. They derive from the neutralization of Thiophosphoric Acids, obtained by ring opening of Phosphorous pentasulfide with alcohols, with Zn-Carbonate or Hydroxides. As a fact, the ZndtP differ strongly by their carbon-chain length. A couple of variants are achieved by choosing different alcohols in the ring opening sequence of Phosphorous (V) sulfide. From the structural perspective, ZndtP may be regarded as chelate complexes rather than a salt (Figure 53).

Molybdenumdithiophosphates contains a Molybdenum [μ-oxo] Core, distinct compared to ZndtP (Figure 54).

11.1.4. Dithiocarbamates

Similar to Dithiophosphates, Chelat Complexes from Zinc, Molybdenum but also Bismuth and others may be formed by reaction of Thiocarbamic Acid with the metal precursors. Dithiocarbamic Acid is synthesized via addition of amines to Carbondisulfide. By varying the chain length of the amine different dithiocarbamates are achieved (Figure 55 and Figure 56):

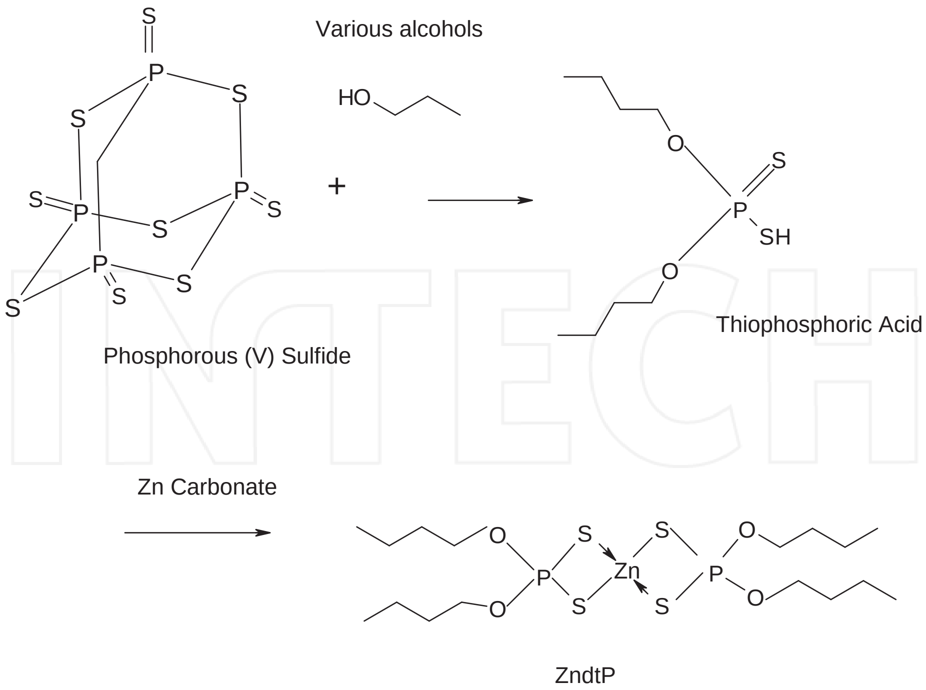


Figure 53. ZndtP from neutralization of Thiophosphoric Acid with Zn Carbonate

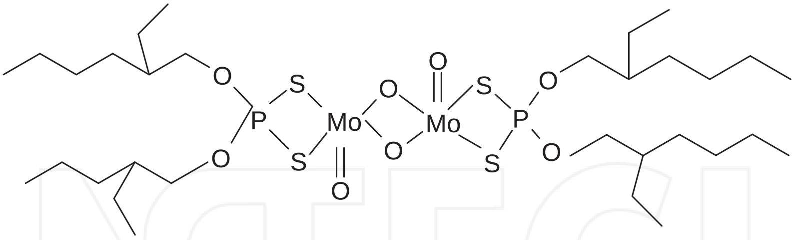


Figure 54. Molybdenumdithiophosphate

11.2. Corrosion protection

11.2.1. General

Within this chapter only iron as a chief element in technical application is considered.

Generally metal surfaces tend to corrosion if water, oxygen and probably salts, like sodium chloride are present. Corrosion may take place either by cathodic reduction of oxygen or by

