

Publication

“THE RHEOLOGY OF LUBRICATING GREASE”

This book has been compiled by Professor Corneliu Balan from “Politehnica” University, Reorom, Energy Faculty, Hydraulics Department, Rumania, and a team of Grease Specialists at the ELGI. It contains chapters on the following subjects:

- ❖ Rheometry of Viscoelastic Materials:
 - General Concepts
 - Constitutive Modelling of Lubricating Greases
 - Influence of Geometry in Rotational Rheometry
- ❖ Dynamics of Lubricating Greases in Simple Shear Motions
- ❖ Lubricating Grease flows in Journal Bearings - Numerical Simulation
- ❖ Lubricating Grease Rheology Visualised by:
 - Nuclear Magnetic Resonance Imaging
 - Reflecting Tracer Imaging

The book puts forward theoretical hypotheses on which some of the rheological properties of grease can be based. It considers experimental work using rotational rheometry to investigate the effect of surface finish at the boundaries in plate - plate and cone - plate geometries and the effect of the gap size between the rotating surfaces. Mathematical expressions are developed to give a basis for grease flow in small gaps and are used to compare the mathematical model to the analytical models for flow in Journal Bearings.

The use of NMR and Reflecting Tracer / laser beam techniques are described to facilitate the visualisation of velocity gradients in a gap under shear conditions demonstrating the occurrence of "wall slip" & regions of constant velocity.

A comprehensive list of references is included for each topic together with an introductory overview of grease composition and properties relating the conventional analytical testing to its performance in the field and to the relationship to its rheology.

Introduction to Rheology of Lubricating Grease Publication

Chapter 1.

Introduction

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1.1. The History and Future of Lubricating Grease

Lubrication has been necessary since the very dawn of human beings becoming intelligent enough to use tools with moving parts. When humans started moving things around, should it be stone blocks to build a pyramid or using a wheel-cart for transportation, a **DE4S** [pronounced "de-force"] (*Dynamic Energy Saving Shearable Surface Separator*), or in other words; a lubricant was needed to reduce the effort. Today lubrication of rolling and sliding parts in a construction is very much taken for granted. The principles of how lubricants work is unknown to most people. It can also be presumed that the first practical application of lubricants was a coincidental discovery and not a direct innovation.

As long as the speeds were low, simple vegetable oils or fats, sometimes even crushed snails, were sufficient for the friction reduction, if ice, snow or water did not already provide the necessary slipperiness.

Over time, many developments have been made to improve transportation, but less to develop lubricants to meet their new demands. From the day of the first steam engines, lubrication has become even more important, the choice of the correct lubricant more difficult and the required lubricant properties more comprehensive.

The future will put ever-increasing demands on long life, higher speed, higher running temperatures and compatibility with the mechanical seals and the global environment. There is a great challenge for lubricating grease developers to find new products that will meet these requirements. This will be accomplished not only by the use of new types of materials but also by new and scientific ways to determine the necessary properties and abilities of modern lubricating greases thus allowing the phasing out of products no longer able to meet the requirements. Fundamental research that can describe the basic principles of lubrication is still just in its infancy and is a great challenge for current and future researchers.

Conservative thinking within our business mitigates against change even though some specific types of lubricating grease are reaching the end of their useful life. Replacement of old conventional water-stabilised calcium greases is still a pending issue. If life cycle graphs for the product types were more frequently used within the business, it can be assumed that the actors in the market would get a rude awakening.

Many improvements have been made to the original concepts of lubricating greases, but few, if any, real innovative "jumps" in the technology can be found. Since the early days of Clarence E. Earle's introduction of

the lithium greases [1], and especially when in combination with 12-hydroxy stearic acid as the anion, only the so-called complex greases are evidence of any innovation in the business. The rest can better be described as *incrementalism*. Such an amelioration process is often driven by cost factors and availability of raw materials, rather than by a targeted development driven by fundamental research.

Development is also normally made by "trial and error" since the complex nature of lubricating greases is little understood and only a scarcity of fundamental knowledge about the chemistry and physics is accessible.

