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Grease-oil compatibility in tribological applications – Supergrease

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Master Thesis in Materials Chemistry
Chemical Engineering
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Performed at ABB AB Corporate Research in Västerås, Sweden

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Master's Thesis in Materials Science
30 ECTS credits

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Abstract

A common reason to malfunctioning of tap-changers is wear of tribological contacts. In order to reduce wear, it would be desirable to lubricate the contacts. Since the tap-changer is working in transformer oil, it is necessary that whatever lubricant is added is compatible with transformer oil. In this work, the compatibility of lubricating grease in transformer oil has been investigated. A wide variety of greases have been studied in order to understand what chemical properties that is desirable for this type of application. Compatibility tests of grease in transformer oil at 80°C have been performed. A ball-on-plate tribological test was performed on the successful grease candidates from the compatibility test. The successful candidates were also exposed to a vapour-phase dehydration process, in order to guarantee that the lubricant could be added to the transformer before delivering the tap-changer to clients. Finally, the transformer oil samples were analysed with FTIR, tan delta and surface tension measurements to evaluate if the greases had, by any means affected the oil. One polytetrafluoroethylene (PTFE) grease was successful in all tests and proved that introducing lubricating grease in the mechanical contacts could decrease the coefficient of friction.

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Acknowledgements

This master thesis project has truly been a great experience and it would not have been possible if it was not for my supervisor Åke Öberg at ABB Corporate Research. Thank you for your encouragement and support throughout the project.

I would also like to send out a warm thank you to Anna Andersson for your kind support and guidance. Thank you Nina Aminlashgari and Christian Mille for helping out in the laboratory.

Thank you Tommy Larsson, Jean Mathae and Per Krainer at ABB Components Ludvika for believing in me and for helping me throughout the whole process. Thank you to Linda Ferm at the oil laboratory in Ludvika for helping me with the oil analysis.

I would also like to send a big thank you to Johan Leckner, Johanna, and Claire at AXEL Christiernsson AB for all help and expertise in the field of lubricating grease. Thank you so much for taking your time and for answering all my questions.

Thank you Åsa Kassman Rudolphi, Elin Larsson and Jonna Lind at Uppsala University, for having patience with me and helping me out with the tribological tests.

Thank you to Rene Abrahams and Thomas Norrby for having me visit at Nynäs, to learn more about transformer oil.

1. Introduction

Power plants are often situated in distant locations, for example the water power plants located in northern Sweden. In order to distribute electricity long distances to the big cities, high voltage power systems are put in place. But the power lines in the cities are low or medium voltage. This conversion from high to low voltage is done by a transformer, via electromagnetic induction [1]. However, there is a large difference between the usage of power in the evenings and in the daytime. This could cause fluctuations in the system, which is prevented by usage of a tap-changer. The tap-changer is coupled together with the transformer, and has the mission to handle fluctuations in power lines and it does so by mechanically changing of taps and thereby fine tuning the transformer winding ratio.

The tap-changer is the most vulnerable part of the transformer due to its many moving contacts; both electrical and mechanical. Malfunctioning of the tap-changer is consequently the most common reason for transformer failure [2]. Both the tap-changer and the transformer are functioning in transformer oil. The transformer oil is protecting the transformer and the tap-changer, by cooling and insulating the system. However, transformer oil is not a suitable lubricant for the contacts working in the tap-changer. Since there is no other lubrication of the contacts, the high friction can cause wear and malfunctioning of the tap-changer.

The overall goal is to find a lubricating grease to use in mechanical contacts that are operating in transformer oil. Transformer oil is a low-viscosity liquid and thus a poor lubricant, its main purpose is to cool the tap-changer and transformer as well as insulate. This results in a high amount of friction in these contacts, causing wear and malfunctioning.

1.1 Aim of this thesis

The aim of this thesis work is to investigate the possibility to use lubricating greases in mechanical contacts in tap-changers. Following actions will be made during this thesis:

- Literature study on the basic know-how about tap-changers, tribology, lubricating grease, transformer oil etc.
- Find appropriate test methods to evaluate the compatibility of lubricating grease in transformer oil
- Perform compatibility tests on a variety of lubricating greases
- Test the successful lubricating greases in tribological experiments
- Based on the results, evaluate the potential of using lubricating greases in transformer oil

1.2 Delimitations

Following delimitations have been made:

- There are several applications, where there is a need for lubricants working in oil. However, only tap-changers were considered in this thesis.
- There are both electrical contacts and mechanical contacts in the tap-changer. Only mechanical contacts were examined in this thesis.
- There are many different types of transformer oils being used in the power industry. ABB recommends NYTRO 10XN (produced by Nynas) to be used in their tap-changers, this is the only type of transformer oil that was considered in this thesis.
- The different types of mechanical contacts that are placed in a tap-changer are numerous. In this project only one type of tribological test was made, simulating a sliding contact.
- The contacts are all made of different types of metals; in this thesis a standard type of steel-steel contact has been considered.
- The steel contacts come in many different roughnesses and hardnesses; this thesis work has considered one roughness and one hardness.

2. Theoretical Background

2.1 Transformer

One of the most crucial and expensive equipment used in combination with power transfer is the transformer. Transformers are needed in many different parts of the power transmission and distribution system to be able to connect networks with different voltages. The transformer is constituted of two windings; the primary winding and the secondary winding. The windings are not connected to each other electrically but magnetically. The primary winding receives electrical energy which it converts to magnetic energy and then again to electrical energy in the secondary winding. A simple explanation can be found in Figure 1 [1].

2.1.1 Tap-changer

There are not any moving parts in the transformer that can vary the input and output of electricity depending on the load in the power system. When there are variations in the power system, a tap-changer is switched on. The purpose of the tap-changer is to keep the voltage constant on the secondary winding of the transformer, it does so by varying the relationship between the primary and secondary winding. The tap-changer is connecting different amount of windings, without breaking the current [3].

Figure 4 shows how the tap-changer looks like in more detail, and Figure 1 shows one possible position on the transformer.

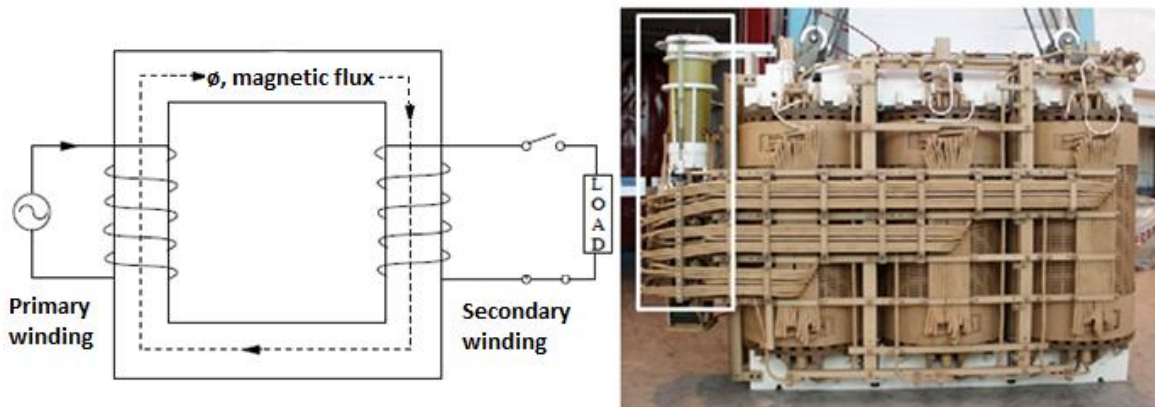


Figure 1 - Left picture; the function of a transformer. Right picture; a tap-changer position in connection to a three-phase transformer.

2.1.2 Transformer oil

Both the transformer and the tap-changer are handling large amounts of electric power, which generate substantial amounts of heat and high electrical fields. This is why transformers and tap-changer are working in transformer oil. Transformer oil is a low-viscous mineral oil with excellent cooling and electrical-insulation properties. The transformer oil is protecting the transformer and tap-changer from short circuits and flashovers. Regular tests need to be done of the transformer oil, in order to ensure its quality.

There are many different types of transformer oils. The most commonly used by ABB is a very low-viscous naphthenic mineral oil (see more information in section 2.3.2) with a small amount of antioxidant 2,6-di-tert-butyl-p-cresol, called NYTRO 10XN.

2.1.3 Working conditions in the tap-changer

The tap-changer is either incorporated in the transformer tank, together with the transformer (see Figure 1 and 4), or in a separate tank outside the transformer. If the tap-changer is incorporated in the transformer oil tank, its tap-selector is sharing the transformer oil with the transformer. However, the diverter switch is always working in a separate oil tank, to prohibit contamination of the rest of the oil tank (see Figure 5). If the tap-changer is put in a separate tank outside the transformer it does not share oil with the transformer.

In this work, the focus will be on the oil that the tap selector (see Figure 5) is working in.

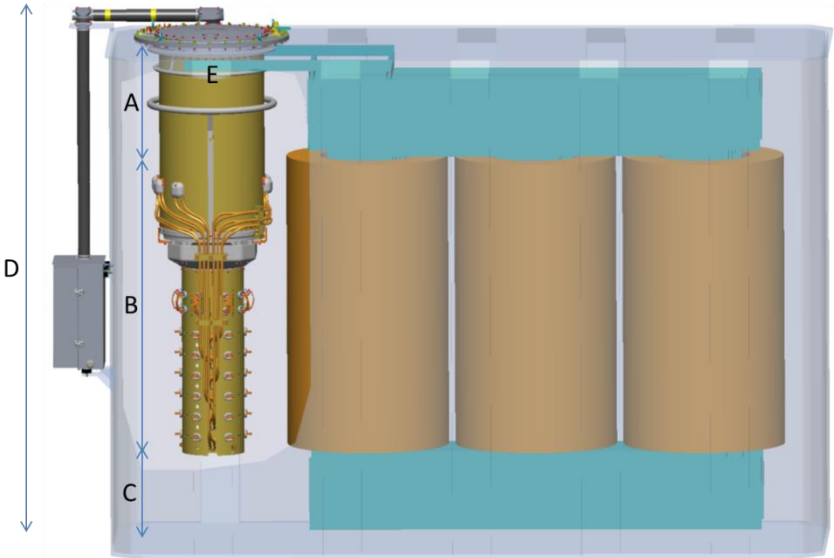


Figure 2 - Different areas in the tap-changer, with different temperature regimes.

2.2 Tribology

Tribology is the science of the interaction between solid surfaces in contact. The most common tribological contact is defined as two solid bodies in moving motion with each other. They are characterized by the material they are made off, the load and velocity they are subjected to, working conditions, such as temperature, environment, lubrication etc.

Friction is defined as the resistance arising when two hard surfaces move against each other. If the surfaces have been subjected to a lot of friction and high forces, small particles of the contacts can fall off; this is referred to as wear.

Lubrication of tribological contacts reduces friction and prevents wear, and will normally lead to a longer, more durable service of the contact. The lubricant is applied on the contact surfaces and its mission is to separate the contacts from each other (see Figure 2). There are three different types of lubricants; solid, liquid and semi-liquid. Solid lubricants are often applied as a coating on the surface; examples of solid lubricants are PTFE (commercial name, Teflon) and graphite [4]. Liquid lubricants usually constitute of oil with or without additives. Liquid lubricants are used in applications where there is a possibility to reapply new lubricating oil continuously [5]. Semi-liquid lubricants, more commonly called greases, are usually very simplistically explained, a mixture between a solid and a liquid lubricant. They are usually constituted of oil, additives and a thickener which role is to give the grease its more viscoelastic properties. The film thickness (see yellow area in Figure 2) of the lubricant is of major importance when studying the impact of lubrication in a contact. Full-film lubrication regime is when the film is sufficiently thick to completely separate the two moving surfaces from each other (see Figure 2), which is desirable [4]. A more detailed explanation off the ingredients in lubricants follows in section 2.3.

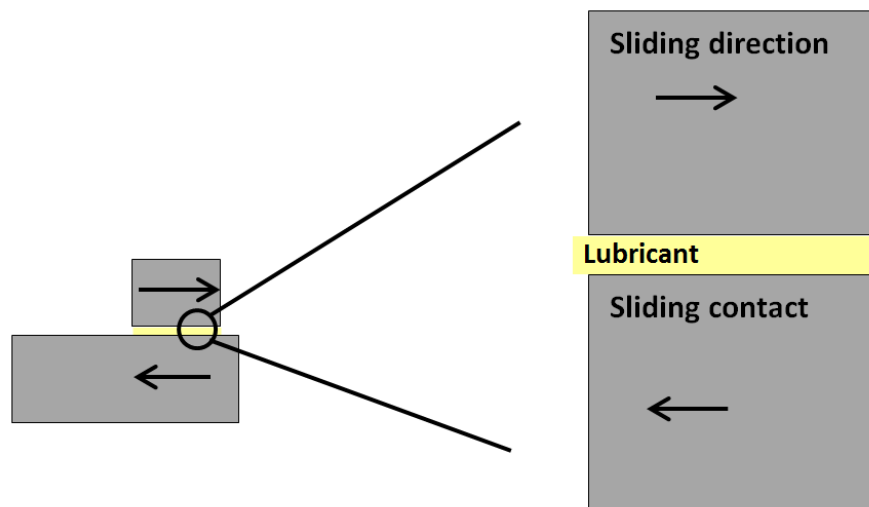


Figure 3 - Schematic picture on how the lubricant works in a sliding tribological contact

2.2.1 Mechanical contacts

There are two different categories of tribological contacts in a tap-changer; electrical contacts and mechanical contacts. The electrical contacts carry electrical current, and are therefore often made of copper or silver. These contacts are not being treated in this thesis. Mechanical contacts have the purpose to run the machinery, for example change tap. Some examples of mechanical contacts that are to be found in a tap-changer are visualized in Figure 3. Every mechanical contact has its own function in the tap-changer, and is subject to different types of forces. Most of the mechanical contacts in a tap-changer are sliding contacts, such as worm gears and sliding bearings, or rolling contacts, such as ball and roller bearings. They are made of different types of materials, but most commonly they are steel-to-steel contacts and steel-

to-bronze contacts. Common types of steel that are found in a tap-changer are; alloy steel, cutting steel, cast steel, structural steel and stainless steel [6].



Figure 4 - Examples of mechanical contacts, from left; worm gear, ball bearing, rolling bearing and pinion gear

2.2.2 Lubricant greases in mechanical contacts

In the literature, there are few publications on the detailed interaction between the thickener, base oil and additives in different mechanical contacts [7]. However, when applying grease to mechanical contacts, three different lubrication mechanisms have been identified:

- Churning phase
- Bleeding phase
- Film break down

The churning phase is describing the first phenomena that occur when starting to run a lubricated contact. This is when the applied grease is being distributed in the whole contact. There is always an excess of grease and the contact is lubricated by the excess of grease. When grease is well distributed in the contact and the excess of grease has left the contact, a steadier phase is initiated. The lubrication of the contact will no longer be through grease flow but through oil bleed. This mechanism is called the bleeding phase. This basically means that the grease is bleeding a little bit of oil every time it gets subjected to a load. This can be compared to a sponge filled with oil and every time the sponge is compressed, a little bit of oil will leave the sponge. In this case the oil bleeds in to the contact, and lubricates it. The bleeding phase is the mechanism that lubricates the contact over the lifetime of the grease. When the grease gets depleted of oil, it can no longer fully lubricate the contact and finally the starvation leads to film break-down and direct metal to metal contact is established [8]. The lifetime of grease varies depending on how well it is fitted for the specific application.

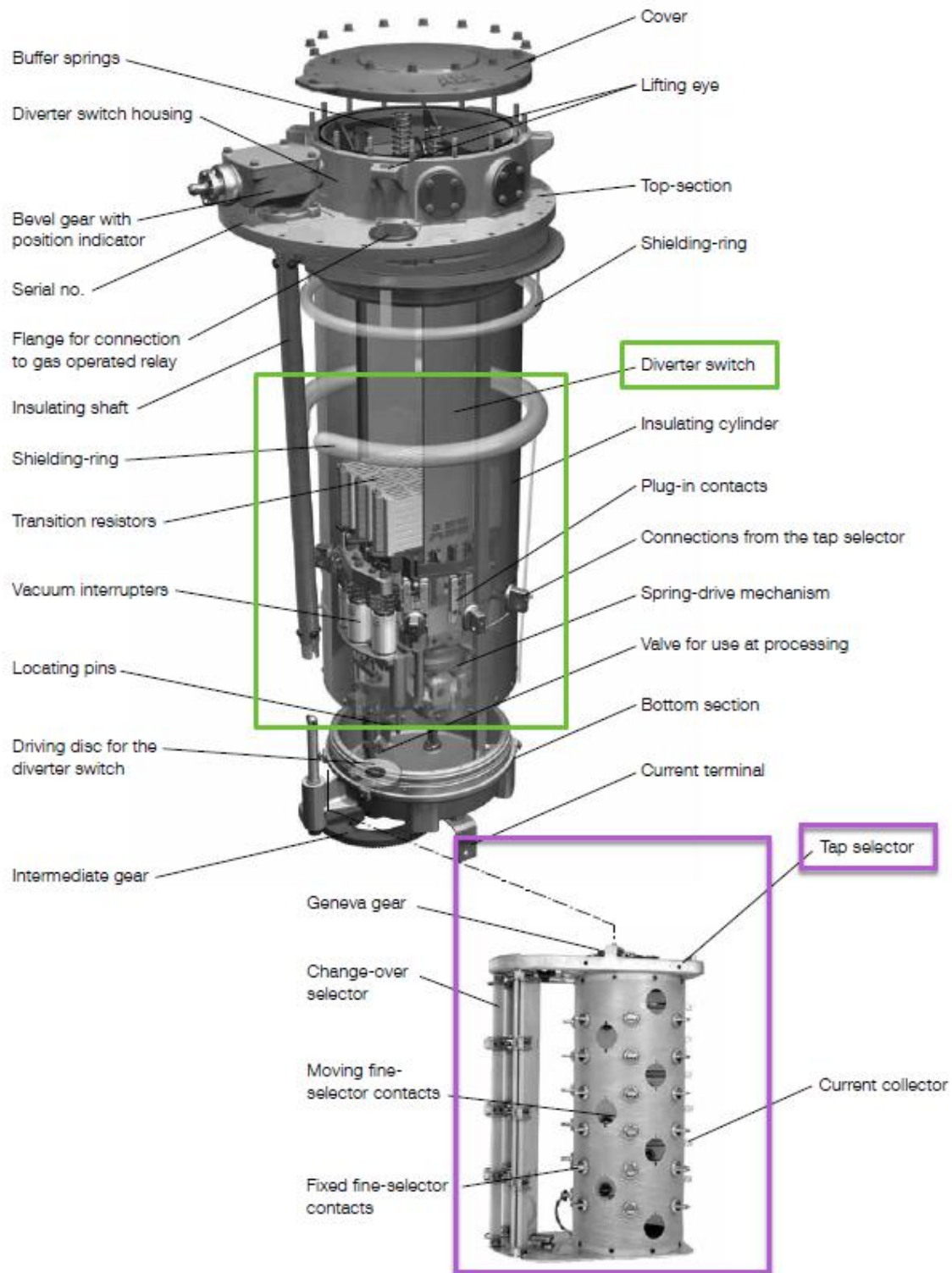


Figure 5 - Detailed description of the tap-changer, with the tap selector and diverter switch marked.