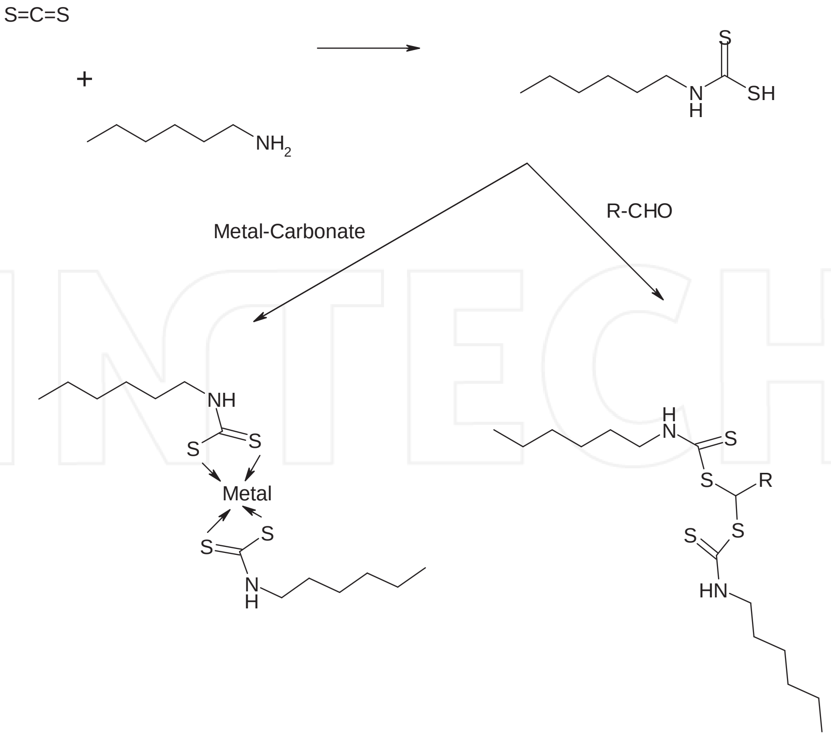


Figure 55. Syntheses of dithiocarbamates

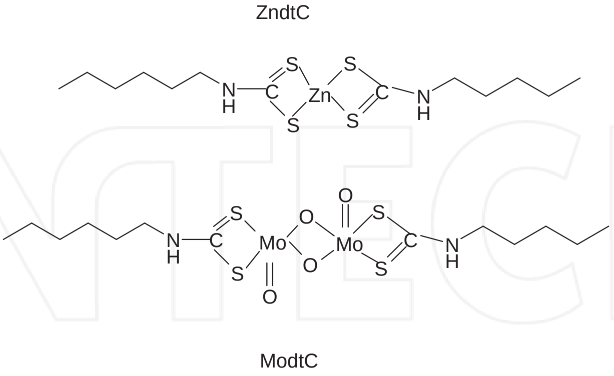


Figure 56. Zincdithiocarbamate (ZndtC) and Molybdenumdithiocarbamate (ModtC)

anodic oxidation of the metal. Charges, either positive (anode) or negative (cathode) pass the surface layer. [2, 3, 9]

Charge transport from the metal toward the outer region is hindered by the surface potential (over potential). Thus, corrosion processes have to overcome this potential and start after a certain induction period. Once, if this potential has been overcome the corrosion starts without hindrances by successive material transport. Materials transport ends up in a drastic change of the surface, mainly accompanied by a loss.

For iron as metal, the transport of the metal ends up in a flaky layer (Rust) that permits water and oxygen to penetrate. Due to this effect the rust process ends up in a total damage of the metal, especially in an environment that boosts corrosive processes.

Counteracting corrosion, the initial processes of charge transportation have to be blocked. Doing so, the over potential, e.g. the natural barrier of charges passing the surface has to be increased by creating additional layers on the metal surface (Passivation) or by creation of stable, insoluble complexes, formed by interaction of the surface atoms with a complex builder.

Passivation of iron surfaces and enhancing the over potential is achieved by deposition of chromium layers that cause a thin and gas-dense closed layer on the metal. Thus, chromium is a powerful inhibitor toward corrosion processes. As the charge transport phenomena occurring on iron surfaces are cathodic or anodic and vice versa, this process could also be stopped by offering an anodic victim like a zinc coating.

Additives that create a corrosion protection are in general dissolved in a carrier base-oil that spreads over the surface. Due to their adapted functional groups a physical binding toward the surface starts to create a layer. In order to create an appropriate corrosion protection this layer has to be packed dense to avoid the penetration of water and oxygen. This is realized by strong dipolar groups and oil soluble tails with a marginal demand in lateral spacing, e.g. long, - unbranched alkyl chains.

Else, passivation also is achieved by placing insoluble complex builders onto the iron surface, like phosphates are. Iron phosphate builds up a close dense insoluble layer on the surface.

Restriction of iron phosphate is indicated by the fact that, under certain conditions, phosphates start to get reduced forming posphanes. Phosph4anes strongly affect metals due to segregation of phosphorous at grain boundaries and releasing hydrogen into the metal. Hydrogen is detrimental to the microstructure by inducing, e.g. hydrogen enhanced local plasticit (HELP) or hydrogen induced cracking (HIC). Presence of phosphanes by reduction of phosphates takes place in acidic and reducing environment, e.g. presence of hydrogen sulfide, chlorides and others.

The following chapter will show some of the most prominent representatives of corrosion protectors.

11.2.2. Sulfonate-chemistry

General

Sulfonates derive from sulfonic acids by neutralization with alkali, earth alkali –metals but also with metals from the transition group, for example zinc. Principally each sulfonic acid may be neutralized. In technical applications mainly alkyl benze sulfonic acids and dodecylsulfonic acid are neutralized. Production starts from alkenes out of petrol chemistry by addition sulfuric acid or SO_3.

Neutralization with either sodiumhydroxide, Calciumcarbonate, Magnesiumcarbonate or Bariumcarbonate leads to sulfonates: A = Sodiumsulfonate, B = Calciumsulfonate and with excess Carbonate to over based Calciumsulfonate (B’), Magnesiumsulfonate (C) and Barium-sulfonate (D) (Figure 57).