Even worse, most of the test methods used today are of poor precision and often have little or no correlation to real life applications. A scientific approach to the use of products based on thickener technology has made it possible to develop many new and reliable products within many other business areas: polymers, cosmetics, paints, drugs and medicines, to mention a few examples of materials not too far removed from lubricating greases.

The use of the cone penetration test method to measure the consistency of lubricating greases and to try to find correlation to the actual rheological behaviour of a product is like trying to life-save a dying fish by the mouth-to-mouth method.

The best way to get a description of consistency would be to use a direct rheological determination of the yield stress value, preferably within a period that correlates to practical use of lubricating greases. The yield stress is also a possible value that could be used as a so-called *engineering value*. A value that is specific for certain types of materials and can be used for the selection of the right product for a given application by itself or, more likely, in combination with other *engineering values*. Engineering values are frequently used in many areas of material specifications, lubricants not excluded.

For a long time, the oil industry has been using specifications like SAE and ISO VG classes to simplify recommendation of appropriate oils for specific applications. A lot of effort has been spent on attempts to make a workable classification system for lubricating greases, so far without too great a success. The complexity of lubricating greases is definitely not best defined by empirical tests and the derived data put into a simplifying table. To make it possible to specify engineering values for lubricating greases, an understanding and determination of fundamental physical properties must first be established. The common resistance to change within our business is understandable considering the complex nature of lubricating greases. If it is difficult to specify the real scientifically derived criteria, it is easy to stick to a set of empirically derived criteria that seem to fit for a given application. In practice, this way of reasoning will create problems for the user since it does not take into consideration the actual application parameters and the complex rheological and tribological behaviour of grease.

Lubrication is of utmost importance in modern society, not least in the impact on the natural environment. The use of proper lubrication will not only reduce costs, but also effect the natural environment in a positive way. The contrary is of course also true. Demands for lower energy input when using a *Dynamic Energy Saving Shearable Surface Separator*, longer lifetime of machinery and the more efficient use of existing

equipment, will all contribute to both the World Economy, as well as to a slower consumption of the non-renewable resources of ore and oil.

By using an appropriate lubricant in any given application, the demand for the energy needed to drive the equipment can be reduced and the machinery can give a higher reliability (less standstill time for maintenance and unexpected breakdowns). The lifetime will be appreciably extended and effective output of the equipment increased. There have been calculations made, which show that billions of dollars in savings every year could be made by changing to the appropriate lubricant for currently running equipment.

Most lubricants are fluids, and most commonly, they are refined fractions of mineral oils. The yield of lubricating oils from crude oil is about 3%. Today more highly refined and hydrotreated mineral oils are used. The polyaromatic compounds have been reduced to levels that, for the moment, are more environmentally acceptable. The development of new technology has increased the need for lubricants that can operate at higher speeds, loads, temperatures and more difficult surrounding environments for an increasingly longer lifetime.

These demands sometimes exceeding the capabilities of mineral oils opening up the use of polyalphaolefins, esters, polyethers and other types of synthetic lubricating fluids. Unfortunately, lubricants in general and lubricating grease in particular are considered as low price products. The volumes required, often lasting for the whole lifetime of the equipment are normally very small particularly for lubricating grease. The cost in comparison with the overall operating expenditure is therefore often negligible. In some cases the volumes needed to ensure adequate lubrication is higher than necessary because an inappropriate product are chosen.

Some suppliers of lubricants provide mainly the lubricating fluids and are not aware of the potential and the shortcomings of lubricating greases. All too often, lubricating greases are looked upon as thick oils, a perception that will inevitably lead to problems in application and in pricing.