The different parts of the tap-changer are divided in to four different areas (see Figure 4). The mechanical contacts are primarily located in area A and B, which is why the temperature in these two areas gives the temperature regimes relevant to this thesis [9]. The average temperature in area A is approximately 60 °C (see Figure 6) and the average temperature in

area B is approximately 50°C (see Figure 7). Max temperature in both areas is 115 °C and min -40 °C.

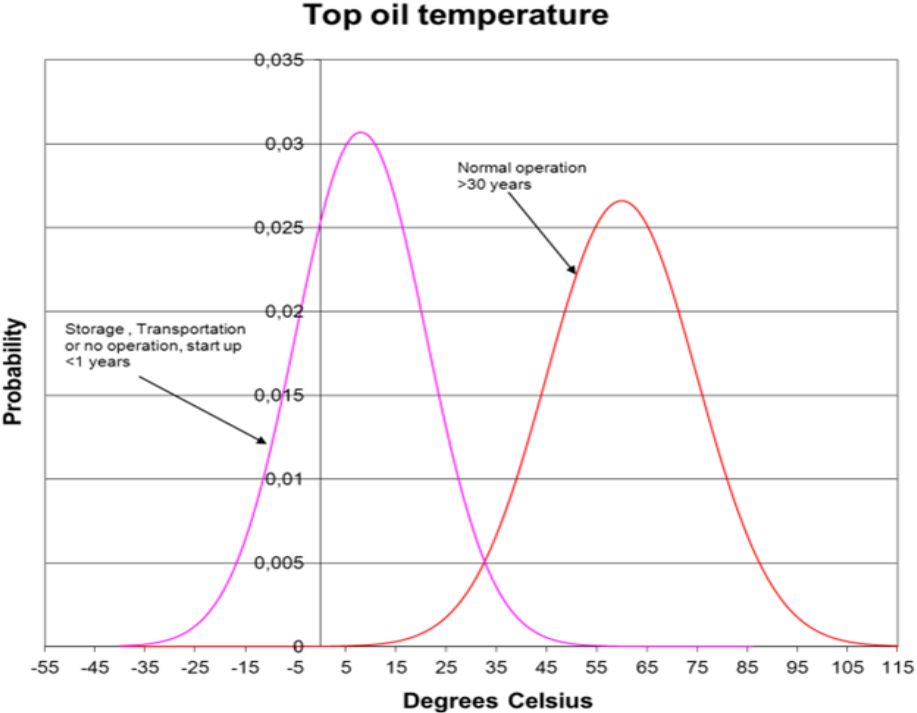


Figure 6 – Temperature distribution area A

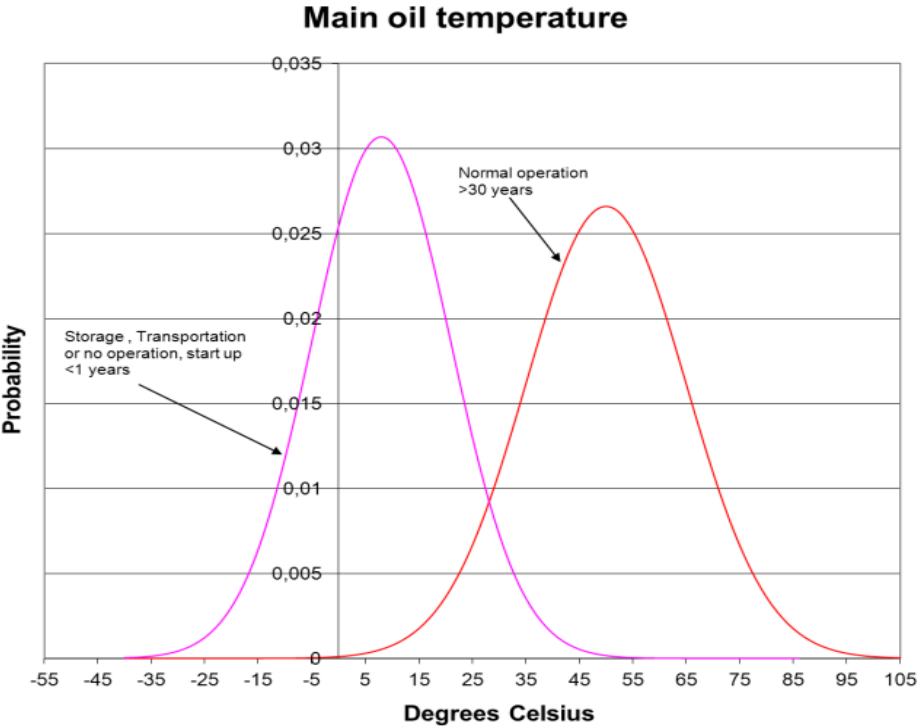


Figure 7 - Temperature distribution area B

The tap-changer is delivered to the customer with an expected life-time of 30 years. The only part that needs to be changed during this period of time is the vacuum interrupter; it needs to be exchanged after 15 years. The lifetime of the tap-changer depends on multiple factors; one

important factor is the quality of the transformer oil. Deterioration of the cooling or insulating properties will shorten the life time of the tap-changer. Factors that could affect the insulating properties are for example metal debris being torn away from mechanical & electrical contacts due to wear. This could lead to problems with conducting particles floating around in the oil.

At ABB a vapour-phase drying method is used to remove all water from the cellulose materials in the tap-changer, prior to oil fill. It will also remove most oxygen and dirt that are present. The tap-changer is put in a chamber with kerosene at 135°C for 1-3 days. This treatment is carried out before the tap-changer is delivered to the customer. Since the tap-changer cannot be reopened after the vapour phase, it is necessary to apply the lubricant in the contacts before the tap-changer goes through vapour phase [10]. It is therefore a requirement that any lubricant used, does not degrade during vapour-phase process.

Another important requirement is that the greases cannot contain silicon; this will cause foaming in tank and may lead to malfunctioning [11].

2.3 Grease chemistry

Grease contains three main ingredients; thickener, base oil and additives. The base oil is the lubricant and the thickener forms a network that traps the oil. One simple description of the thickener is a sponge, keeping the oil in place and releases a little bit of oil every time it is squeezed [12]. The additives are added to enhance properties such as corrosion resistance [4].

2.3.1 Thickeners

The thickener is responsible for the semi-liquid consistency of lubricating grease. This type of behaviour is called viscoelastic response. The base oil exhibits a pure viscous response and the thickener shows elastic response when subjected to an external force. Consequently, when the grease is subject to an applied stress, both elastic and viscous forces work together counteracting the deformation [7]. Another example of a viscoelastic liquid is honey.

Thickeners can be divided in to three different categories [13]:

- *Polymorphic thickeners* do not interact with base oil at room temperature, but becomes colloidal dispersed in the oil with increasing temperature. Commonly, polymorphic thickeners are metal soaps.
- *Solid hydrocarbons* do not show a polymorphic behaviour, these thickeners form a homogenous network with the base oil at temperatures exceeding their melting temperature. The low melting temperature hinders these thickeners from being used above 60-70 °C. Examples of solid hydrocarbons are paraffin and petrolatum.
- Thickeners that neither form homogenous networks with the oil, nor improve dispersion at elevated temperatures are so called heat-resistant thickeners; they can be either organic or inorganic. Examples of organic types are various *polymers*. Inorganic thickeners include; silica gels, carbon black, pigments. These thickeners form networks from aggregated particles that stick together with molecular forces. The oil penetrates the network and is kept there by capillary forces and adsorption to the cells.

Most thickeners (such as metal soap, polymer or clay) have polar characteristics, which is why they get adsorbed to a metal surface [4].

2.3.1.1 Polymorphic thickeners

Polymorphic thickeners are often referred to as metal soaps. Metal soap thickeners are produced from mixing fatty acids with an aqueous solution of corresponding metal hydroxide. There are alkali metal soaps (Li, Na, K) but also alkaline-earth metal soaps (Ca, Ba) and soaps made of Al, Pb from group thirteen and fourteen in the periodic table. Soap thickeners do not dissolve or disperse in oil in room temperature. But when heated, they transform to a mesomorphic state through a phase transition and can be colloidal dispersed in oil during agitation.

The concentration of the alkali metal soap decides at which state the produced grease is. The different types of states are; isotropic melt, simple gel, oleogel and lastly suspension. An oleogel is a system where the dispersed particles are ordered in a three-dimensional lattice, with elastobrittle solid properties. This behaviour is different from a simple gel, which contains a two dimensional lattice with high elasticity. It is the elastobrittle solid properties of an oleogel that is desirable when producing grease. To be able to obtain this type of oleogel, the formation needs to pass through the stage of becoming an isotropic melt. The melt is then cooled down to become a stable jelly with big lumps and later it is mechanically processed to become an oleogel. This type of behaviour is characteristic for alkali metal soaps. When producing anhydrous calcium (alkaline-earth metal) grease, no isotropic melt is observed. This explains the importance of which type of cation that is incorporated in the grease.

The most important factors that influence the formation of an oleogel are presence of surfactants, aggregation, adhesion, bonding interactions. There are no studies made on the interactions between the colloiddally dispersed soap particles or interactions between the soap particles and the dispersed medium (oil).

In conclusion, the soap thickener is believed to form a three-dimensional skeleton with colloidal-size particles in two dimensions and macroscopic size in the third dimension. The base oil, which is the dispersed medium, is being trapped in this skeleton by capillary forces, adsorption and other physical bonds. A thixotropic dispersion, which means dispersion that exhibit a time-dependent shear-thinning behaviour, has been formed. This explains the plastic behaviour of a lubricating grease.

Complex thickeners are constituted by a higher fatty acid together with a salt of a low molecular weight organic or mineral acid, sticking together by adsorption or molecular forces. The composition of the soap gives the grease different properties; alkali metal soaps differ from alkaline-earth metal soaps as well as pure soap differ from complex soap. The optimum thickener content varies with working temperature [13]. Soap greases are held together with weak van der Waal forces [14].

Most soap thickeners are created from hydroxisteric acid (se Figure 8).

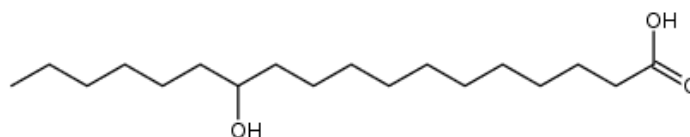


Figure 8 - Hydroxisteric acid

2.3.1.1.1 Lithium soaps

Lithium soaps are made out of Li-12-hydroxy stearic acid (see Figure 9), which is produced from an aqueous solution of LiOH that is added to molten hydroxistearic acid. Lithium soaps exhibit excellent mechanical stability and good water resistance [13]. These characteristics makes lithium greases an excellent choice for high working temperatures [15]. Since lithium soap is one of the most commonly used thickeners, it is often used as reference grease in

literature when comparing to other greases. Figure 9 shows a very simplified picture of how lithium-soap molecules adsorb at the metal surface, due to their negative charge [16].

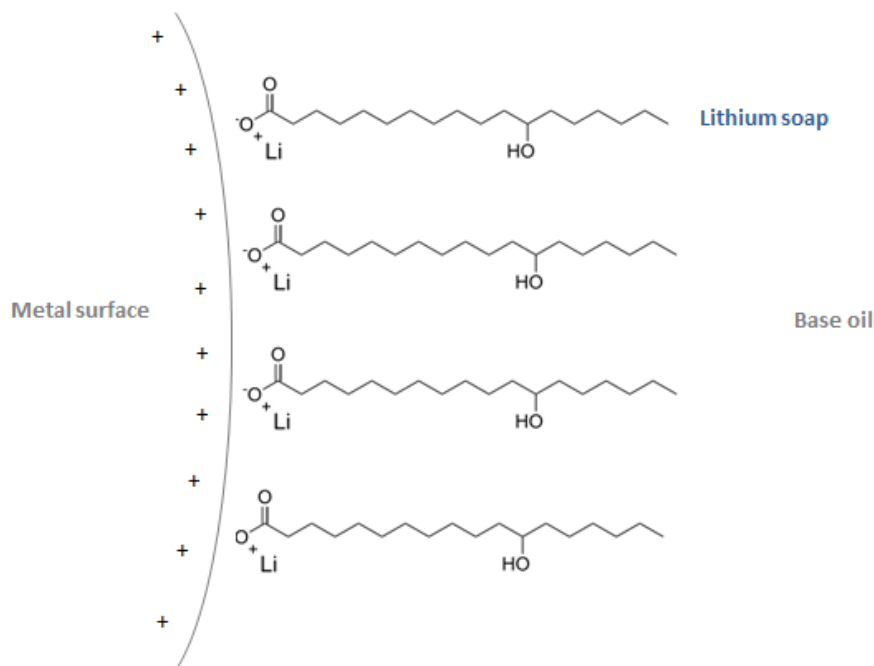


Figure 9 - Li-12-hydroxy stearic acid affinity for metal surfaces

2.3.1.1.2 Lithium Complexes

An even better lubricating performance is received when using lithium complex thickener. Lithium complexes are formed from mixing 12-hydrostearic acid with LiOH and boric acid and terephthalic acids. The complex lithium soaps have small polar acids linking the Li-12-hydroxy stearic acid molecules together (see Figure 10), which forms a dense network. This dense structure results in a network that better protects the trapped oil from oxidizing, due to prohibited heat flow. This is the reason to why lithium complex soaps have a higher thermal stability than pure lithium soaps [15].

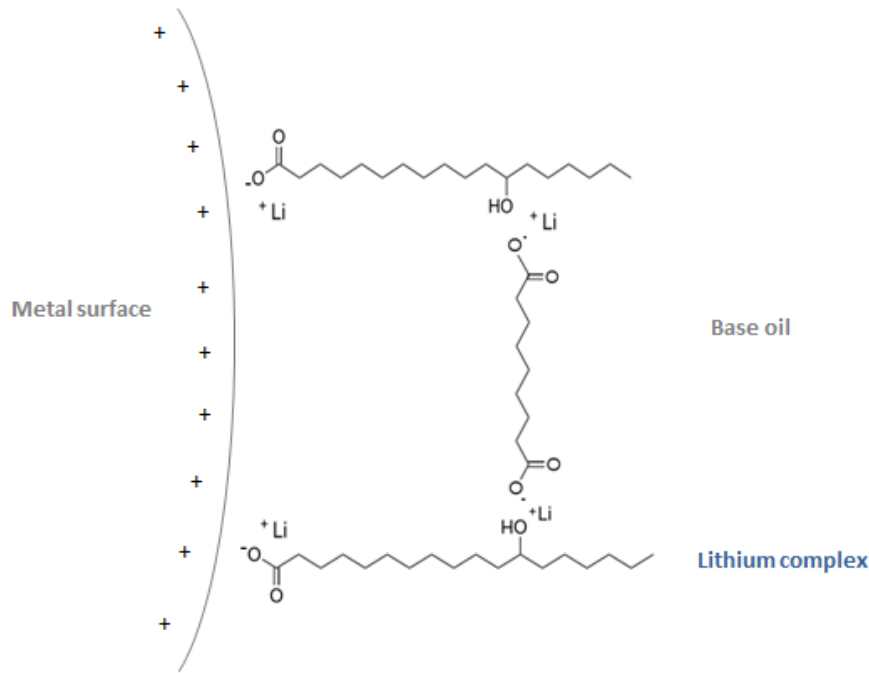


Figure 10 - Interaction between lithium grease molecules at the metal surface

2.3.1.1.3 Anhydrous Calcium

The first ever developed grease thickener was the calcium thickener. However, it has a limited functionality due to its low melting temperature at 100 °C. Temperatures in bearings and other tribosystems commonly exceed this temperature. However, the thermal properties can be enhanced when using anhydrous calcium soap, which means that the soap is not stabilized in water. Anhydrous calcium soap can be used at working temperatures around 110 °C which is similar to lithium and sodium greases. The advantages of anhydrous calcium soaps are that they are strongly adhesive, can work at low operating temperatures and can withstand water very well. Anhydrous calcium molecules want to adsorb to the metal surface in the same way as lithium thickeners do, due to its negative charge (see Figure 11) [17].