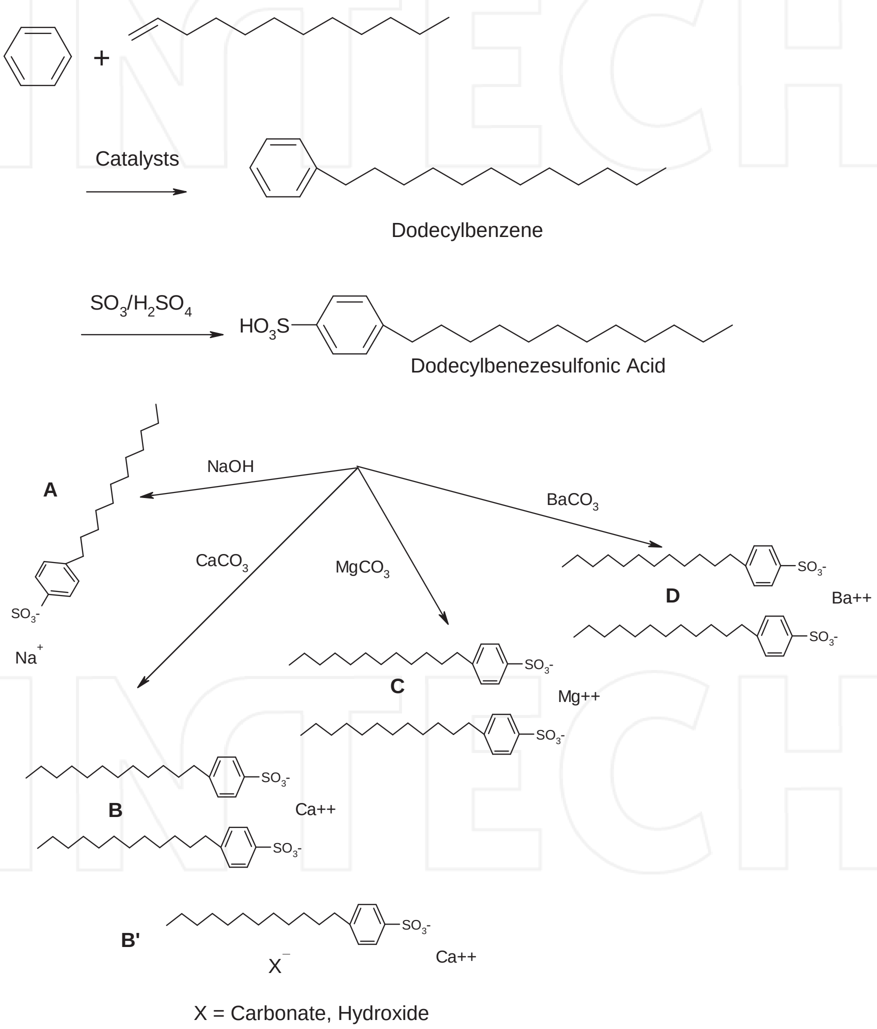


Figure 57. Sulfonic Acids and their Salts

11.2.3. Carboxylic acids and derivatives

Carboxylic Acid and their derivatives, e.g. esters may act as metal corrosion protectors. While carboxylic acids are supposed to cause corrosion, some of them prevent. Rust preventing carboxylic acids are derivatives from α-Aminoacids, like N-Oleylglycine. (Figure 58)

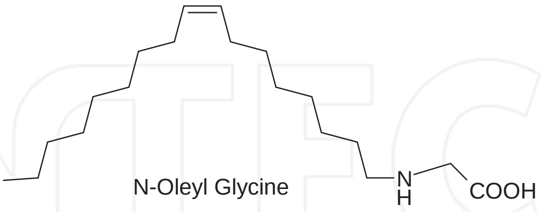


Figure 58. N-Oleylglycine

N-Oleylgylcine acts as powerful emulsifier, even at low dosage. Rust protecting is due to the spread of water in the formulation over a big volume. N-Oleylglycine, even at low percentages also counteracts with EP/AW additives, driving their activity down.

Carboxylic Acids, derived from Phenoles such as Nonyl-phenoxiaceticacid is a non emulsifying corrosion protector but under prohibition, due to its irritating effects (Figure 59).

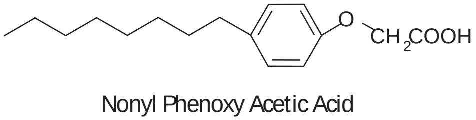


Figure 59. Nonylphenoxyaceticacid

Succinic Acid Derivatives, such as Succinic Half Ester of Octanole are powerful metal protectors, but also strong counteracting with EP/AW additives. Synthesis is carried out by reacting succinic acid anhydride with alcoholes (Figure 60).

Carboxylates, derived from neutralizing carboxylic acids with transition metals like Zinc, Lead, Bismuth lead to corrosion protection. Common acids are Napthenic acids or medium chain carboxylic acids like octanoic acid (Figure 61).

11.2.4. Amine phosphate esters

Amine Phosphate Esters may act as anti-corrosion additives in addition to their anti-wear properties. Due to their synergistic properties and due to the fact, that certain amine phosphates are allowed as additives for incidental food contact, they are often found in all kind of lubricants (Figure 62).

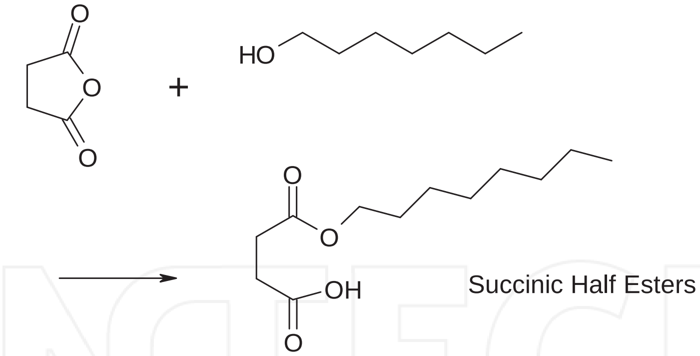


Figure 60. Succinic Half Ester

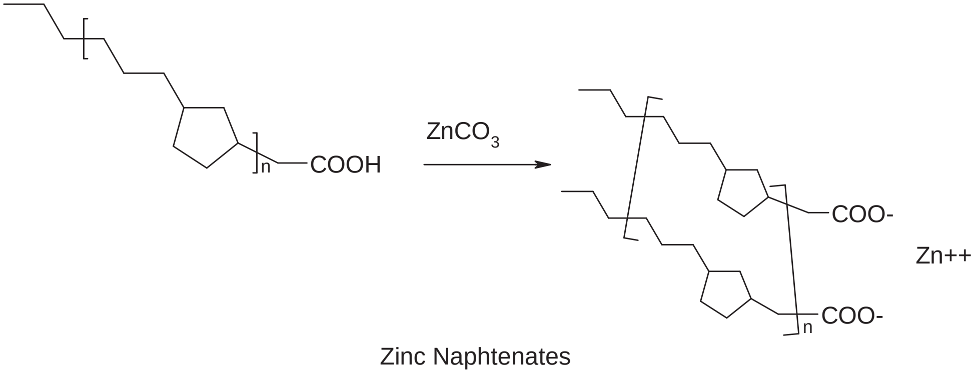


Figure 61. Zn (Bi) Carboxylates (Napthenate and Octoate)

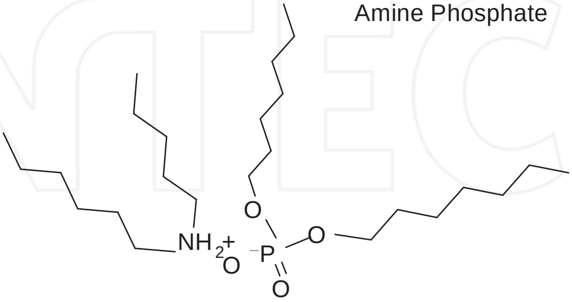


Figure 62. Amine Phosphate Structure

Amine Phosphates are powerful activators of copper and zinc and cause leaching of those metals from brass cages in bearings. Adding Amine Phosphates copper deactivators like benzotriazoles have to be present (Figure 63).