Lubricating greases can act as problem solvers. They are very "forgiving" because of certain properties they possess. The bulk form keeps the lubricant in place, without any auxiliary equipment needed to feed the lubricant to the application point (except for occasional replenishing). When using a lubricating grease, the fluctuations in temperature, loads, vibrations and surrounding environment conditions, within reasonable limits, can all be handled by just one type of product. The matrix of the bulk lubricating grease can absorb contaminants, such as particles and water, in relatively high amounts without a reduction in its lubrication properties. This is possible since only a small part of the lubricating grease is taking part in the lubrication, with the larger part acting as a seal. The solid state of the grease simplifies the choice of conventional seals and helps to keep contaminants from penetrating into the surfaces that are to be lubricated. This not only prevents detrimental particles getting access to the surface but also gives good protection against corrosion. When required by the surrounding environment, additional components can be added to reinforce the corrosion protection properties.

The ability to keep solid contaminants within the bulk and prevent them from reaching the lubrication point excludes the need for costly filtering equipment as needed for lubricating fluids.

The matrix of a lubricating grease also makes it possible to include solids in the composition, without any fear of solids settling when in a static condition. The use of additives not soluble in the lubricating fluid is even beneficial as such additives will have a better chance of reaching the metal surface to be lubricated.

The bulk surrounding the lubrication contact can act as a reservoir for replenishment. If grease starvation in the contact zone occurs, the frictional heating increases and the flow of new grease into the contact zone is possible. Vibration, should the frequency and amplitude be high enough, can also make lubricating grease slump into the contact zone.

Considering all said above, lubricating greases should be regarded as high technology products, but this is often not the case.

Since the beginning of the 50's, so called *multi-purpose greases* have been available. These are lubricating greases that can meet most lubrication demands and is true, in about 80% of all applications. With the increasing technical development of applications, this figure is diminishing and more often *special greases* are needed. The use of commodity, relatively simple lubricating greases manufactured in large volumes is decreasing and forcing the producers to close down unprofitable manufacturing units. This is especially true in Europe, while in other parts of the world simple commodity products can adequately maintain the new markets and/or differences in application technology.

The increasing demand for special lubricating grease stress the need for appropriate and reliable methods and equipment to test and control the special properties required. The test methods used today were developed many years ago and often modified from oil test methods (also old and sometimes obsolete). Almost all of the available test methods have poor precision, compared to modern analyses available in other business areas. The major reason for this is a more or less fruitless effort to measure the complex behaviour and composition of lubricating greases (together with a general constitutive relationship for the material) by the use of cheap and simple empirical tests.

There is also a trend to internationally standardised test methods. The criteria to be met in such Standards, especially the demand for an established precision, are necessitating improvements to the test methods in use.

All measurements, whatever is measured, are erroneous, but by eliminating all systematic errors, it is possible to achieve acceptable precision for a well thought out test method. This has to be consistent with a theoretical model in the frame of a scientific theory. If the number, or sizes of random errors, impact unacceptably on the precision, assuming systematic errors are eliminated, the test method may be impossible to use. In such cases, a new test method must be developed.

The resources available for the development of new and improvement of older test methods are today very limited. The Standards organisation bureaus carry out a large part of this work, with little or no contribution

from academia or equipment manufacturers. Merging of companies within the business is not improving the situation since there will be fewer representatives participating in Standards work and an overall loss of expertise and commitment.

The CEN and ISO organisations are not principally involved in development of new test methods, but rather for examination and approval or disapproval of existing ones. If this trend continues, a severe lack of truly standardised test methods will create serious problems within the near future. This would pose problems for all parties involved, since there would be arguable ways to define what, and how, to measure lubricating grease properties.

This book attempts to give a basic understanding of the possibilities that can be realised by the use of grease rheology. A lot of practical development work, however, still lies ahead before a clear understanding can be achieved. As will become clear for the reader, the use of rheology is fundamental for understanding the physical properties of lubricating greases. [2],[3],[4] In combination with other sophisticated analyses, the structure and interaction with incorporated lubricating fluids can be investigated and understood. It is essential for future research to use a multi-disciplinary approach with tribologists, rheologists and chemists working closely together. A rule of thumb used by many chemists in particular, is that "like dissolves like", indicating a complex co-operation between many different sciences to solve the complex nature of lubricating greases.