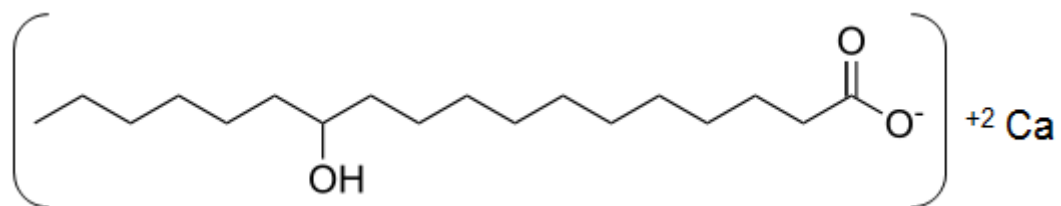


Figure 11 – Anhydrous calcium

2.3.1.1.4 Calcium Sulphonate Complex

Calcium Sulphonate Complex is not a soap thickener, but a complex grease with calcium sulfonate adsorbed on a calcite (CaCO₃) crystal structure (see Figure 12). These types of thickeners are called *functional thickeners*. The best suited base oil for calcium sulfonate greases has turned out to be high-viscosity paraffinic oil. This differs from the low-viscosity paraffinic or naphthenic oil preferred in lithium greases [18]. This thickener can withstand

extreme pressures and work at high temperature, due to the complexity of the grease with calcium sulphonate derivatives crystallized in to the thickener structure. This also results in an excellent water resistance and very good shear stability [15].

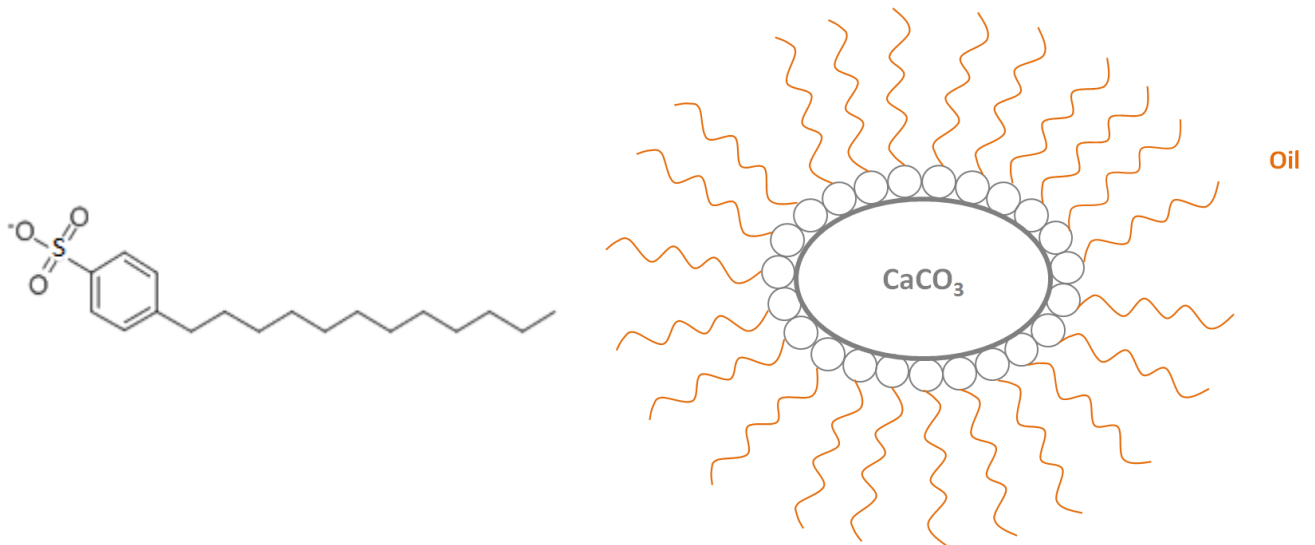


Figure 12 – Left: calcium sulphonate Right: Schematic picture of calcium sulphonate complex

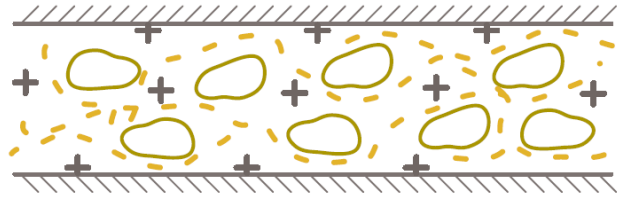
2.3.1.2 Polymer thickeners

A polymer is defined as a molecule constituted by many monomers linked together with covalent bonds [19]. The urea group that are marked with a blue box in Figure 15 is an example of a monomer. With this wide definition of what a polymer is, it is easy to imagine that the variety of polymers is endless. In greases, different polymers are used as additives, dispersion medium and thickeners. A description of the type of polymer being used as dispersion medium and additives follows in the following two sections.

Polymers used as thickeners are generally high-molecular weight polymeric compounds. These polymers form networks that do not dissolve in hydrocarbon oils, but rather swell. When the polymer network swells, it allows solvent molecules to enter its structure and a highly viscous liquid is formed, a grease [19]. The solubility of a polymer in hydrocarbon oil depends on the type of polymer. The most commonly used polymer thickeners are polypropylene and polyethylene. Polymer thickeners are often used instead of traditional thickeners to improve cohesion and adhesion. Polymer thickeners are neutral in their charge and do not have a high affinity for the metal surface, in contrast to soap thickeners (see Figure 13). Additives are charged molecules that are designed to reach the surface of the metal in order to fulfil its task; for example, extreme pressure additives (see Figure 21). In the case when a soap thickener is used, there are charged thickener and additive molecules competing for the surface. In comparison, polymer thickener molecules are not charged and have no high affinity for the metal surface, which results in the additives more easily getting through to the surface and the polymers staying in the dispersion medium (see upper part of Figure 13). As can be seen in Figure 13, the polymer thickener is making it possible for the additives to come through to the surface. Other desirable features, using a polymer thickener, are better chemical and mechanical stability, as well as usable at high and low temperatures. [20]

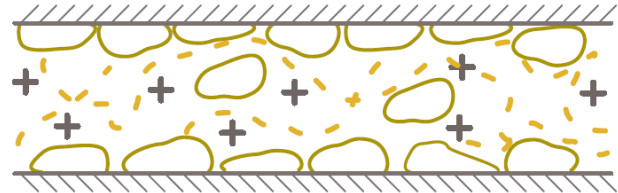
Epoch

Based on a non-polar thickener system (polypropylene) – the additives can reach the metal surfaces and do their job.



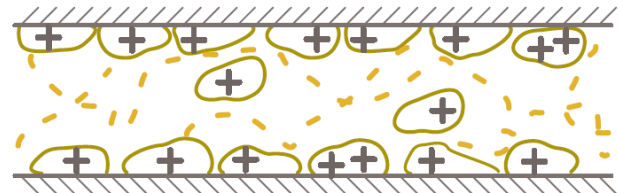
Soap

Soap has a higher polarity than additives – many additives will never reach the metal surfaces.



Functional soap

Soap and additives are bundled together – more additives will reach the metal surfaces, but some will inevitably be blocked in the middle.



○ Thickener system + Additives - - - Oil

Figure 13 - Showing the difference in affinity for the metal surface between soap greases and polymer greases (17).

Polytetrafluoroethylene (PTFE) is a type of polymer thickener (see Figure 15) that is built of only carbon and fluorine atoms. This bond is the second strongest single bond there is, which is why PTFE greases have outstanding properties such as high thermal stability and chemically inertness [21]. Another name for PTFE is Teflon, which is used as non-stick coatings in frying pans. It is often used when high temperature grease (up 200°C with peaks at 270°C) is needed in an application with moderate load. PTFE greases are also very adhesive, which is a desirable property in many applications, and they also have high density [15].

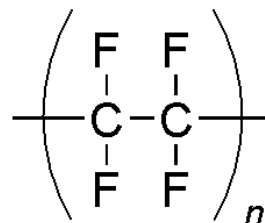


Figure 14 - Molecule structure of a the repeating unit in PTFE

Polyurea is a polymer built up of many urea monomers (see blue area in Figure 15). The carbon chains connected to these urea molecules can vary in length and composition, which is why they are marked R' and R in Figure 15. Polyurea greases are performing well at very high temperatures and they are water resistant. However, they do not perform well in moderate temperatures. Polyurea is a product from a reaction between iso-cyanates and

amines. One drawback is that it is made out of toxic raw materials, which has kept the price at a high level [15].

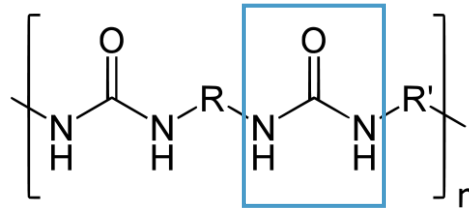


Figure 15 - Polyurea, blue area represents the molecule structure of urea

2.3.2 Base oil

There are certain characteristics that need to be considered when choosing which type of base oil to be utilized for grease. Since grease is constituted to 85% by base oil, its properties affect the grease in a major way. Following parameters are important properties for base oil:

- Solubility
- Viscosity
- Oxidation stability
- Evaporation loss
- Low and high temperature properties

Solubility of the thickener in the base oil is crucial. As mentioned in the section 3.1, different thickeners behave differently when interacting with the base oil. A soap thickener is forming a stable colloidal system; the stability of the colloidal system is highly affected by the solubility between the thickener and the base oil. In this case, the soap thickener should not be soluble in the base oil. This differs from the way polymer thickeners interact with the base oil; a polymer thickener should have a similar solubility parameter as the base oil. However this does not result in a homogeneous blend, but a swelling of the polymer matrix, allowing base oil molecules to enter the matrix [15] [19]. Normally, the solubility between the thickener and the base-oil is the only solubility to consider. However, in this work it is important to also consider the solubility with transformer oil. The solubility of oil in oil can be described with Hansen-Solubility parameters. There are three different parameters describing the total contribution of each cohesive force [22]:

- The *non-polar interactions* raises from atomic forces, often called dispersion forces, and are represented in the term E_D . These are practically the only cohesive forces in aliphatic saturated hydrocarbons, such as paraffinic oils.
- Permanent *dipole-dipole interactions* are described with the term E_P , they influences strongly the cohesion forces within a material. The polarity depends on the dipole moment.
- The third parameter is *hydrogen bonding*, E_H . Hydrogen bonding is a molecular interaction, which strengthens the cohesive energy, since bonds between molecules are strong.

The sum of all parameters gives the total cohesive force holding the medium together;

$$E_{TOT} = E_D + E_P + E_H$$

Low-viscosity oil is used when there is a need for good heat transfer or ability to work at low temperatures. These are reasons why a low viscosity is preferred for the transformer oil. High viscosity base oils in greases will induce less oil bleed and a lower soap concentration is therefore needed. High viscosity oils will perform better at high loads and at low speeds. These greases also tend to have better adhesion and better water resistance [15]. Another important point is that diffusion through highly viscous materials are slower, which results in a slower dissolving process of, for instance, two oils.

Good low-temperature properties are useful in this application since the temperature in the tap-changer could go down to -50°C .

The origin of the base oil is mineral oil, synthetic oil or vegetable oil. Different oils are chosen; depending on the type of environment they are to be used in [4].

2.3.2.1 Mineral oil

Mineral oil are distilled from crude oil and contain many different hydrocarbons and other chemical components [4]. There are three hydrocarbon structures present in petroleum, see Figure 16. The degree of distillation is chosen depending on fractions of each hydrocarbon the produced mineral oil will contain. Transformer oil is an example of a highly distilled mineral oil; it contains almost only naphthenic hydrocarbons.

In grease production, it is common to use a mixture of naphthenic and paraffinic mineral oils, this way it is possible to customize the grease properties [15].

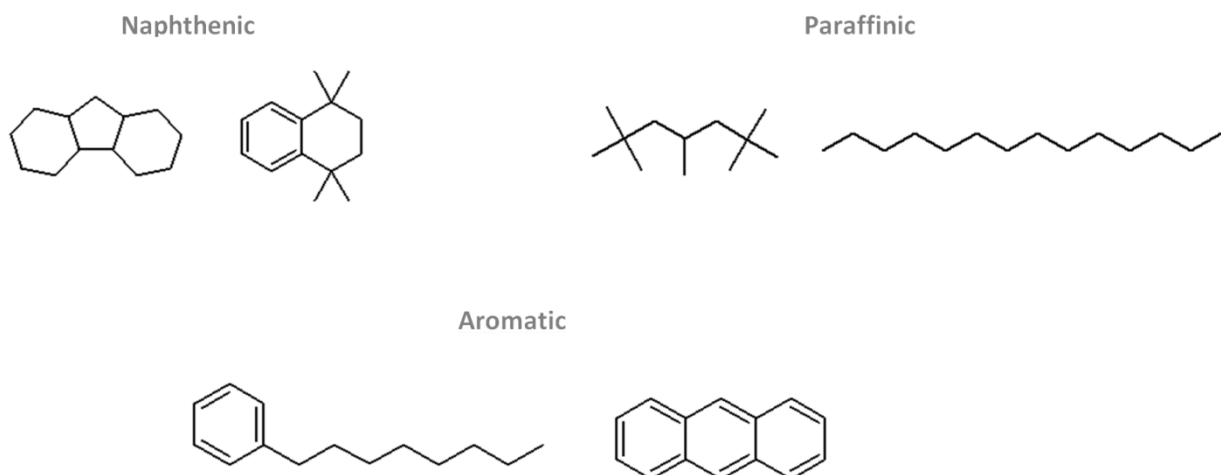


Figure 16 - Hydrocarbon structures

- *Naphthenic* base oils contain mostly naphthenic structures, but also a lower proportion paraffinic and aromatic structure. The aromatic content is very low, which gives these oils their light yellow colour. Naphthenic oils dissolve additives very well, which is an advantage when used in lubricants [4]. The high solvency is beneficial in grease

production since a smaller amount of thickener is needed to find the right consistency [12]. Moreover, naphthenic oils have a low viscosity index, which means that they have a high pumpability in comparison with paraffinic oil [4].

- *Paraffinic* oils have a high viscosity index. Paraffinic greases need higher thickener content, which is beneficial for high temperature regimes [12].
- *Aromatic* structures are to be found in small amounts in both paraffinic and naphthenic oil. The higher amount of aromatic compounds the more yellow will the oil get in its colour. In general, aromatic and naphthenic oils exhibit better flow properties at low temperatures due to their branched and ring structures.

2.3.2.2 Synthetic oil

Synthetic oil is a product of chemical reactions, and cannot be distilled directly from crude oil. However, the chemicals used often originate from petroleum. It is easier to customize synthetic oils since the reacted chemicals decide which properties the oil will get. In fact, all properties are improved when comparing synthetic oil to mineral oil. The only drawback is its significantly higher price, in comparison to mineral oil. This is the reason why synthetic oil is most commonly used when there is a need for enhanced thermal stability or a need for better chemical resistance [23]. Here are some examples of common synthetic oils used in greases:

- *Polyalphaolefins (PAO)* are synthesised from polymerization of n-decene together with a catalyst [23]. They contain oligomers with an average degree of polymerization from 2 up to 8 [24]. However, additives do not easily dissolve in PAO, due to the low polarity of PAO. This is due to absence of double bonds or aromatic compounds (see molecule structure in Figure 16). Naphthenic oils can be added to improve this ability [4].
- *Ester* oil has greater lubricity than mineral oil and is fully compatible with mineral oil and PAO, which means that it can be used instead of mineral oil or in a mixture with mineral oil. Ester groups are polar, which means that ester oil molecules want to adsorb at the metal surface. This means that there is a competition between ester oil molecules and additives at the metal surface. If the oil is too polar the ester groups will be adsorbed rather than the anti-corrosion additives, and the lubricity goes down. The non-polarity index can be calculated with the van der Waals formula [25]:

$$\text{Non - polarity index} = \frac{[\text{Total number of C atoms} \times \text{Molecular weight}]}{[\text{Number of carboxylic groups} \times 100]}$$

The higher the non-polarity index, the more non-polar the ester is and the lower is the affinity to the metal surface.

- *Polyalkyleneglycols (PAG)* are random copolymers. The type of starting components decides which type of PAG will be formed. Two common starting materials are propylene oxide and ethylene oxide (see the molecule structure in Figure 17), which creates a polar PAG. The more ethylene oxide that is incorporated in the ether, the higher is the water solubility. There are PAGs that are water soluble and non-miscible in mineral oils, as well as there are PAGs that are non-soluble in water and miscible with mineral oil. If higher alpha-olefin oxides are used as starting material, the

miscibility in mineral oil will be enhanced, and the polar characteristic decreases. Polar PAGs are only soluble in ester oils (see figure 19) [26].

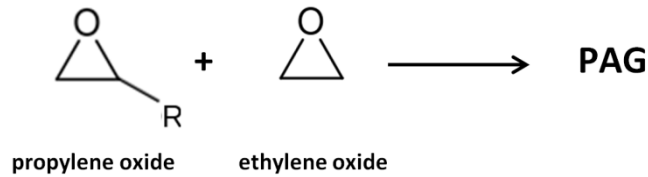


Figure 17 - Schematic picture of production of PAG

- Perfluoropolyether oil (PFPE) have good thermal stability, chemical resistance, resistance against corrosion, low viscosity index and is referred to as being inert. The only drawback is its high price [13]. One example of a PFPE molecule can be visualized in Figure 18. This type of PFPE oil has two CF_3 -groups, which are non-polar, making this type of PTFE oil non-polar and inert. This is in contrast to PTFE oils that have -OH end groups, which are polar [27]. Two examples of PFPE oils that have CF_3 end groups are FOMBLIN Y and Z, often used in PTFE greases.