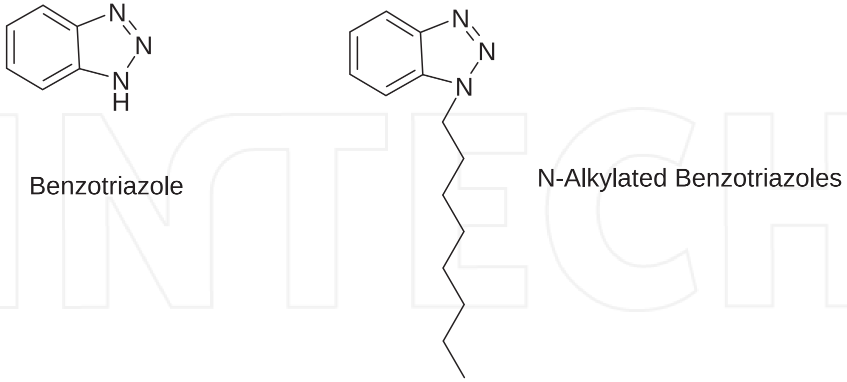


Figure 63. Benzotriazole and N-Alkylbenzotriazoles as Cooper Passivators

11.3. Antioxidants (AO)

AO prevent lubricants from oxygen attack. Oxygen is, by nature, a diradical that undergoes several transitions. Electron uptake from metal surfaces by a cathodic transfer, leads to varieties of activated oxygen specie, powerful attacking hydrocarbon sites by abstraction of hydrogen, leading to peroxides, and carbon radicals. The carbon radical itself starts to stabilize by abstraction of hydrogen leaving an alkene as new product [10]. (Figure 64)

Due to radical stabilization the new formed alkene starts to continue the oxidation by sequential abstraction of hydrogen, forming di-, tri- and polyalkenes, but also benzene rings. Apart from the hydrogen abstraction, also oxidation takes place by attacking carbon radicals by oxygen. At least the products created by such this procedures are carbonyl compounds, e.g. alcohols, ketones, aldehydes, carboxylic acids and sometimes esters. PAO oxidation at metal surfaces, e.g. iron beyond 120°C results in the formation of lactones (esters that come up by internal reaction between an alcohol group and terminal carboxylic group) (Figure 65).

Hence oxidation sequences dramatically change the original hydrocarbon chain. If once started it is self accelerating till new, different and stable products are reached. Oxidation is unselective and takes place everywhere in the chain. Hence, plenty of products are formed by radical oxygen assisted processes.

Antioxidants in general prevent the base oil, quenching the oxygen attack by formation of stable radicals. Stabilization of the radicals is realized by a delocalization of the persistent AO radical, created by oxygen attack due to the presence of aromats in the structure (Figure 66).

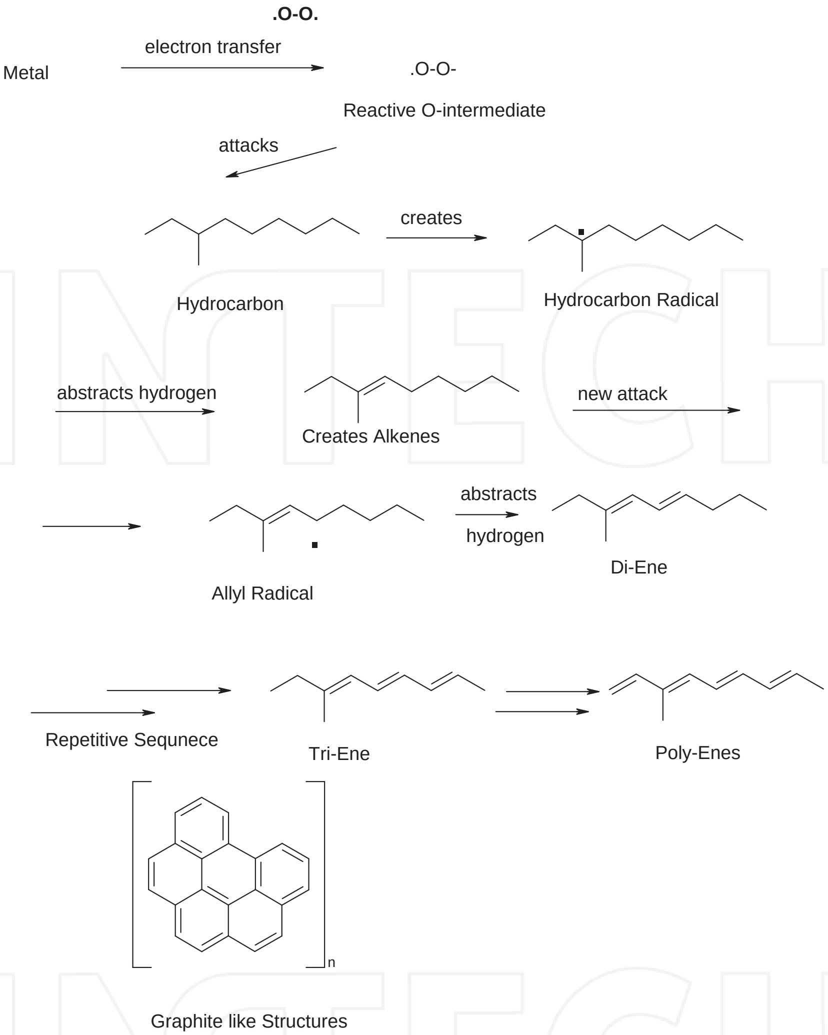


Figure 64. Oxygen – Hydrocarbon Attack sequence

The AO radical subsequently stabilizes to form new products like quinones. The quinone structure may form a dark colored charge transfer complex with the original antioxidant. Very often this causes strong discoloration of AO stabilized lubricants since the charge transfer complexes are very intense in color. Sometimes, for example in the case of polyurea greases, such charge transfer complexes may interfere with the grease structure in terms of solidification.