1.2 What is a Lubricating Grease?

Definition

The American Society for Testing and Materials (ASTM) defined lubricating grease as:

"A solid or semi-fluid lubricant consisting of a thickening agent in a liquid lubricant. Other ingredients imparting special properties may be included".

This definition describes the major components in lubricating grease and has been used since 1955, but nothing is mentioned about the required properties or how it will work.

In 1952 Vold and Vold [5] suggested a different and more practical definition:

"A grease is a lubricant which has been thickened in order that it remain in contact with the moving surfaces and not leak out under gravity or centrifugal action, or be squeezed out under pressure. Thus, a major practical problem is the provision of a structure that will stand up under shear and at all temperatures to which it may be subjected during use. At the same time the grease must be able to flow into the bearing through grease guns and from spot to spot in the lubricated machine as needed, and must not of itself add significantly to the power required to operate the machine, particularly at the start. This is an exacting set of rheological requirements".

Already in the 1950's people were aware of the need to describe lubricating grease by their rheological properties.

Even in 1937 Klemgard wrote [6]

"Incidentally, flow studies of grease at various shear rates and temperatures are of considerable value in predicting service performance".

More recently, in 1974, Sinitsyn [7] suggested a new definition of lubricating grease incorporating the rheological properties.

"A grease is a lubricant which under certain loads and within its range of temperature application exhibits the properties of a solid body, undergoes plastic strain and starts to flow like a fluid should the load reach the critical point, and regains solid-body properties after the removal of the stress".

Altogether these attempts to define lubricating greases, among many others, try to give a picture describing lubricating grease as a multiphase product with a complex rheological behaviour. Since there are no clear limits differentiating today's fluids (for example, many motor oils contain dispersed polymers for improvement of viscosity behaviour), an exact and clear definition might be impossible to give.

Lubricating grease is maybe best described as a thickener or gellant diluted by a lubricating fluid. To improve certain properties and functions, additional components are sometimes included (often called "additives"). This controversial way to define the thickener as being diluted by a lubricating fluid, rather than the more common way to describe it as thickening the fluid, comes from recent research. This work shows the active part, the gellant, at least when being a metal soap, takes in the actual lubrication contact zone (see next chapter for more information).

Lubricating grease properties depend on both its composition and the manufacturing process used. The actual possible compositions and the different available processes are too large a subject to be covered within the scope of this book, but the generalised principles are given below.

1.3 Composition

To give a complete description of possible compositions of lubricating greases is far beyond the scope of this book but can be found elsewhere. [8],[9] This contribution will only cover the general aspects and principals, without focusing on any specific details.

The most common composition of a lubricating grease is a Lithium-12-hydroxy stearate thickened mineral oil with anti-oxidant(s), anti-corrosion and extreme pressure (EP) improving agent(s) added. Several other metal cations are used; Calcium, Aluminium, Sodium and Barium being the more common metals.

Whilst 12-hydroxy stearic acid, in its refined fatty acid form or as the triglyceride (hydrogenated castor oil), is the most commonly used anion, several other anions are used. Tallow, lard, stearic acid, oleic acid and many other fatty acids or fats are used either as the major anion or as modifiers for the desired soap structure.

When combining different types of anions, normally diacids like acetic, adipic or azelaic acid, with the same metal cation, so-called complex greases are formed.

By the use of different types of metal cations, but with one major type of anion, so called mixed base greases are formed.

Mineral oils are the most common base fluid for lubricating greases, even though synthetic fluids like polyalphaolefines and synthetic and natural esters are gaining importance every year. Other types of synthetic fluids seem to play a minor role and are mostly used for very special applications

The use of esters from natural sources is increasing due to environmental concern encouraging the use of raw material from renewable sources. Refined rape seed, sunflower and corn oils have already been introduced in the market and more types are expected in the future

Additives are often, although not always, used in lubricating greases. Typically, antioxidants, corrosion inhibitors, anti-wear and EP agents are added. Solid lubricants (usually graphite or Molybdenum disulphide), metal deactivators and polymers are also examples of additives used in lubricating greases.