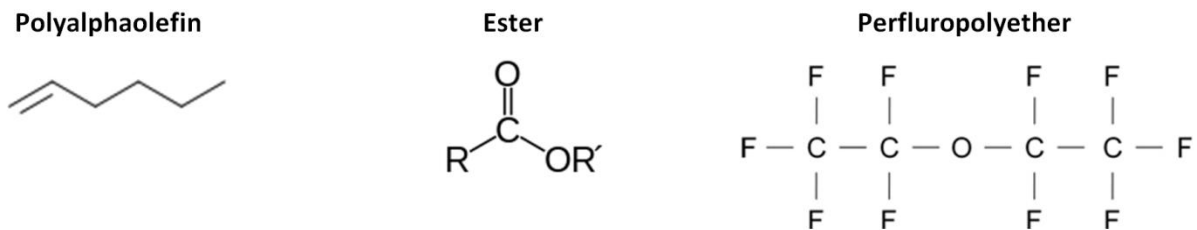


Figure 18 - Examples of synthetic oils

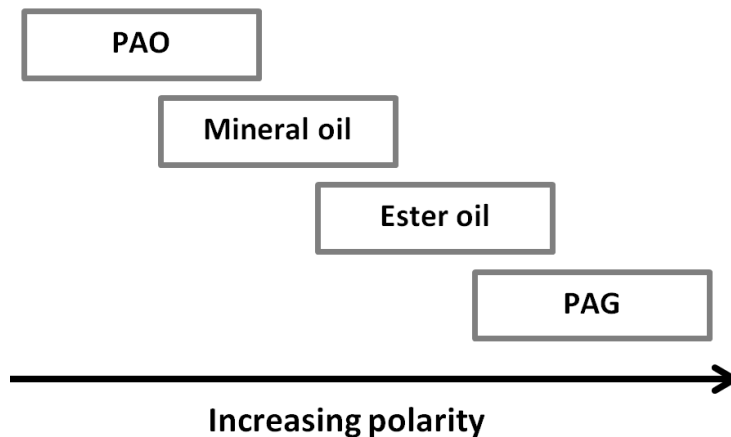


Figure 19 - Explanation of oil miscibility

2.3.3 Additives and fillers

Additives and fillers can be described as a third group of compounds incorporated in lubricating greases. Additives contribute to the formation of the thickener skeleton and are not

present in the dispersed medium. Fillers on the other hand, do not affect the skeleton of the thickener but are dispersed in the base oil.

Most *additives* are surfactants (see Figure 20), which mean that they are surface active [13]. Additives are added to grease to enhance grease properties. Some examples are [15]:

- *Antioxidants*, these are added to protect the grease from aging. Oxidation processes are triggered with increased temperature and antioxidants are therefore one of the most important additives in greases working in high-temperature regimes.
- *Anticorrosion agents* adsorb at the metal surface and form a thin film that protects the metal surface from corroding. Calcium sulphonates are often used as anticorrosion agent (see Figure 20).
- *Extreme pressure additives (EP)* are added when high pressure otherwise will give rise to hot spots (see Figure 21). EP additives are chemically activated at a certain critical temperature, most commonly this causes the hot spot to become brittle and fall off.
- *Anti-wear (AW)* agents are added when there is an additional need for anti-wear protection. Usually these agents work at less stressful situations or at lower loads, than the grease itself is dimensioned for.

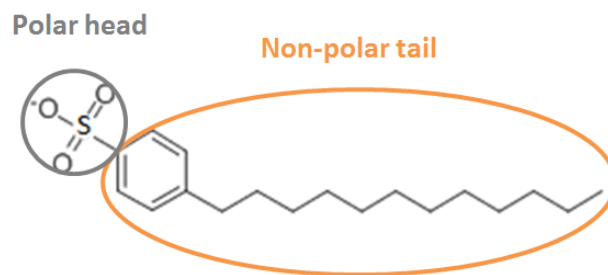


Figure 20 - Surfactants are built up of two parts, a polar (hydrophilic) head and a non-polar (hydrophobic) tail

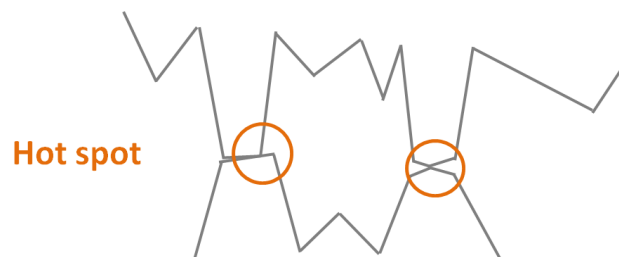


Figure 21 - Examples of where hot spots arise

Some additives can serve multiple tasks in the grease at the same time. For example they can serve as antioxidant as well as anticorrosion agent. Oxidation processes are accelerated by increased temperature. The temperature is rather high in mechanical contacts, which is why antioxidants almost always are needed. Antioxidants can also prolong the shelf time of the grease.

Adhesion to the metal surface can be improved by adding polymeric additives such as; latex, rubber, polyisobutylene, etc. These additives are oil soluble and their function is to improve viscosity, adhesion and in some cases protection. They do not however affect the thickening effect, colloidal stability or rheological properties. Surface modifiers are added to improve the

interaction between the surface of the thickener and the dispersion medium. In other words, the ability for the thickener to form a stable colloidal system with the dispersion medium is improved (see Figure 22). Surface-modifying additives are often added when the grease production needs to be controlled. Examples of surface modifiers are: free fatty acids, high molecular-weight mono- and polyhydric alcohols, ethers, naphthenates of metals, salts of organic acids etc. See how the surface modifiers work at the surface of the thickener/water droplet in Figure 23 [13].

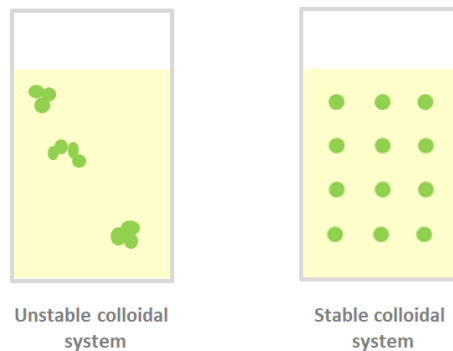


Figure 22 - Left picture shows an unstable colloidal system, the micelles aggregate. Right picture shows a stable colloidal system where the micelles are well separated.

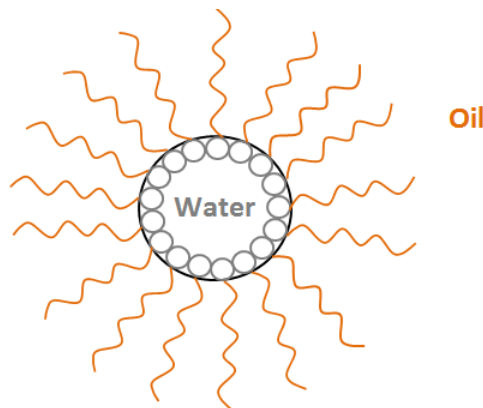


Figure 23 - Micelle

Fillers are added to improve properties of the dispersed medium (base oil). They do not affect the colloidal stability as additives, but are dispersed in the oil. The purpose of having fillers is often to improve lubricity or thermal stability. PTFE was mentioned before in section 2.3.1 thickener chapter, but PTFE can also be added as a filler to improve lubricity. Other common fillers are molybdenum disulphide (MoS_2), graphite and boron nitride [13].

3. Literature survey of analysis methods

The analysis methods used in this work emanate from the requirements for lubricants in transformer oil. This means that the grease should lubricate a steel-steel contact while in contact with transformer oil. At this point, there are no prior studies on compatibility between lubricants and transformer oil. In general there are few publications to be found regarding the chemistry of grease. The way to proceed was therefore to look at analysis methods for grease and oil separately.

3.1 Grease analysis methods

There are numerous studies on how to evaluate the performance of grease. One method is to age the grease in an oven at its maximum working temperature [28]. To analyse the aged grease Goncalves et al. used FTIR to receive information about oxidation [28]. Hurley et al. also received information about the influence of brass debris on the oxidation process of the grease. They could also distinguish base-oil evaporation taking place, when comparing the spectra [29]. Another method that Goncalves et al. used was a bleed-oil extraction process, in which information about how the bleeding rate differed between aged greases and fresh greases were obtained [28]. The method was claimed to be similar to the standard method ASTM:D4425, which is a method that is used to simulate the bleeding rate in an application where grease is subjected to centrifugal forces, for example in shaft couplings, universal joints and rolling elements [30]. Other methods are rheology measurements, where the storage modulus and loss modulus is obtained. The storage modulus measures the amount of stored energy, while the loss modulus measures the amount of energy that dissipated by the material [19]. Information about changes in storage modulus gives information about the thickener content, thus the elasticity in the grease, whereas oil loss is described with the loss modulus, in other words the loss of viscosity [28] [31] [12]. Many different techniques have also been used to study the difference in film thickness for aged greases vs. fresh greases.

3.2 Transformer oil analysing methods

Analyses of transformer oil are important in order to assure the quality. It is important that the cooling and insulating properties are intact during the operation, for safety reasons and to prevent damage to the tap-changer. There are multiple tests that need to be done on regular basis, recommended by the transformer oil manufacturer. When new materials shall be approved to operate in the tap-changer, the following tests need to be done:

An *aging process* is the first step. A sterilized beaker is filled with transformer oil plus the material to be tested. The beaker is put in an oven at 90°C for 7 days. Firstly, the *appearance* of the oil is examined. It is important that the oil has not changed in colour or has become turbid.

The next step is to analyse the oil with two different analysing methods [11] :

- Tan delta measures the amount of energy that is dissipated or lost as heat. This test is performed in order to guarantee that the insulating properties of the oil stay intact. Possible impurities that conduct electricity will be detected here, such as metal debris or water.
- Surface tension is measured to see possible changes in polarity. If the oil has oxidized, there will be a drop in surface tension.

4. Materials and methods

4.1 Assumptions

- The only flow mechanism in the tap-changer is self-convection. The driving force of self-convection is the temperature difference.
- The amount of particles that gets liberated from the contacts in the tank is neglected. This describes a perfect situation when all the contacts are properly lubricated and there is no wear.
- The working temperature is assumed to be constant, corresponding to the mean temperature in the tap-changer.

4.2 Materials

As mentioned before, the aim of these tests is to understand the compatibility between grease and transformer oil. The greases that were tested in the first screening are presented in Table 1. These greases are commercially existing products, consisting of different types of thickener, additives and base oils. The base oil in grease number 1-8 is a mixture of paraffinic and naphthenic mineral oil and in number 9-11 it is PAO. Number 12 contains PFPE oil. Known polymeric additives are added in column 5 (Table 1), the greases contain other additives as well but they are not specified. AXEL Christiernsson has delivered all greases except from Fomblin OT 20 that was produced by Klüber.

Table 1 - First screening

No	Name	Thickener	Base oil	Polymer additive	Viscosity at 40°C (cSt)
1	Hycal 272 WR	Calcium Anhydrous	Mineral	8,8 % poly-isobutene	1000
2	Hycal 262 WR	Calcium Anhydrous	Mineral	4% poly-isobutene	500
3	Callsullence 162 WR	Ca-Sulphonate complex	Mineral	1,2% hydrogenated styrene diene polymer & 1% poly-isobutene	500
4	Calsullence 1615 WR	Ca-Sulphonate complex	Mineral	2 % hydrogenated styrene diene polymer	500
5	Calsullence 152 WR	Ca-Sulphonate complex	Mineral	1,2 % hydrogenated styrene diene polymer & 0,88% poly-isobutene	200
6	Axellence 262 EPWR	Lithium complex	Mineral	3,6% poly-isobutene	500

7	Axellence 162 EPWR+ TACK 30	Lithium complex	Mineral	<1% poly-isobutene & 0,2 hydrocarbon polymer	500
8	Acinol 172 EP	Lithium	Mineral	2,5% poly-isobutene	1000
9	Noion	Polypropylene	Synthetic (PAO)	-	-
10	Noion + TACK 38	Polypropylene	Synthetic (PAO)	1,6 % hydrogenated styrene diene polymer	-
11	Noion + Vistamaxx 6202	Polypropylene	Synthetic (PAO)	1,6 % propylene-based elastomer	-
12	Fomblin OT 20	PTFE	PFPE	Unknown	-

The greases that were tested in the second screening round are listed in Table 2. A new approach with a different base oil; ester oil, was performed. As well as a couple of samples with varied thickener concentration, a high viscosity PTFE-grease and a high viscosity polymer grease.

Table 2 - Second screening

No	Name	Thickener	Base oil	Polymer additive	Viscosity at 40°C (cSt)
L1	"Axellence 752 EPBD" BG	Lithium complex	Ester	-	320
L3	"Axellence 752 EPBD" BG softer grease	Lithium complex + 10% high viscous ester	Ester	-	370
H	Hycal 762 EP EF	Anhydrous calcium	Ester	Styrene- Ethylene/Butylene- Styrene block copolymer	500
C	Calsullence	Ca-sulphonate complex	Mineral	2 % hydrogenated styrene diene polymer	500
P	Stabox 9415	PTFE	PFPE (Fomblin Y45)	-	140
L6	Axellence 152 EP BG high soap	Lithium complex	Mineral (less)	-	150
L5	Axellence 152 EP BG diluted	Lithium complex	Mineral	poly-isobutene	215
L4	Axellence 152 EP BG diluted	Lithium complex + 20% high viscous	Mineral	-	250

complex ester					
L2	Axellence 152 EP BG diluted	Lithium complex + 40% high viscous complex ester	Mineral	-	300
POL	Polypropylene	Poly propylene	Synthetic (PAO)	-	100 (at 100°C)

The transformer oil used is a very low viscous naphthenic mineral oil with a small amount of antioxidant 2,6-di-tert-butyl-p-cresol, called NYTRO 10XN. was NYTRO 10XN, produced by Nynas. Polyalkylene glycol oil made out of ethylene oxide and propylene oxide has also been used. It is called SYNALOX 40-D-150 and is produced by DOW Chemicals.

4.3 Compatibility test on glass plates

This test aims to investigate the compatibility between grease and transformer oil. The test has not been prepared according to any standard method, due to lack of relevant methods found in literature. It is however very similar to the test method used at the oil laboratory in Ludvika to characterize new materials (see section 3.2).

A thick layer of each grease sample was distributed on a 1 mm thick optic glass. To assure the thickness of 1mm, two optic glasses were put on each side of the optic glass, as a template, and the grease was applied with another optic glass (see Figure 23). When all the greases were applied to glass plates (see Figure 24) they were placed in separate beakers filled with 75 ml transformer oil. The oil did not completely soak the oil film, but let a small piece of the grease film stay above the surface.

The beakers were covered with aluminium foil and put in an oven holding 80°C. This temperature was chosen since it is an intermediate temperature between the average temperature in the tap changer (70°C) and the temperature used in the compatibility tests in the oil laboratory (90°C). This test was only performed on the greases in the first screening.

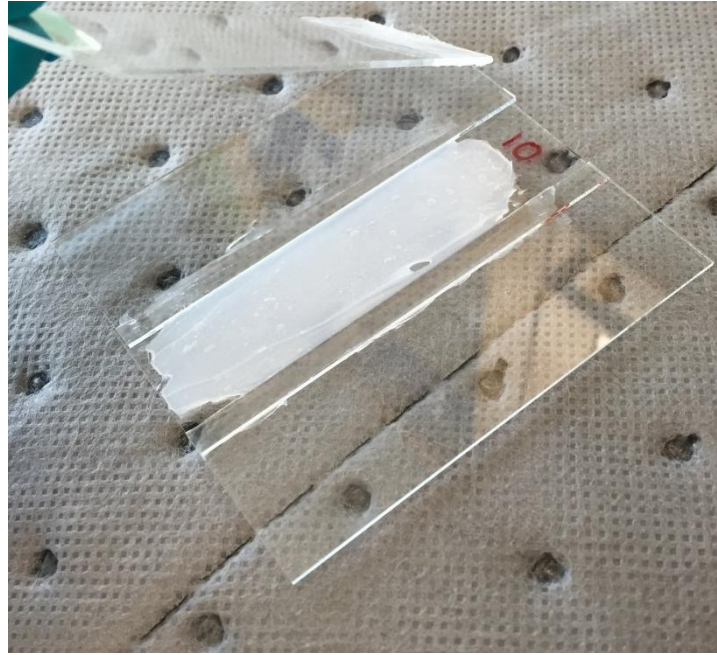


Figure 24 – Application of grease on glass plate

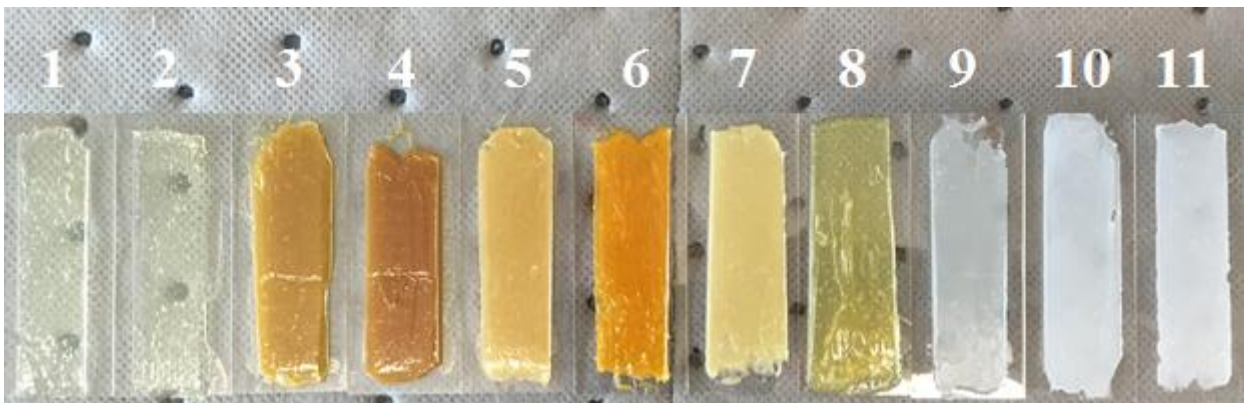


Figure 25 - Greases applied to glass plates

4.4 Compatibility test on metal foil

The same compatibility test was also performed on metal foil. Since the metal surface is rougher and not inert, it differs from glass. This test method is thought to be a better simulation of the surfaces in the mechanical contacts. Also, the applied layer was not as thick as the films applied at glass plates (see Figure 25) to eliminate the risk of gravitation pulling the thick grease film downwards. This test was performed on all greases from the first and second screening. The second screening contains greases with a new type of base oil, that is ester oil. The thickener content was also varied to see how that influenced the dissolving process.