Persistent radicals formed by AO are dangerous in some cases. In the case of their accumulation in the system they are able to boost oxidation rather than to prevent. Dosage of AO hence

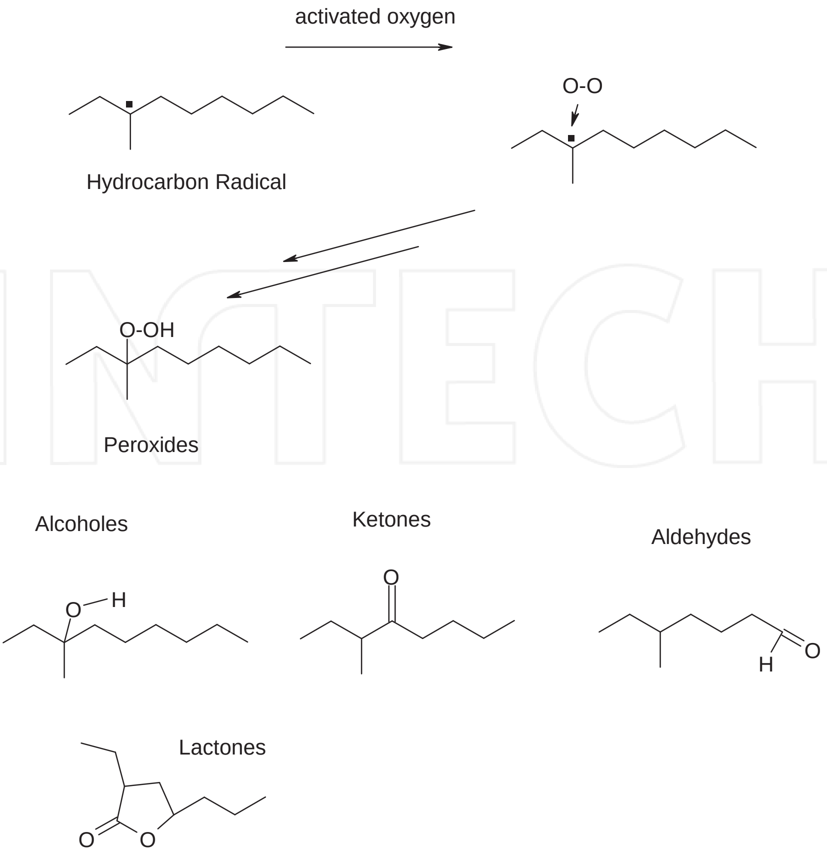


Figure 65. Oxidation sequence of Hydrocarbons toward carbonyl compounds

should be carefully tested. Formation of either charge transfer complexes or oxidation products by the presence of AO may cause increased formation of sludge in the lubricant if the dosage balance is not appropriate.

Nearly all AO contain aromats as a base principle. Prominent AO candidates are Butylhydroxitoluene (BHT) (A), Alkyldiphenylamine), Phenyl-α-Naphtylamine (PAN) (C) and various others (Figure 67).

12. Greases

12.1. General remarks

Greases are defined apart from their chemical composition by the manufacturing processes. Thickener and oil, getting heated by stirring, start to dissolve. Getting cold, the process of

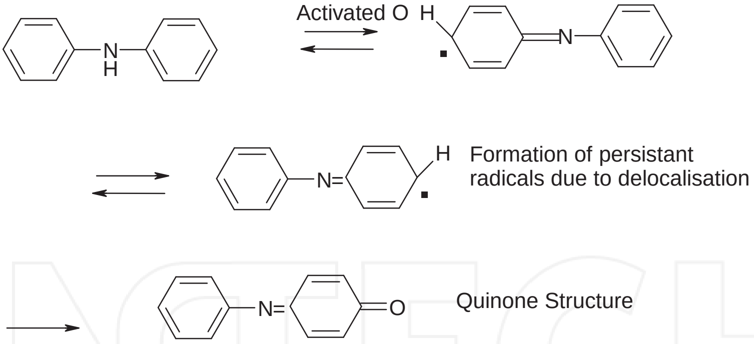
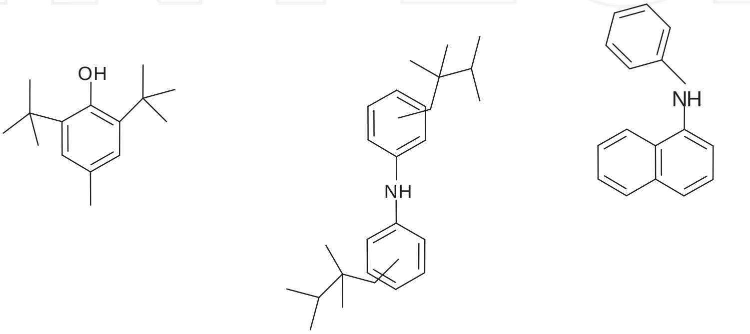


Figure 66. Principal delocalization of radicals created by oxygen attack.



A

Butylhydroxitoluene
BHT

B

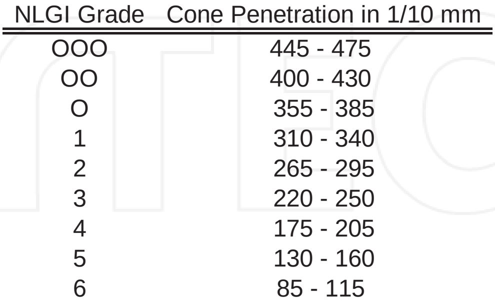
Octyldiphenylamine

C

Phenyl-α-Naphtylamine
PAN

Figure 67. Structures of AO: (A): BHT, (B) Alkyldiphenylamine, (C) PAN

stirring leads to a raw material where amorphous and crystalline structures are merged. The amount of crystals and amorphous materials depends on the nature of the raw materials on the one side and on the rate of heating and cooling on the other side. Rapid cooling causes homogeneous and amorphous structure, as particles are not able to grow to a large size. The raw grease, as effect of the mixture of solid structures has to be homogenized carefully. Homogenization leads to a smoothened appearance of the grease with a scale distribution of thickener particles as effect of the cooling process. Slow cooling generally leads to material with large sized particles as an effect of nucleation and crystal growth. Oil embedding in such structures is different due to the solid structure of the thickener. Stiffness and flowing capability may change as an effect of the merged structure. Greases, even in the case of identical chemical composition may differ significantly by their manufacturing process. Stiffness of greases is defined by the NLGI grade declaration, measured by penetration of standard cone into the grease. The deeper it’s penetration the more liquid the grease will be. To get a constant value, the grease is worked by 60 strokes, then tempered to 25 °C and measured by cone penetration. NLGI grades are presented in table 2: [3]



NLGI Grade	Cone Penetration in 1/10 mm
OOO	445 - 475
OO	400 - 430
O	355 - 385
1	310 - 340
2	265 - 295
3	220 - 250
4	175 - 205
5	130 - 160
6	85 - 115

Table 2. NLGI Grades of Greases

12.1.1. Oil bleeding

Within grease the base oil is bound in different states. Some oil is weakly bound to the thickener nuclei and gets easy released. Oil, bound in micelles and large structures with van-der-Waals and dipolar bonding releases less. Oil release takes place due to centrifugal effects in speeding machinery elements, e.g. bearings, creeping across walls e.g. sealings enhanced by temperature. Successive loss of oil in grease may lead to its change in performance, accompanied by a malfunction. Oil bleeding is measured with different techniques. Within the most popular one the grease is sat on a sieve and pressed by a static load through it a given temperature. Bleeding is measured as a function of time. For bearings the long term bleeding rate should be less than 5 % per weight in 7 days. [3]

12.1.2. Dropping point

Greases - if heated - start to get liquid at a certain point. Molten grease will leak out at sealing edges and may cause a malfunction of the grease. For bearings the thumb rule is given by dropping point minus 50 °C as the upper point of applicability. [3]

12.2. Soap based greases

Greases are soft solids, created by a thickener that gelates in suitable base oils. Gelling takes place by intense mixing of thickeners with the base oil, often accompanied by heating till the gelation is reached [3]. (Figure 68):

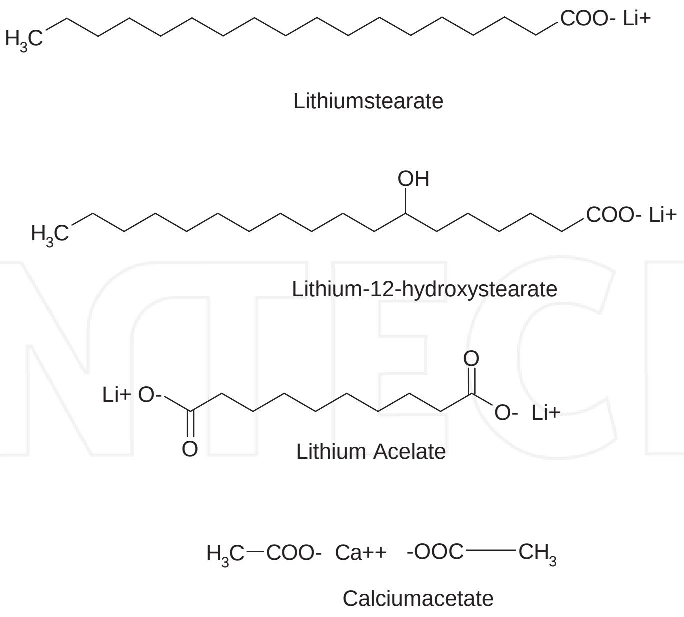


Figure 68. Prominent representatives of thickeners for grease production

Thickeners are all substances where gelling in the base oil is achievable. Prominent representatives are lithium and calcium salts of carboxylic acids, for example Lithium Stearate, Lithium-12-hydroxistearate, Calciumstearate, Calcium-12-hydroxistearate but also Calciumacetate. Lithium Complex Greases are created by the co-existence of lithium-12-hydroxistearate with dicarboxylic acids like Acelaic or sebacaic acid.

Calcium Complex Greases are composed by calcium acetate, Calcium Stearate and calcium-12-hydoxistearate as thickeners.

Salts of magnesium, barium and alumina are used for grease production but to minor extent.

12.3. Di and Polyurea greases (PU-greases)

Urea Greases are often called PU-Greases in technical language.

Urea structures are realized by adding amines to isocyanates (Figure 69):

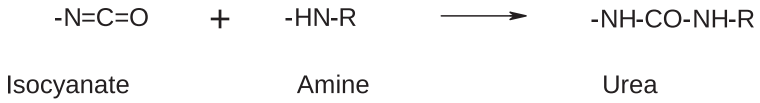


Figure 69. Urea Formation

Di-Urea grease production take aromatic Isocyanates, like Diphenylmethane Isocyanate (Methylenbisdi-isocyanate, MDI) reacted with various aliphatic amines, like Cyclohexylamine, Alkylamines from C8 to C18 chain length.