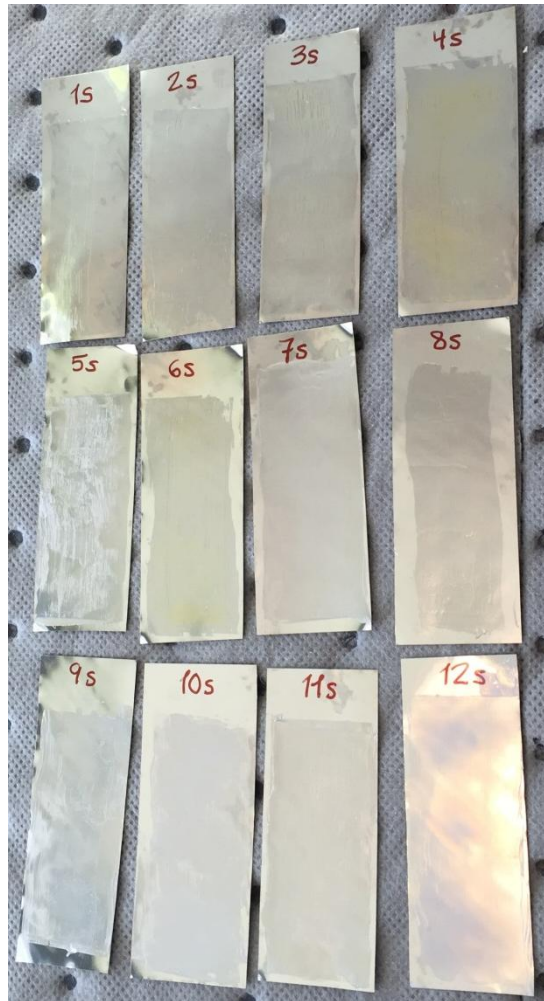


Figure 26 - Grease samples applied to steel foil

4.5 Compatibility test in glycol oil

In the compatibility tests with grease in transformer oil, there was a problem with the greases dissolving in the transformer oil. In order to understand this problem better, a compatibility test with glycol oil was performed. The glycol oil used in this test is a polar and water-soluble oil, which means that the difference in polarity is considerable between the base oils in the greases and the glycol oil. This test is thought to give information about how two different types of oils affect the solubility of the base oils in the grease. A selection of greases from screening number 1 were applied on metal foil (in the same manner as in the compatibility test on metal foil) and then put in beakers containing highly viscous glycol oil. This experiment is supposed to give some guidance on how it would work the other way around, meaning; if the base oil in the grease would be glycol oil and the surrounding oil be transformer oil. It should be noted however, that this test might be a bit misleading since there is a considerable difference in viscosity between the chosen glycol oil and transformer oil. A higher viscosity will give a hindered mass transfer.

4.6 Vapour phase dehydration

The vapour phase measurements were performed in Ludvika on the successful candidates from the compatibility tests. The greases were applied on metal foil and put in a basket to go through the process. The chamber is heated and at the same time evacuated until vacuum is obtained. Kerosene vapour is introduced when the chamber is at 135 °C. The kerosene vapour condensates on the tap-changer and falls off. This process continues for approximately 1-2 days.

4.7 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a fast and simple characterizing method. It is a qualitative analysis method that can be used to detect for example, additives in greases [28] [32]. A beam with infrared light is hitting the sample at a certain wavelength. The sample absorbs some of the light, while some radiation is transmitted. The absorption of light causes the atoms in the molecules to vibrate. Absorption and transmittance spectra are received, which is a molecular fingerprint for the sample (see the schematic setup in Figure 27) [33].

Oil from the compatibility tests on glass plates were recorded. The received spectra were compared to corresponding spectra for pure grease and then the spectra for pure NYTRO 10XN. If characteristic peaks from the grease were detected in the spectra from the oil sample, the grease has dissolved in the oil.

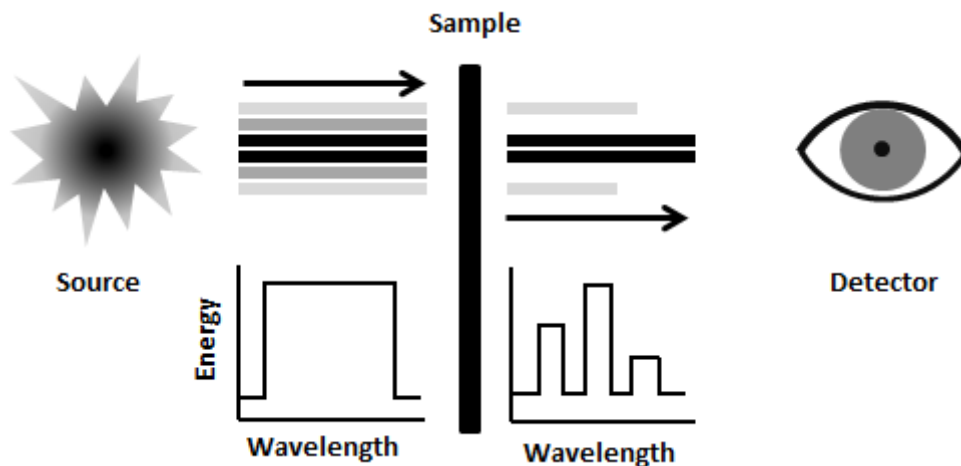


Figure 27 - Schematic picture that describes FTIR

4.8 Dielectric loss factor

Materials have different electrical characteristics; these depend on the dielectric properties. A material is dielectric if it has the ability to store energy when applied to an electrical field [34]. This test is performed in order to guarantee the insulating properties of the transformer oil. Impurities, such as water or soaps, may cause the dielectrical loss tangent to increase, this leads to impoverished insulating properties of transformer oil [34].

The test is performed on BAUR OIL Tester DTL according to the standard method IEC 60247:2004, at 90°C.

Two different greases were analysed in this test equipment; Fomblin and AXEL PTFE. In order to simulate how the grease would affect the properties for the oil after a longer period of time. Prior to the analysis, all samples are aged in 90°C for 7 days. These samples were compared to pure transformer oil in order to see any differences.

4.9 Surface tension

The ring method is performed with a tensiometer, in order to measure the interfacial tension between two liquids. This method is used to verify that no polar groups from the grease have entered the transformer oil, and in that case raised the surface tension.

4.10 Tribological test – Ball on plate test

Tribological tests were performed in Uppsala in a ball on disk test equipment. A schematic picture of the setup is shown in Figure 13. The lower parts of the equipment made the sample move in an oscillatory movement, while the ball was fixed in the same position. The ball is a standard bearing ball with a diameter of 1 cm, the applied load was 5N and the stroke length 10 mm. All grease samples were applied on steel plates with the dimensions 3x3x0.3 cm and put in an oil bath holding approximately 80°C. The steel plates were not polished before the tests, which resulted in a quite rough surface. The test was initially performed on a non-lubricated steel plate in transformer oil, in order to get a reference. The test was then performed on lubricated steel plates with Fomblin and AXEL PTFE grease, in duplicates. The sample plate moved reciprocating for a total number of 1000, 1800 and 3600 cycles, with the frequency of 1 cycle/s. Coefficient of friction, μ was recorded vs. time.

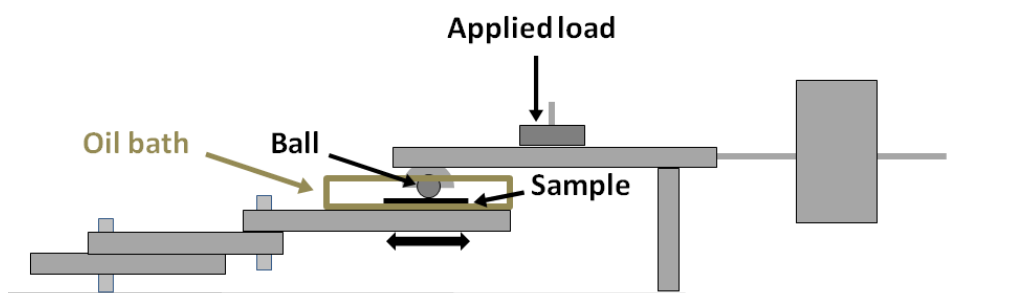


Figure 28 - A schematic picture of the tribological test. The lower part is moving, while the ball is stationary. The olive green box indicates the position of the oil bath.

5. Results and discussion

5.1 Compatibility test on glass plates

Figure 29 show the results from batch 1 after 2.5 hours in an oven holding 80°C, applied on glass plates. The figure shows that all greases have slipped off the glass plate (nr 1 and 8 did as well when moving the glass plate slightly upwards). Grease no 1 and 2 (calcium anhydrous thickener) are still quite cohesive since the whole film fell off in a uniform piece, even though the adhesion to the glass plate had ceased to exist. In greases number 3-5 (with calcium-sulphonate complex thickener), both the adhesion to the glass plate and the cohesion within the grease have relaxed. This was shown from the grainy texture in the bottom of the beaker as well as by the split of the grease film being in contact with the oil and the grease above the oil. Number 6-7 both contained lithium complex and their behaviour is similar to number 1-2, the cohesion is stronger than for number 3-5. Number 8 (lithium thickener) was still quite cohesive, similar to nr 1-2. Number 9-11 (polymer thickener) was still quite cohesive, but not as good as nr 1-2.

Another observation was that the transformer oil (normally transparent) had changed its colour in those cases where the grease was coloured. Also, the smell was no longer pure transformer oil but smelled of the grease present in the beaker.

The first batch of greases consisted of different types of thickeners but the same type of base oil. This base oil is a mixture between naphthenic and paraffinic hydrocarbon structures, which means that the base oil is chemically similar to transformer oil. As mentioned in section 2.1.2, transformer oil consists of mostly naphthenic carbon structures. This means that the base oil in the greases is soluble in the transformer oil. One probable explanation to why the greases do not stay on the glass plates is that the base oil in the greases have dissolved in the transformer oil, at the same time the transformer oil is penetrating the grease to dilute it.

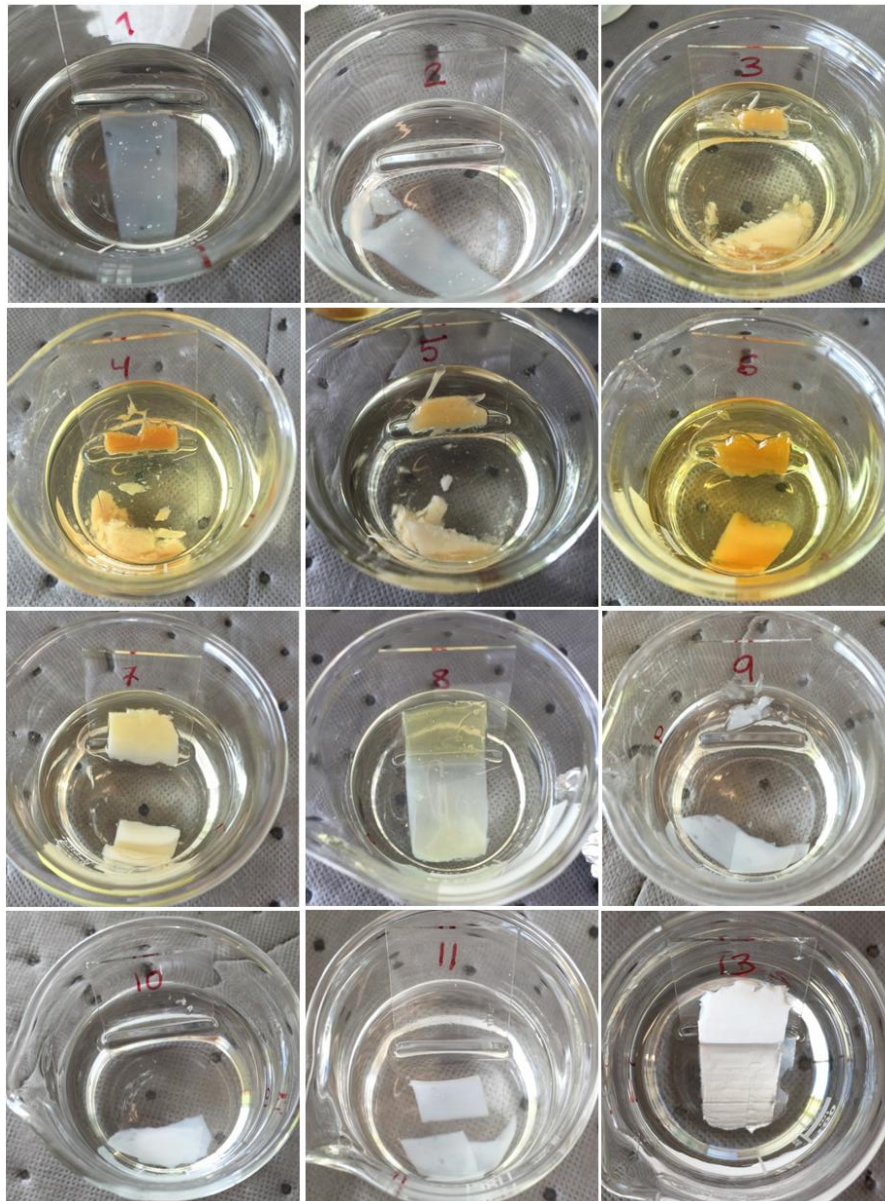


Figure 29 - Results from compatibility test on glass plate after 2.5 hours in 80°C

The results after 6 days treatment in 80°C are presented in Figure 30. Number 1 and 2 are not cohesive anymore; the film has broken down to pieces. It looks like the pieces are thinner than the original film, which indicates that the grease is dissolving in the oil. Number 3, 4 and 5 have lost most of its colour. Number 6 and 7 are still cohesive, which means that it does not seem to dissolve as easily in the oil. This could be explained by the dense structure of its thickener, lithium complex (see Figure 10), which seems to efficiently keep the base oil inside the thickener structure. Grease number 9, 10 and 11 have not changed much visually, which probably have to do with their base oil, PAO, which is chemically different from mineral oil (see section 2.3.2.2 and Figure 19). This could slow down the dissolving process. Number 13 is almost intact, the only difference is that the film had formed a crack and the lower part moved down approximately 1 mm. The explanation to this could be a combination of gravity and the high density of Fomblin.

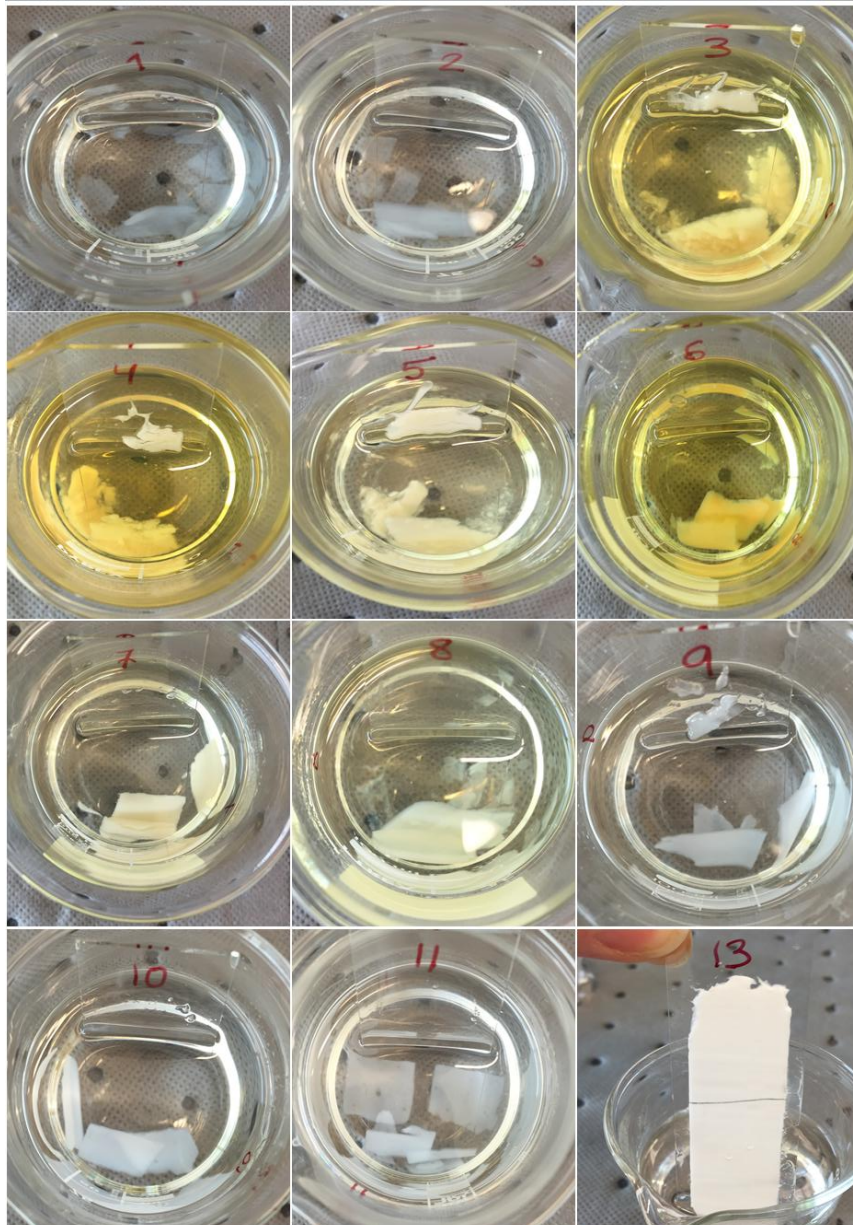


Figure 30 - Compatibility test on glass plate after 6 days

5.2 Compatibility test on metal foil

The results from the compatibility test on metal foil after 2,5 hours are found in Figures 31-33.

The results from the first screening are presented in Figure 31 and 32. Number 3 and 4 still had a substantially part of the grease film left on the metal foil. For number 12 the grease film was intact, except for a thin vertical strip of space. The grease film is to a large amount still sticking to the metal foil for grease number 7 as well. But for grease number 1,2, 6, 8, 9, 10 and 11 it had almost completely fallen off.

The results vary considerable from the results received from the compatibility test on glass plate (see Figure 30). The only grease that exhibits the same behaviour on both glass and steel plate is Fomblin (number 13 in Figure 30 and number 12 in Figure 32). It seems like grease number 3 and 4 have a stronger adhesion force to the steel plate than the other greases. This

indicates that the calcium-sulphonate thickener have a stronger affinity for the metal surface than the other thickeners. This conclusion can be made if the amount of additives is assumed to be very small, and therefore negligible, and if the greases in the first screening is assumed to be the same.

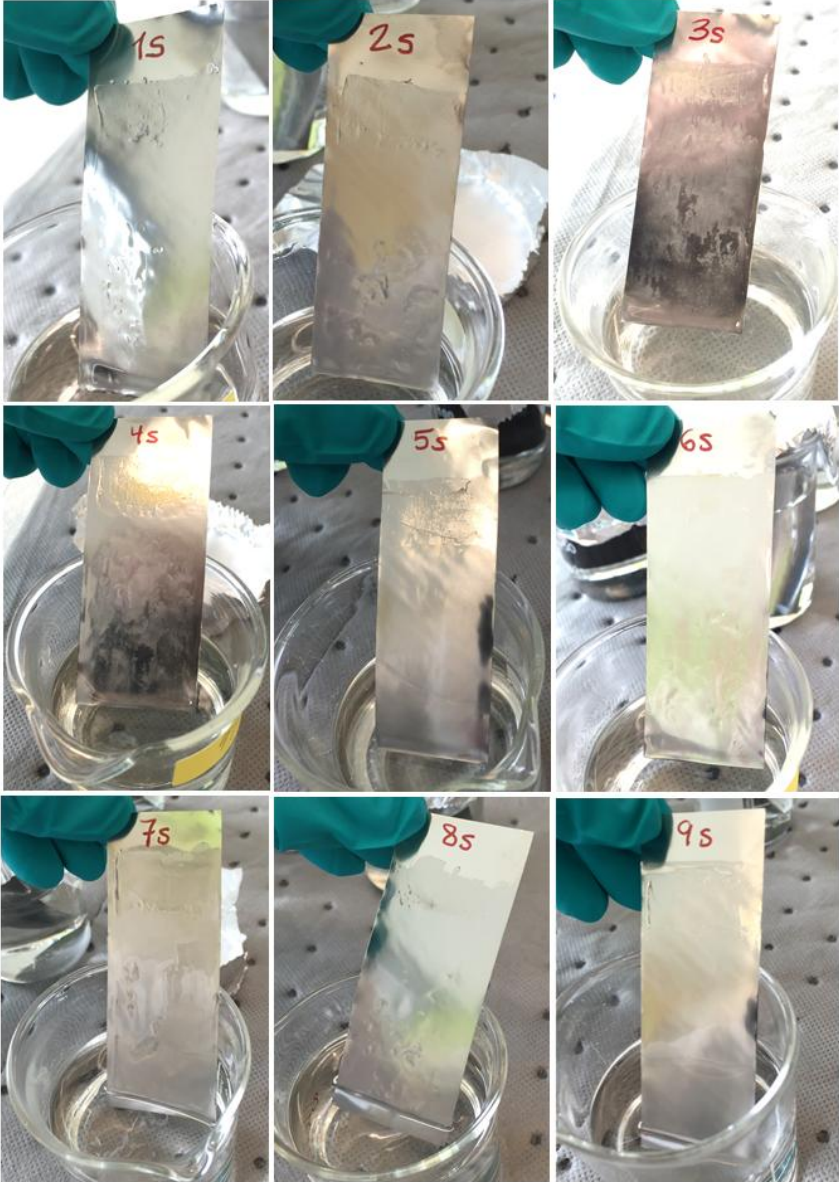


Figure 31 – Results from compatibility test on metal foil after 2.5 hours, grease nr 1-9

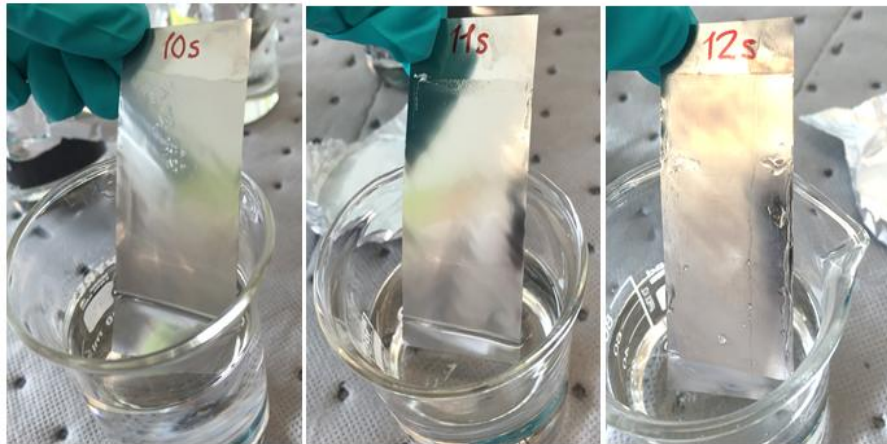


Figure 32 - Results from compatibility test on metal foil after 2.5 hours, grease nr 10-12

To further analyse how the thickener and base oil content in the grease affect the interaction with the metal foil and the transformer oil, a second screening was applied on metal foil and put in the oven in the same manner as with the first screening. The results from this test are presented in Figure 33. All greases except C and P have fallen of the metal foil. C is very similar to grease no 4 (from the first screening), it is therefore reasonable that it behaved in the same manner. P (will be referred to as AXEL PTFE from now on) is another type of PTFE grease, similar to Fomblin but with a higher viscosity, and is therefore thought to behave in the same manner.

Greases no L1, L3 and H dissolves in the same manner as the corresponding grease containing mineral oil as base oil. This means that it does not matter whether or not the base oil in the grease is ester oil. There are however different types of ester oils, the amount of polar groups in the oil affect the polarity of the oil and also the solubility in transformer oil. Consequently, a more polar ester base oil would probably result in less dissolving of the grease in transformer oil.

L5 and L6 contains different amount of thickener. Both grease films have fallen of the metal foil and been divided in smaller pieces, in the same manner. This indicates that the amount of lithium complex thickener in the grease does not affect the solubility in transformer oil.

POL contained high viscous PAO oil, but this does not influence the solubility of the grease in transformer oil (compare POL Figure 33 with number 9, 10 and 11 in Figure 31 and 32).

Moreover, L2 and L4 have fallen of the foil in large pieces. This cohesiveness can be explained by the addition of a high viscous complex ester. The complexity and high viscosity could in this case indicate that the dissolving of the grease in transformer oil is slower.

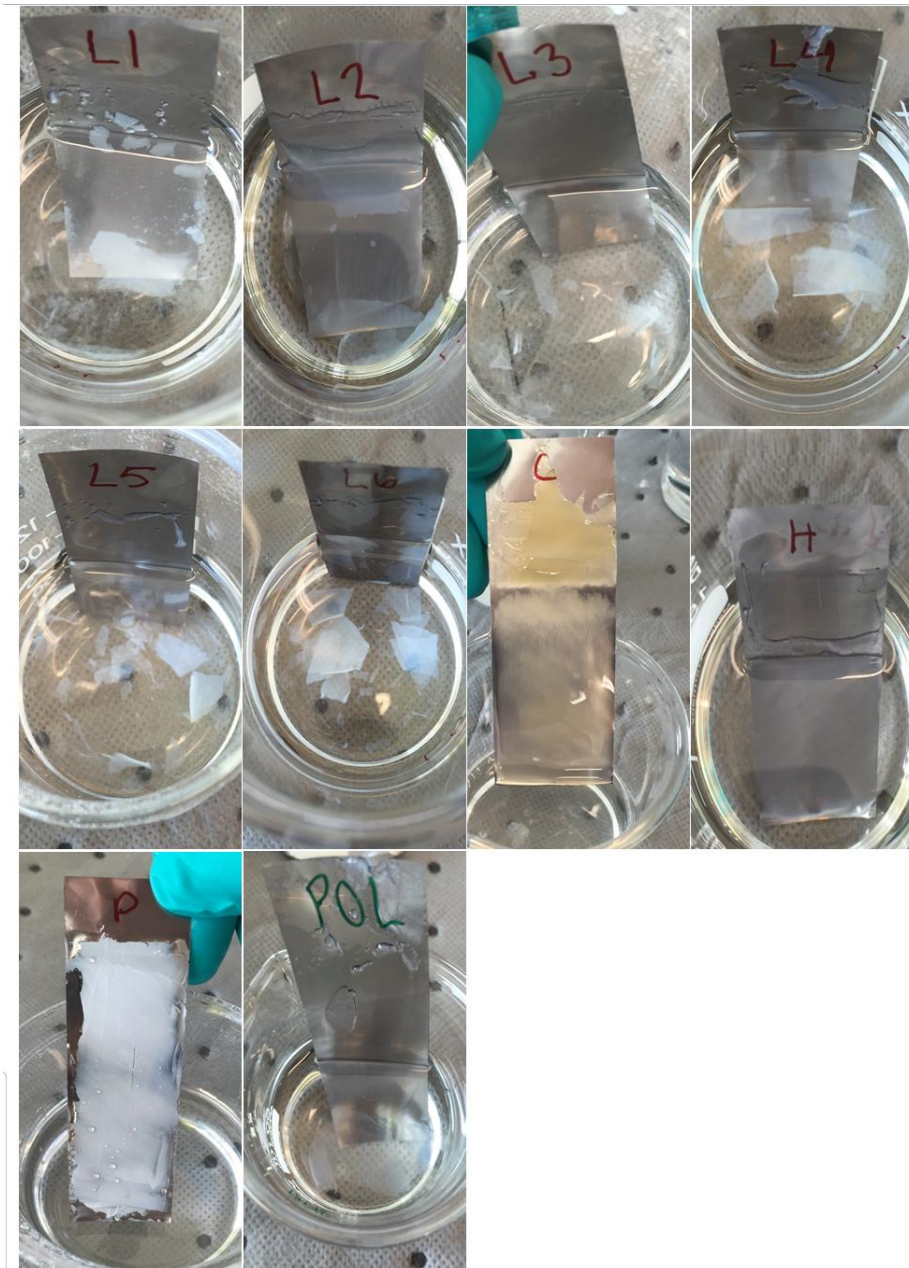


Figure 33 - Compatibility test on steel foil, batch no 2

5.3 Compatibility test in glycol oil

The results after 2.5 hours in 80 °C in glycol oil are shown in figure 35. All grease films are still sticking to the metal foil. Grease number 1 and 10 was not wetted by the glycol oil, the glycol oil drops off the grease film when removing the plate from the oil (see Figure 35). Grease number 3 and 6 have more interaction with the glycol oil at this point. The probable reason why the glycol oil is less willing to blend with the greases is due to a substantial chemical difference between the base oil in the greases and glycol oil. SYNALOX is a polar glycol oil that is water soluble and not soluble in mineral oil. Number 10, containing an inert polymer thickener and PAO base oil, is the best performer. This makes sense when looking at Figure 18 in the section 2.3.2.2, where PAO and PAG have the biggest difference in polarity.

The reason why grease no 1 performs better than 3 and 6, has probably to do with other ingredients than the base oil. The water content might be high in grease number 3 and 6, this could influence the compatibility with SYNALOX, since SYNALOX is water soluble.

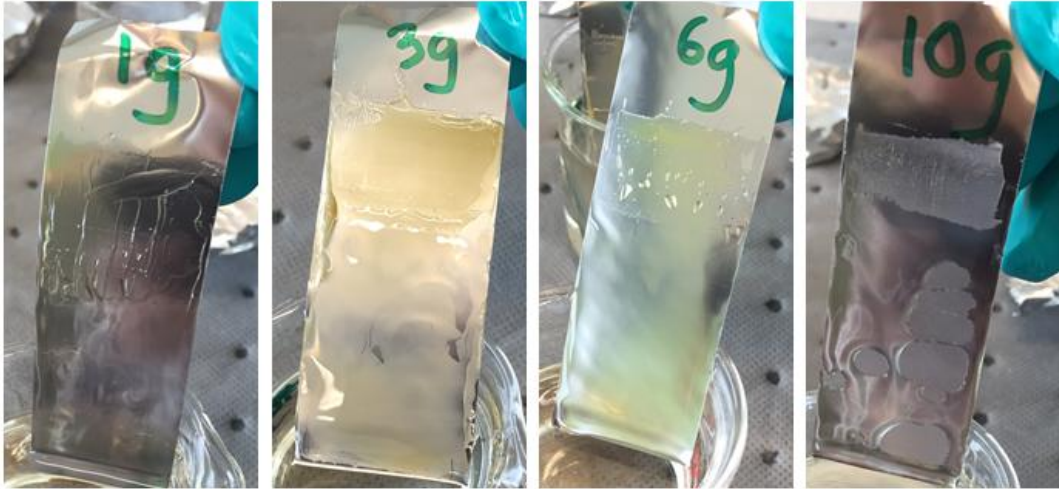


Figure 34 - Results from compatibility test on grease nr 1, 3, 6 and 10 after 2.5 hours

The results after 8 days in the oven are presented in Figure 35. Number 1 and 10 have started to migrate from the steel plate, which can be visualised through horizontal lines, as well as fallen of pieces around the edges of the foil. The glycol oil blends more with the greases at this point. Big flakes of grease have fallen of the steel plate for grease no 3 and 6.

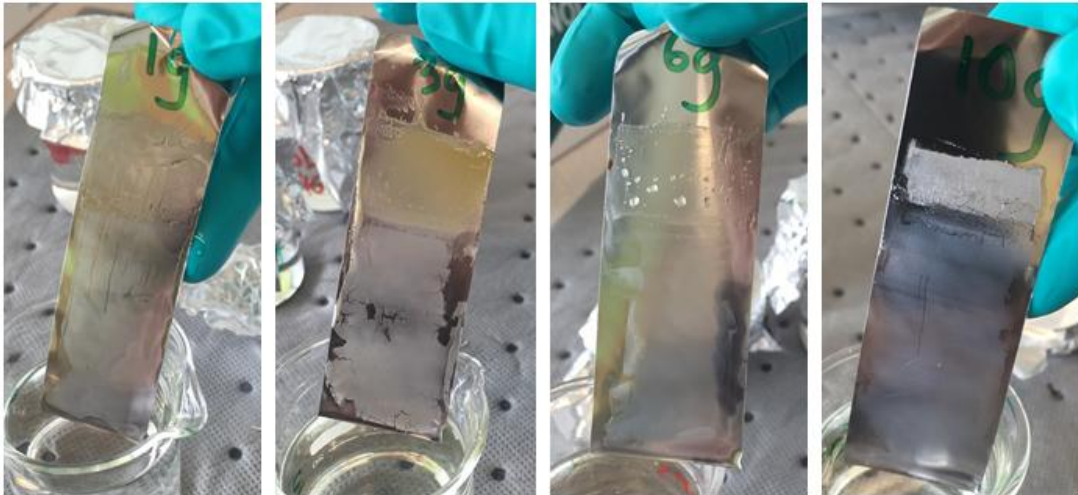


Figure 35 - Results from compatibility test on grease nr 1, 3, 6 and 10 after 8 days

In conclusion, it takes longer time for the greases to dissolve in the glycol oil than in transformer oil (compare Figure 36 with 32, 33 and 34). Difference in polarity (between base oil in grease and surrounding oil) could be one reason to why the adhesion to the metal surface has improved. However, the high viscosity of the glycol oil could influence the results in the sense of slowing down the solution process.

5.4 Fourier Transform Infrared Spectroscopy

The hypothesis from the compatibility tests was that the greases have dissolved in the transformer oil. The chosen analysis method to evaluate the hypothesis was FTIR. The results from FTIR on grease number 1 and Fomblin is presented in Figure 36 and 37. Each figure contains three spectra; pure grease, pure transformer oil and transformer oil after 6 days treatment with grease in 80°C.

Figure 36 shows spectra for grease no 1. The red spectra represent the spectrum for pure grease with a characteristic peak at approximately 1600 cm^{-1} , the peaks at approximately 2800 cm^{-1} and 1400 cm^{-1} correspond to the base oil. If the grease has dissolved in the transformer oil, a peak around 1600 cm^{-1} should show in the blue spectrum. This is not the case (see Figure 36), the blue spectrum is identical with the black spectrum, which means that there is now sign of grease in the oil after 6 days. This could still mean that the oil in the grease dissolved in the transformer oil, since the chemical composition on transformer oil and the base oil is similar.