Synthesis of the thickeners and grease formation is carried out simultaneously. Ester Oils, like trimellitic acid esters facilitate the synthesis by solving the precursors before the reaction takes place (Figure 70):

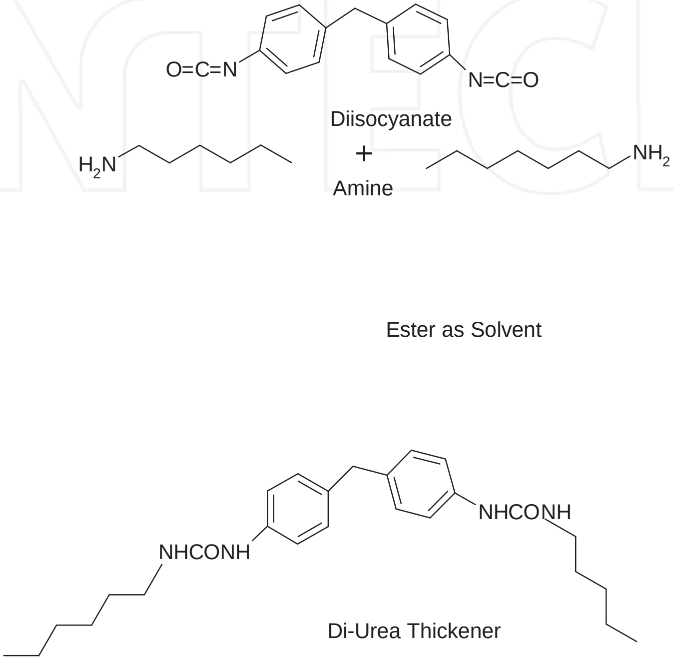


Figure 70. Formation of Di-Urea Grease

Tetra- and polyurea Greases are created by mixing Di-Isocyanates like MDI or Toluenediisocyanates (TDI) with diamines, like ethylene diamine and monoamines, like Octadecylamine in suitable base oils (Figure 71):

Urea Greases offer plenty nitrogen-hydrogen bridges within their structures. Concordant with the presence of temperature resistant aromatic nuclei and in junction with high temperature resistant base oils, they represent the group of high temperature grease “per se”. As to the high variability of taking precursor amines, PU greases offer the possibility to adapt the grease to a given application, much more than soap greases do.

Polyurea Greases that start from tallow amine, tolyenediisocyanate and ethylene di-amine are in accordance with the US FDA regulations H1 (incidental food contact) if H1 base oil (like

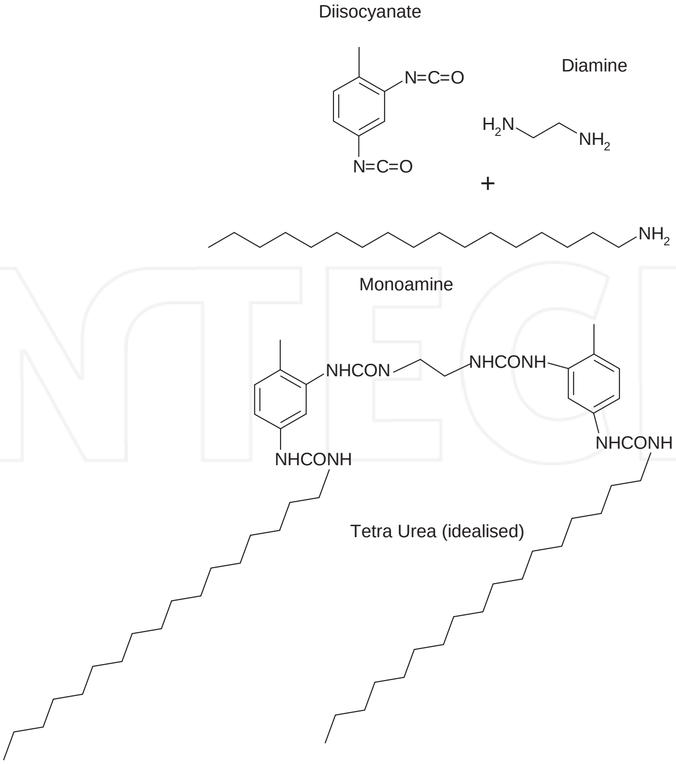


Figure 71. Formation of Tetra-and Polyurea Greases

white mineral oil or PAO) is used. Also the modern EU REACH regulations are valid for polymeric structure.

As the polymeric degree increase, the thickeners may get insoluble and crystalline. Greases are no longer available due to this because a lack of gelling. Due to this fact, variances of PU Greases are restricted.

MDI and especially TDI are ought to be highly toxic by inhalation. Production of PU greases have to take care, than none of the precursors are free in air, nor present in the grease.

Some isocyanates tend to polymerize during production, rather than to react with the amine, especially at the end of the syntheses. Polymeric Isocyanates may remain in the grease and cause severe toxicitiy, especially if the greases are up -heated.

PU Greases are very sensitive toward ingress of OH – groups (e.g. alkalines, water, polyglycoles) as the nitrogen-hydrogen bridging is disturbed. Ingress of such pollutants may cause a change in consistency. Polyglycoles, if heated emit aldehydes that interfere with the NH groups in PU greases. This reaction may end up in making the solid PU liquid! PU greases thus should be monitored to those facts (Figure 72):

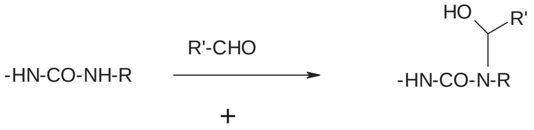


Figure 72. Reaction of PU Grease and Aldehydes

Other incompatibilities of PU Greases arise from mixtures with clay thickeners due to the presence of either OH (Si-OH) or NH functional groups if the clay is modified by organic amines.

12.4. Other thickeners

12.4.1. Clay greases-structure and use

Clay Thickeners derive from Alumina-Silicates. Due to their high surface and modification they are suitable for gelling base oils, e.g. Esters, Napthenic Base Oils, sometimes Silicones and Phosphoric Acid Esters. Clay Structure is generated by tetrahedral arrangement of Silica with insertion of alumina (see figure) in layers of approximately 1-2 nm distance. Water and other cations may be inserted in the space in between the two layers. Other cations, e.g. magnesium, may also be inserted in between. [3] (Figure 73).

Gelling takes place by adhesion and insertion of organic molecules in the structure, assisted by polar additives like propylene carbonate. Clay grease is produced by multiple milling the clay with appropriate base oil by addition of water suppliers like glycerol or Propylene carbonate at temperatures below 100°C. If water is lost the structure may break down during the manufacturing. Doing so, the grease produced is a buttery solid with no dropping point.