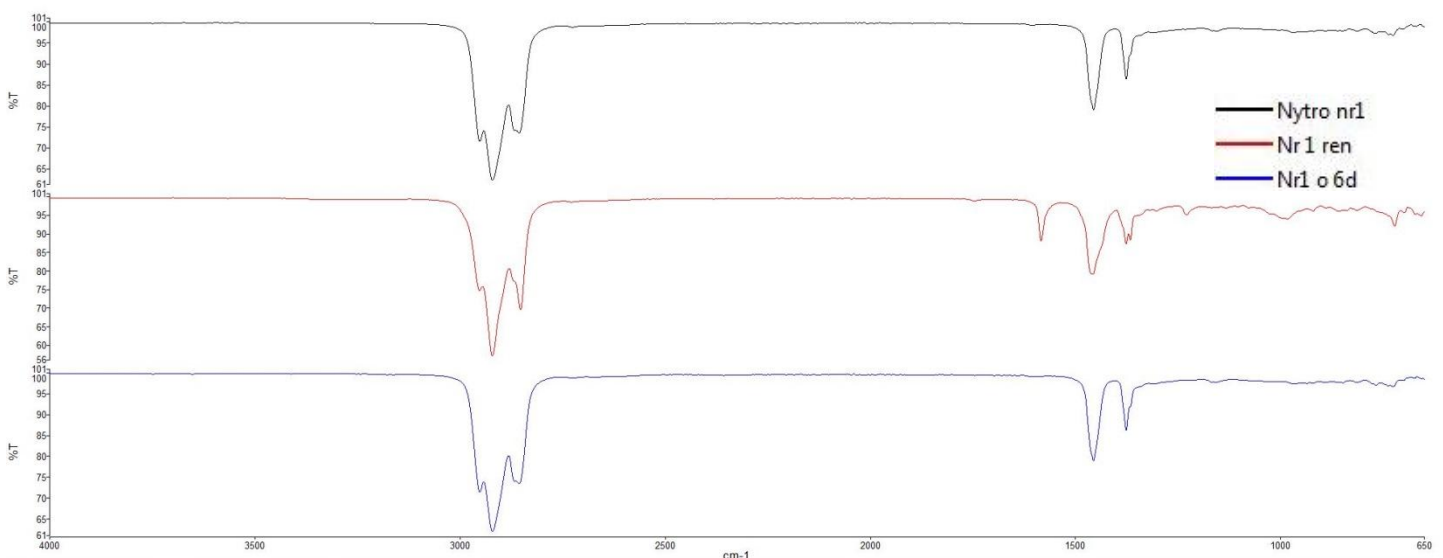


Figure 36 – Results from FTIR analysis on Grease number 1. From top; pure transformer oil, pure grease, and transformer oil that has been treated with grease no 1 for 6 days.

The corresponding spectra for Fomblin are to be found in Figure 38. There are a couple of characteristic peaks for Fomblin in the fingerprint region; however, none of these peaks are to be found in the oil (see the pink spectrum). This indicates that Fomblin did not dissolve in the transformer oil. This is reasonable since Fomblin did not show any sign of dissolving in the compatibility test either.

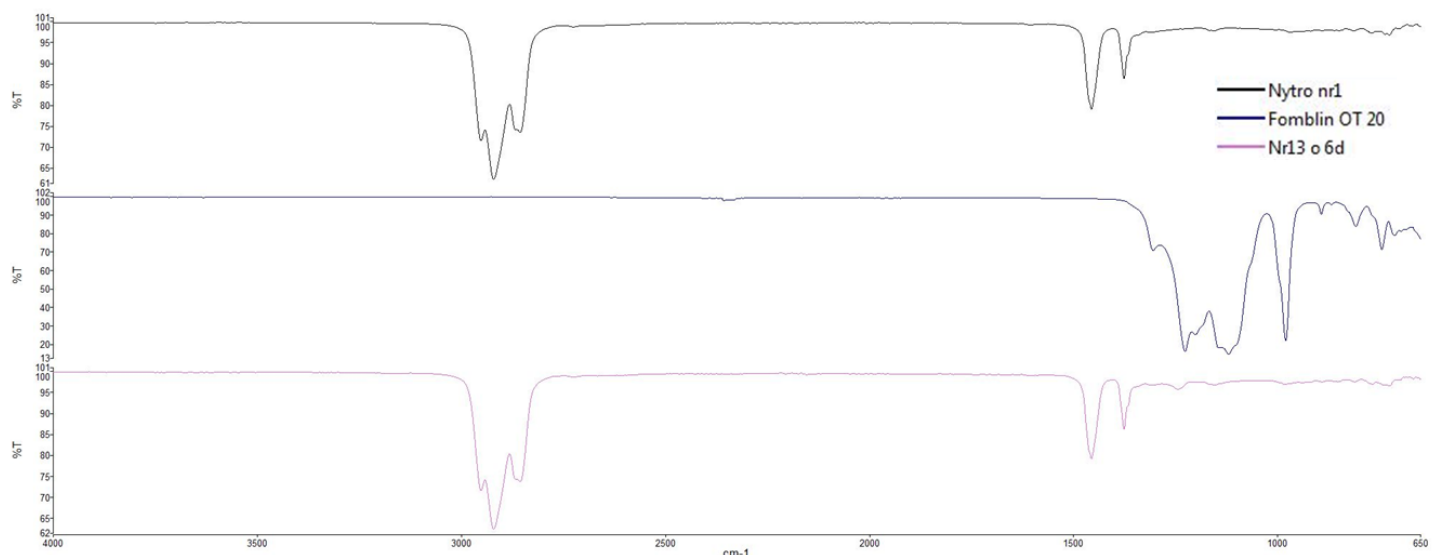


Figure 37 - Results from FTIR analysis on Fomblin. From top: pure transformer oil, pure grease and transformer oil that has been in contact with Fomblin for 6 days.

The same pattern is to be seen for all other greases from the first screening. There are no signs of the thickener or additives in the transformer oil. FTIR spectra for all greases are to be found in a separate document.

5.5 Tribological test on fresh greases

Tribological tests were first performed in transformer oil; this test is referred to as a reference test to demonstrate a non-lubricated contact. Results from this test are found in Figure 38. Tribological tests were then performed on two greases; PTFE AXEL and Fomblin, in transformer oil. These results are presented in Figure 39-42. All tests were performed in duplicates, resulting in graph No 1 and No 2. All tests are carried out in 80°C.

The results from test on metal plate in pure transformer oil are found in figure 38. The friction for both curves stays low for a few seconds, followed by a large increase in the coefficient of friction that indicates that the contact is no longer lubricated. The first couple of seconds, there is an oxide layer present that is lubricating the contact. When the oxide layer is pulled off there is no longer any lubrication of the contact. That is why the coefficient of friction is suddenly increasing rapidly. These results are believed to be reasonable since the transformer oil is a poor lubricant, which should result in high friction.

There are however a big differences between curve No 1 and No 2. The friction became instantly very low at two points (500 seconds and 620 seconds) in curve No 2; this could be caused by the ball passing over a very fine area on the steel plate or by some type contamination entering the contact. However, curve no 1 is thought to better describe the conditions in a non-lubricated contact.

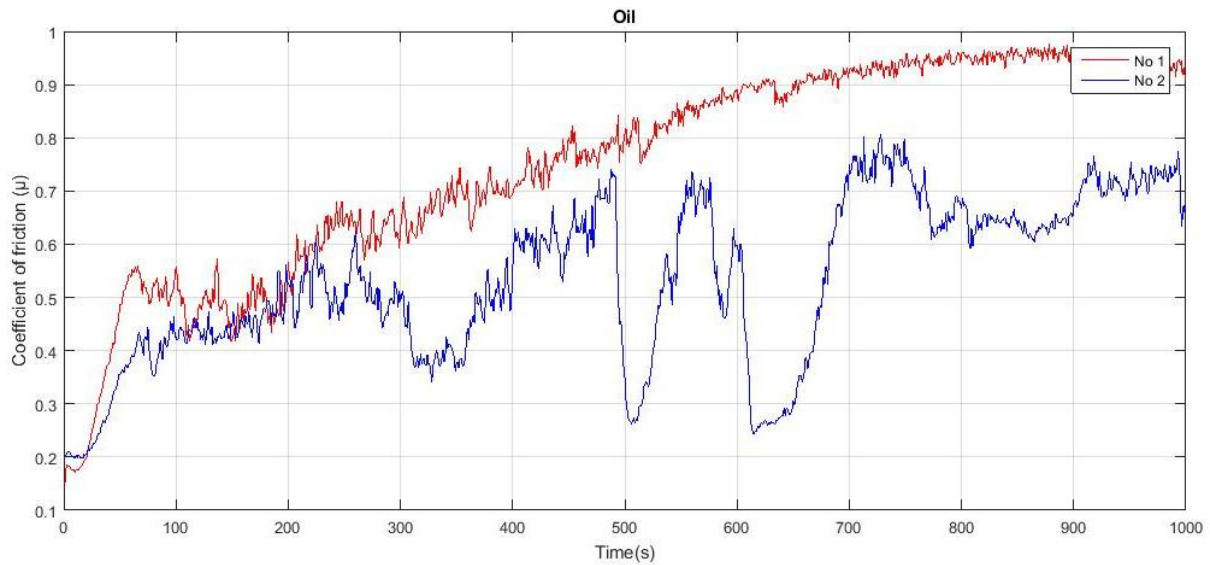


Figure 38 - Results from tribology tests in transformer oil

Figure 39 shows the results from ball on disc measurements with AXEL PTFE grease. The coefficient of friction stays under 0.2 for 100 seconds for No 1 and for about 70 seconds for No 2. This represents normal values for full-film lubrication of grease. However, there is a probable film breakdown around 100 seconds and steel-steel contact is obtained, resulting in a large increase of the coefficient of friction. But the coefficient of friction does not climb to the high values that were observed in Figure 38, but stayed rather constant around 0.45-0.5. This could indicate that a break-in period with AXEL PTFE creates a smoother surface, which lowers the friction in a steel-steel contact. Another hypothesis is that the grease re-enters the contact during the test. Curve No 1 and No 2 are similar which indicates that the reliability of these tests are high. The difference between the two curves during the first 100 seconds could be due to that test No 1 was performed on newly applied grease, while No 2 was performed on a grease film that had been in the transformer oil during test No 1.

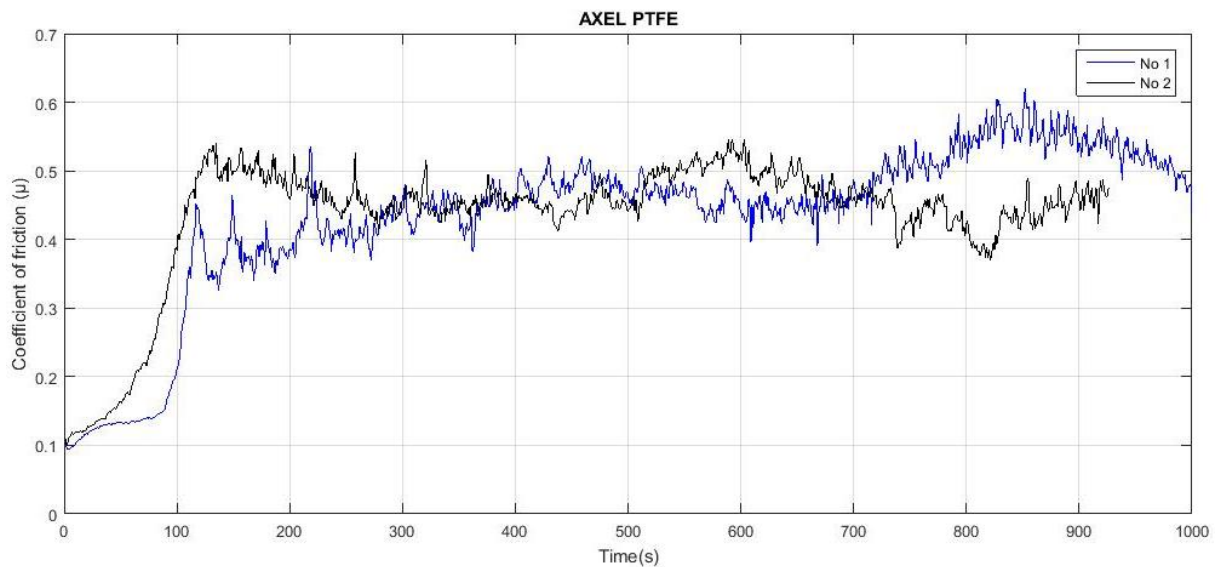


Figure 39 - Results from ball on disc tests on Axel PTFE in transformer oil

There was a somewhat larger spread between the two measurements on Fomblin, see figure 40. During the first 150 seconds, the coefficient of friction increased continuously for both No 1 and No 2. But the curves tend to reach different coefficients of friction over time. However, the values for both No 1 and No 2 are lower than the values in figure 38.

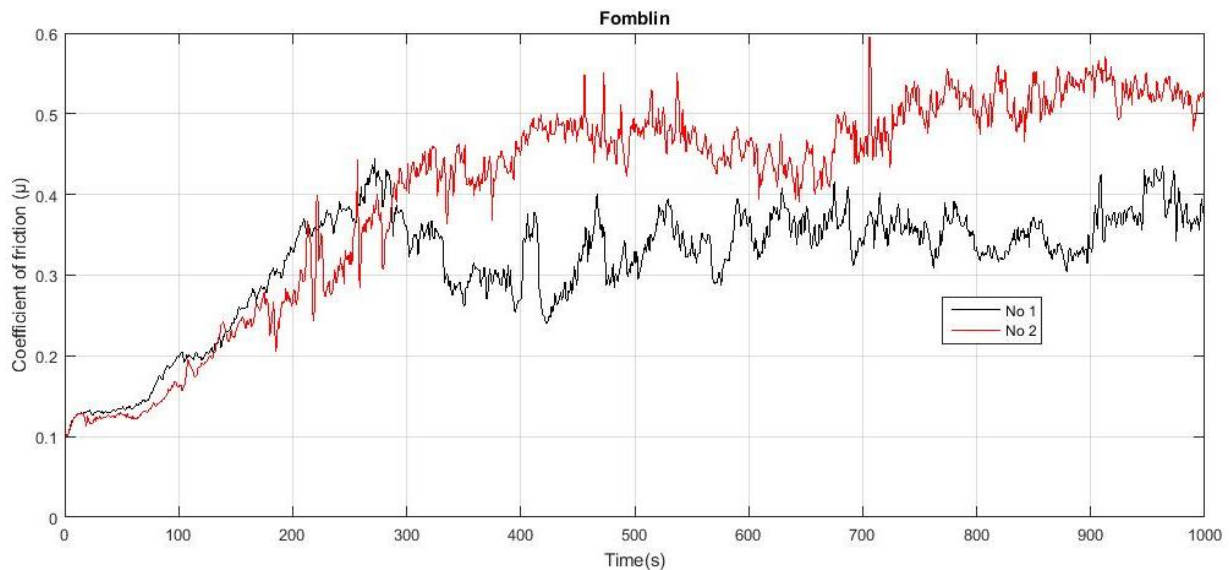


Figure 40 - Results from ball on disc test on Fomblin in transformer oil

In conclusion, both greases seem to give rise to more favourable conditions for the steel-to-steel contact, resulting in a lower coefficient of friction than the same test on a non-lubricated plate.

In order to better understand what happens after a long period of time, the same tribology test was performed during a longer period of time for both greases. These tests were only performed one time for Fomblin and one time for PTFE AXEL. The results are presented in figure 41 and 42.

The results from Fomblin 1h (see Figure 41) is rather startling, it seems like the friction goes up rather quickly and then decreases to extremely low values, corresponding to a coefficient of friction in a lubricated contact. Perhaps this means that Fomblin re-enters the contact after approximately 750 seconds. Another hypothesis is that PTFE particles are pushed into the interface, resulting in a low friction lubricated film. However, it should be noted that this test was performed once and therefore might not be representative. What is interesting is that the first 600 seconds corresponds quite well to the obtained results in Figure 40.

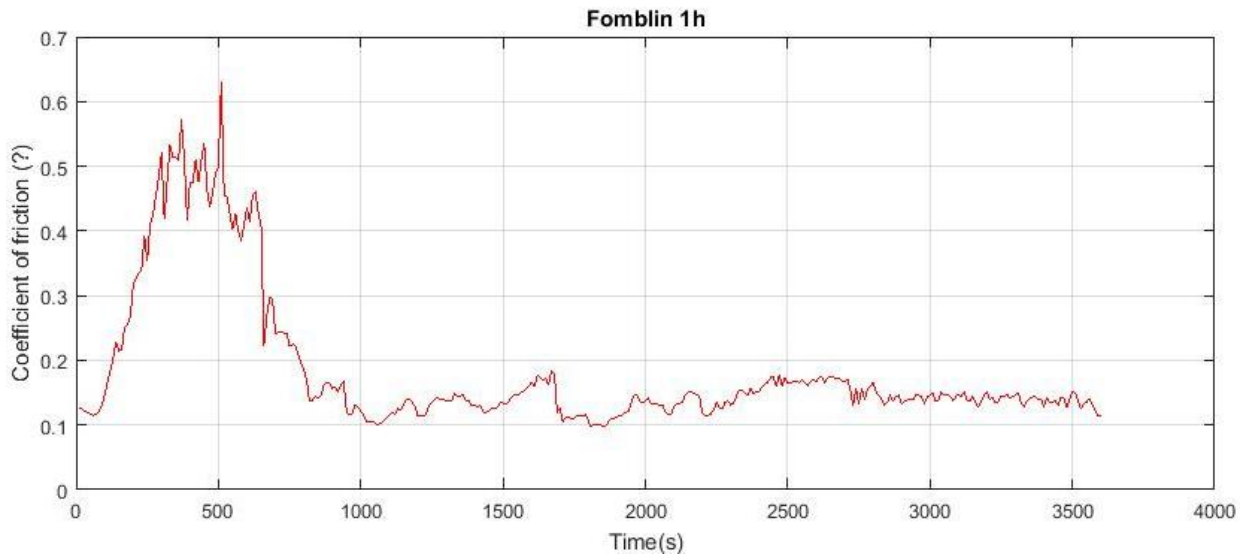


Figure 41 - Results after 1 hour on Fomblin in transformer oil

The results from 1-hour tribology testing on PTFE AXEL are presented in Figure 42. The coefficient of friction shows a much more irregular behaviour in this test, and it reaches higher values than in Figure 39. There might be some type of irregularity in the steel plate or other conditions causing these results. The test needs to be performed a couple of more times in order to get a reliable trend.