12.4.2. Use of clay greases

Clay greases are used for applications where the grease should not move out and for special high temperature applications, e.g. cement industry in slow motion bearings. Due to the inertness of the inorganic structure toward alkaline and acids, clay greases are preferred in applications where water, alkaline and acids are present, e.g. chain or bearing lubrication with such ingress. Clay is declared as safe for incidental food contact and allowed for lubricants in food industry (USDA H1 regulated) in junction with base oils like white mineral oil, PAO or esters that are allowed for this purpose.

12.4.3. Restrictions in the use of clay greases

Restrictions for the use of clay greases are the presence of Lithium, - Calcium or Polyurea Greases that may interfere with the hydrogen bonding of the clay structure. Mixtures of clay

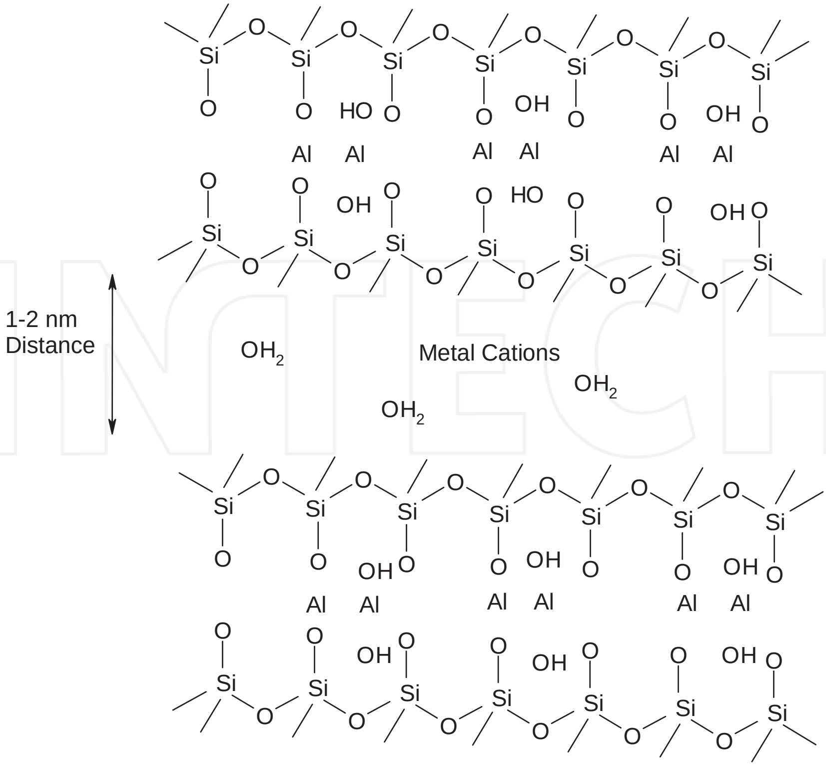


Figure 73. Estimated basic structure of clay

and conventional greases should be evaluated very carefully. Clay greases are restricted in bearing lubrication strictly due to over rolling speed. In general the speed factor is limited to ndm (Average of outer and inner diameter of the bearing times the speed (revolution per minute)) of 100.000. Only slow moving bearings could bear clay lubrication.

13. Silica

Silica is in use for thickeners as amorphous material, obtained by flame decomposition of Silica Tetrachloride (Figure 74):

Silica, due to its powerful surface activity may be used as powerful thickener in low percentage for each kind of base oil. Greases obtained by mixing silica with base oils are transparent. The inorganic structure causes no dropping point for such greases. Silica Thickened greases cause steep and irreversible thickening by heating up due to the increase of internal hydrogen bonding. They never should be in use for high speed and high temperature rotating bearings,

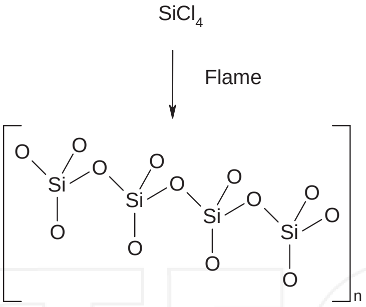


Figure 74. Principal formation of amorphous SiO2 by flame combustion

since they block their motion. The ndm (Average of Bearing Size times revolution per minute) is restricted to 100.000, hence slow motion. Due to the possible entrance of water, silica thickened grease is poorly water stable and should not be in use in applications where water (especially hot water) and alkalines are present. Alkalines react with silica to silicates, starting its degradation.

14. Polytetrafluoroethylene (PTFE)

PTFE is a convenient thickener in base oils for the purpose of incidental food contact, low friction properties and high temperature. The fluorine entity causes low activity toward oxygen. PTFE Grease is used in oxygen application (valves under oxygen impact), especially with PFPE.

15. Conclusion

Tribology is highly guided by physics and chemistry of the lubricants. Functionality of lubricants is given by their physics and their chemical structure. Modern understanding of lubrication hence allows the construction of lubricants appropriate to a given application to a certain extent. Under the conditions of full lubrication their physical properties, e.g. viscosity, viscosity-temperature and viscosity –pressure properties dominate over the chemical structure. Under such circumstances, the lubricant takes away heat (cooling function) from the mating contacts, but also wear and debris (cleaning function). Within a running – in period some reaction layers of lubricant constituents (additives) may be created. Basically those layers stay constant over time and do not change. On the other hand, if lubrication undermines the given roughness’s of the mating partners, or overtakes the natural temperature limit given by the restrictions of organic chemistry (e.g. temperatures beyond 150°C), chemistry starts to perform reaction scenario highly related to the nature of the chemical structure of the ingredients in the lubricant. The basic reactions found here are radical reactions, as a fact of the presence of oxygen and iron. Within such radical reaction sequences hydrogen is abstracted, alkenes and alkynes are formed and their oxidation products (aldehydes, ketones, carboxylic acids and their derivatives). Additives, in general improve the lubricants by expanding their limits.

In general, lubrication fundamentals in tribology have overcome the alchemy of the past by numerous efforts taken by the scientific community.

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