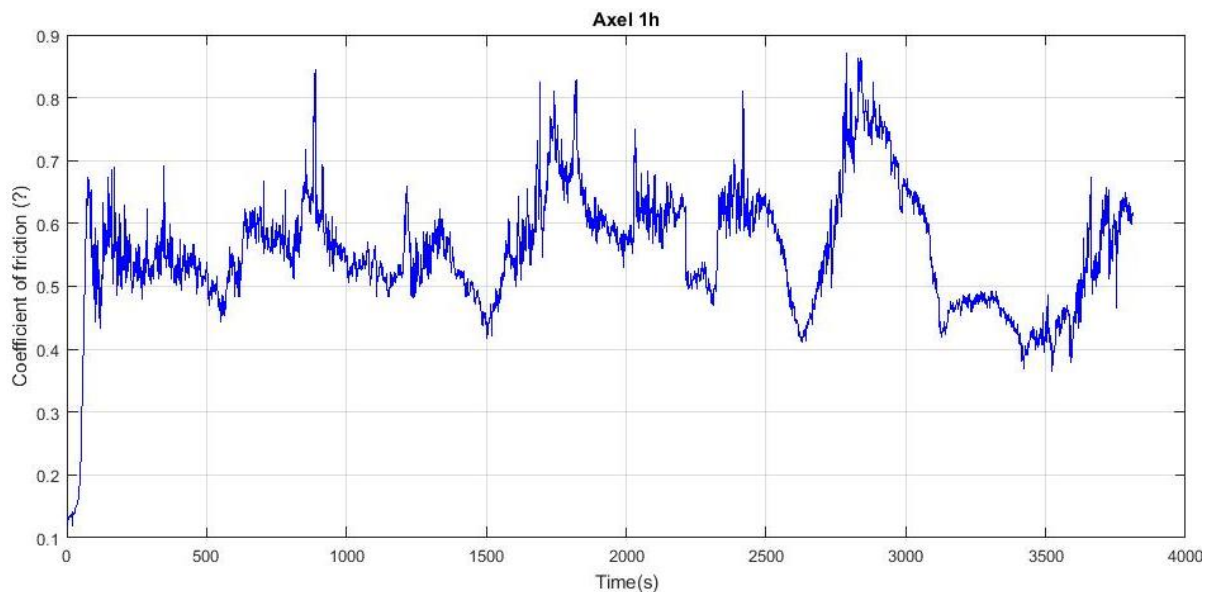


Figure 42 - Results after 1 hour on AXEL PTFE in transformer oil

In conclusion, both AXEL PTFE and Fomblin seem to create more favourable conditions for the steel contact. Although, a couple of more tests on both short and long term behaviour are needed in order to better understand how the grease behaves in the contact. The steel surfaces could be examined to understand how the greases behaved in the contact. It would also be interesting to do tribological tests with different loads.

5.6 Vapour phase dehydration

The visual results after treating Fomblin and AXEL PTFE in the vapour phase dehydration process are shown in Figure 43. Grease AXEL PTFE did not seem to be affected by the vapour phase process. However, Fomblin was no longer a grease but a white powder. The reason for this could be that Fomblin contains additives that are activated when exposed to this type of conditions.



Figure 43 - Results after vapour phase. Left: AXEL PTFE, Right: Fomblin

5.7 Oil analysis - Tan delta and surface tension

Results from tan delta and surface tension methods are presented in Table 3. The following conclusions can be drawn; neither Fomblin nor PTFE AXEL affects the performance of the transformer oil. In other words, both Fomblin and PTFE AXEL can be used in tap-changers.

Table 3 - Results from tan delta and surface tension measurements

Test object	Dielectric loss factor at 90°C	Surface tension against water at 25°C	Appearance
Oil with Fomblin	0.3×10^{-3}	45	No changes
Oil with AXEL PTFE	0.3×10^{-3}	46	No changes
Reference oil	0.3×10^{-3}	46	No changes
Requirements	Value $< 5 \times 10^{-3}$ Max allowed increase (from reference): 3×10^{-3}	≥ 30	No changes

5.8 Tribological test after vapour phase dehydration

Since Fomblin became pulverized after the vapour phase dehydration process and tribology tests could not be performed. Results from tribology test on AXEL PTFE are viewed in Figure 44. What can be seen is a low friction in the beginning, but with time, it increases continuously. This type of behaviour was not seen previously, on tests prior to vapour phase treatment. It should be noted however that these tests were performed on a new type of steel plate, with a different roughness and hardness than before.

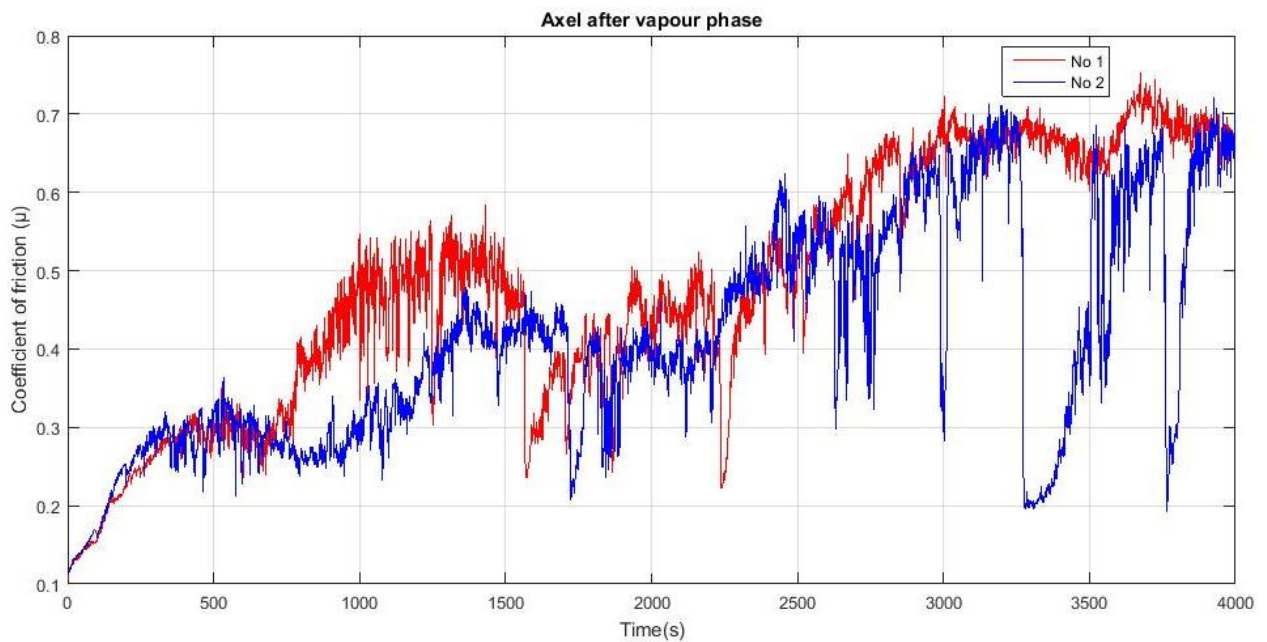


Figure 44 - Results on AXEL PTFE after vapour phase testing

6. Conclusion

In conclusion, successful results were obtained, showing that there are greases that do not dissolve in transformer oil. Results from tribological tests show a decrease in the coefficient of friction. If further studies are made on how to optimize certain ingredients in the grease for this specific purpose, there is a big chance that an even more successful candidate will be found. More conclusions drawn from this work are:

- Greases containing mineral base oil dissolve in transformer oil, due to the chemical similarity base oil being similar to transformer oil. The thickener however, does not seem to dissolve in the transformer oil, according to FTIR analysis.
- Type of thickener influences the affinity for the metal surface. Calcium-sulphonate thickened grease gave the best results, with a high affinity for the metal surface.
- Teflon greases are inert towards transformer oil, both in appearance and from oil analysing tests.
- The results obtained from the tribological test (ball on disc), shown a decrease in the coefficient of friction when using AXEL PTFE and Fomblin. Slightly lower values were received with Fomblin.
- Fomblin did not withstand the vapour-phase dehydration process. AXEL PTFE was intact in its appearance, but the results from tribological tests are different from before the vapour-phased dehydration process.

For further studies

- Results from a long-term test with PTFE AXEL grease in a tribological contact, for example a worm gear, would be a natural continuation of this project.
- The surfaces from the tribological tests could be examined further; in order to better understand how the PTFE greases affects the interface.
- A wide selection of PTFE greases could be examined in order to custom fit a specific PTFE-grease for this application.
- The successful results from the compatibility test in glycol oil opens up a possibility to investigate greases with polar base oil, for instance glycol oil. For this approach it would be interesting to use thickeners that have shown high affinity for the metal surface in transformer oil, for example calcium-sulphonate thickened grease. Another choice of thickener could be a polymer thickener.
- Since the presence of PTFE grease in transformer oil does not affect the cooling or insulating properties, the possibility to apply PTFE tribocoatings could be examined.

References

1. **S.A.Khparde, S.V.Kulkarni.** *Transformer Engineering – Design and Practice.* s.l. : CRC Press , 2004.
2. *A statistical approach to processing power transformer failure data.* **Rogier Jongen, Peter Morshuis, Johan Smit.** 546, Vienna : CIRED, 2007, Vol. 1.
3. *Kompositmaterial – Fiberkompositer med ökad mekanisk och elektrisk prestanda för lindningskopplare.* **Anders Strömbeck, Tommy Larsson.** 1999, ABB Tidning nr 5 , pp. 38-42.
4. **Marika Torbacke, Åsa Kassman Rudolphi, Elisabet Kassfeldt.** *Lubricants – Introduction to Properties and Performance .* Chichester : John Wiley, 2014. pp. 54-55.
5. *New Method of simulation to Evaluate the Sensitivity to Oxidation of Lubricating Oils: An Aging Cell Coupled with Fourier Transform Infrared Spectroscopy .* **Priéri F, Gresser A, Le Dréau Y, Obiols J, Kister J.** 2008, Applied Spectroscopy, pp. Vol. 62, pp. 810-816.
6. **Mathae, Jean.** *Components.* Ludvika, 10 03 2016.
7. *The influence of bearing grease composition on friction in rolling/sliding concentrated contacts.* **Nicola De Laurentis, Amir Kadiric, Piet Lugt, Philippa Cann.** 94 pp.624-632, London : Tribology international, 2015.
8. *Modern advancement in lubricating grease technology.* **Lugt, Piet M.** 2016, Tribology International 97, pp. 467-477.
9. **Mathae, Jean.** *Components.* Ludvika, 01-04-2016.
10. **Larsson, Thomas.** *Principle Engineer.* Ludvika, 01-04-2016.
11. **Ferm, Linda.** *Power Grids / Power Transformers.* Ludvika, 16-03-2016.
12. *Oil/Thickener Interactions and Rheology of Lubricating Greases.* **Salomonsson L, Stang G, Zhmud B, Ab Nynas Petroleum,.** 3, pp. 3029-309, Nynäshamn : STLE Tribology Transaction, 2007, Tribology Transactions, Vol. 50, pp. Vol. 50 pp. 302-309.
13. **Ishchuk, Yu.L.** *Lubricating Grease Manufacturing Technology.* s.l. : New Age International, p.3, 2005.
14. *Robsut Polyurea Grease for Wide Range of Industrial Applications .* **Anoop Kumar, Steve Humpreys, Bill Mallory.** Tulsa : Royal Manufacturing Co. LP.
15. **Constantin Madius, Willem Smets.** *Grease fundamentals - Covering the basics of Lubricating Greases.* NOL : Axel Christiernsson, 2015.
16. *On the film thickness behaviour of polymer greases at low and high speeds.* **David Gonçalves, Beatriz Graça, Armando V. Campos, J. Seabra, Johan Leckner, René Westbroek.** 2015, Tribology international, Vol. 90, pp. 435-444.
17. **G.Gow.** *Lubricating Grease.* [book auth.] M.F. Fox, S.T. Orszulik R.M. Mortier. *Chemistry and Technology of Lubricants.* 3rd. New York : Springer, 2010, pp. 420-421.
18. *Calcium Sulphonate Greases.* **Fish, Dr. Gareth.** 16, Wickliffe : AXEL Christernsson, White paper Lubrisense, 2014.
19. **J.M.G Cowie, Valeria Arrighi.** *Polymer: Chemistry and Physics of Modern Materials.* Boca Raton : CRC Press, Taylor & Francis Group, 2007. 978-1-4200-0987-3.
20. *Evaluation of different polyolefins as rheology modifier additives in lubricating grease formulations.* **J.E. Martín-Alfonso, C. Valencia, M.S. Sánchez, J.M. Franco, C.Gallegos.** 2011, Materials Chemistry and Physics, pp. Vol. 128 pp. 530-538.
21. **Ellervik, Ulf.** *Organisk Kemi.* Lund, 2009.
22. **Hansen, Charles M.** *Hansen Solubility Parameters - A user's handbook.* Boca Raton : CRC Press LLC, 2000. 0-8493-1525-5.
23. **Bruce, Robert W.** *Handbook of Lubrication and Tribology Vol. 2, chapter 28.5.1.* s.l. : CRC Press., 2012.

24. *Polyalphaolefins, Radiolysis of synthetic Oils Based on polyalphaolefins.* **A.Olejniczak, A.G.Shostenko, S.Truszkowski and J.Fal.** 2008, High Energy Chemistry, pp. Vol.42 9.92-94.
25. **M. Brown, J.D. Fotheringham, T.J. Hoyes, R.M. Mortier, S.T. Orszulik, S.J. Randles and P.M. Stroud.** Synthetic Base Fluids. [book auth.] M.F. Fox, S.T. Orszulik R.M. Mortier. *Chemistry and Technology of Lubricants.* New York : Springer, 2010.
26. **Tocci, Lisa.** Building a better base fluid. *Lubes 'n' greases magazine.* November, 2013.
27. **Liu, Bharat Bhushan and Huiwen.** Nanoscale Boundary Lubrication Studies. [book auth.] Bharat Bhushan. *Nanotribology and Nanomechanics: An introduction.* Berlin : Heidelberg, 2008.
28. *Formulation, rheology and thermal ageing of polymer greases-Part I: Influence of the thickener content.* **David Gonçalves, Beatriz Graca, Armando V. Campos, J.Seabra, Johan Leckner, René Westbroek.** 2015, Tribology international, pp. 160-170.
29. *Thermal Degradation of Greases and the Effect on Lubrication Performance.* **S. Hurley, P.M. Cann, H.A. Spikes.** pp. 75-83, London : Elsevier Science B.V., 1998.
30. **International, ASTM.** www.astm.org. [Online] 01 01 2014. [Cited: 18 03 2016.] <http://www.astm.org/Standards/D4425.htm>.
31. *Rheological Behaviour of Greases: Part II - Effect of Thermal Aging, Correlation with Physico-Chemical Changes.* **I. Couronne, P. Vergne.** 4, pp. 788-794, Villeurbanne Cedex : Tribology Transactions, 2000, Vol. 43.
32. *Lubrication and Reflow Properties of Thermally Aged Greases.* **S. Hurley, P. M. Cann, H.A. Spikes.** 2000, Tribology Transactions, pp. Vol. 43 pp. 221-228.
33. mmrc.caltech.edu. *mmrc.caltech.edu.* [Online] Thermo Nicolet Corporation, 2001. [Cited: 29 04 2016.] <http://mmrc.caltech.edu/FTIR/FTIRintro.pdf>.
34. **Staffan Jacobson, Sture Hogmark.** *Tribologi-Friktion Smörjning Nötning.* Uppsala : Ångströmlaboratoriet, 2011.
35. *Effect of Loads on Other Key Factors on Oil-Transformer Ageing: Sustainability Benefits and Challenges.* **Radu Godina, Eduardo M.G.Rodrigues, Joao C.O.Matias,Joao P.S.Catalao.** 2015, Energies, pp. 12148-12149.
36. **Olsson, Karl-Olof.** *Maskinelement.* Stockholm : Liber, 2006. pp. 160-162.
37. **Krainer, Per.** *Transformers, ABB.* [interv.] Anna von Krusenstierna. 10 03 2016.
38. **Braithwaite, E.R.** *Solid Lubricants and Surfaces .* s.l. : Elsevier Ltd., 1964. chapter 6, p.664.
39. **Jawad Faiz, Behzad Siahkolah.** *Electronic Tap-changer for Distribution Transformers.* New York : Springer, 2011. pp. 1-3.
40. *White Paper Lubrisense - Polymer Thickened Lubricant.* **Jacobson, Emeritus Bo.** Nol : AXEL Christiernsson AB, 2007, Vol. 07.