1.4 Typical Processes

There are two main processes used for producing lubricating grease:

- i. Lubricating Grease with the soap thickener produced *in situ*, within the desired lubricating fluid (Table 1)
- ii. Lubricating Grease with a pre-made soap thickener or inorganic thickener added to the lubricating fluid. (see Table 2)

Table 1

Lubricating greases with soap thickener produced *in situ*, within the desired lubricating fluid

Saponification of		
Glyceride fats or other fatty acid esters	Fatty acids	Mixtures of fatty acids and glyceride fats or other fatty acid esters
Dehydration		
Dissolution or heating to phase transition of soap crystallites in oil		
Cooling and crystallisation of the soap		
High shear treatment for distribution of agglomerates		
Adjustment of consistency and additivation		

Table 2

Lubricating greases with pre-made soap thickener or inorganic thickener added to the lubricating fluid

Mixing with low or moderate shear	Mixing with high shear
Dissolution or heating to phase transition of crystallites	Activation by alcohol or water
Cooling and crystallisation	
High shear treatment for distribution of agglomerates	
Adjustment of consistency and additivation	

The process described in Table 2 often gives products with less mechanical and thermal stability when compared to products produced by the process in Table 1.

Both processes for soap thickening involve a step which includes a tempering of the soap in oil mixture until a phase transition into a waxy phase is achieved. If it is only necessary to reach this phase shift and the cooling step takes place in the same way, similar product properties should be expected whichever process was chosen. This does not seem to be the case, since products made from pre-made soap exhibit a less stable structure

It is the authors belief that small quantities of water or other strongly polar components are needed to achieve a mechanically and thermally stable product. The amounts of polar component can be very low, in parts per million, but are necessary for hydrogen "bridging" of the soap molecules.

When comparing the processes in Table 1 and Table 2, the only difference is in the actual saponification step, which can be done in a humid environment or at least form water in the actual reaction. The water formed during the saponification reaction might be enough to get some stability to the structure, but it is widely accepted to use additional water in the saponification process to get a repeatable and stable product.

Before the introduction of 12-hydroxy octadecanoic acid, or 12-hydroxy stearic acid, most lubricating greases made needed a small amount of water if a structure was to be formed at all. Water stabilised soap structures are still needed for conventional Calcium greases, and is the reason for their limited application temperature range (water evaporating from the grease at temperatures around 50°C). If the stabilising water content exceeds a lower critical limit, the whole structure collapses, and this is commonly known as the "mayonnaise effect".

The structure forming or the actual structural composition is far from, if at all, known or understood. Practice, in combination with "trial and error", have given the "rules" of manufacture from the differing raw materials that can be used in lubricating grease. The structure formed can be both tough and sensitive at the same

time, having an ability to "heal" when sheared repetitively for a long time at the same time as being sensitive to contaminating chemicals like strong alkalis or acids. Ionic detergents also have a detrimental effect on soap thickened lubricating greases, as is their intended effect, to degrease. The use of sodium cations for ion exchange of the soap thickener will result in a water-soluble soap. Detergents that are free of metal ions can still detrimentally affect the lubricating grease thickener, in very much the same way as when adding certain types of additives in relatively large quantities, especially other types of soaps. Such incompatibility is also found for mixtures of fully formulated lubricating greases and can lead to serious problems in real life applications. The mechanisms for this are not understood but might involve changes in solubility parameters as well as destabilising effects on the structure.

1.5 Chemical Characteristics

The analysis of lubricating grease is often very complicated, not the least for chemical analysis. Many chemical analyses are made either in a water environment or postulate that the specimen is fluid. The use of "wet" chemistry analyses is very limited and the thickener structure makes it impossible to feed the untreated product into sophisticated analysis tools like chromatographs.

Since lubricating greases are supposed to withstand water spray off and the thickener is insoluble in most solvents, it is difficult to dilute the product without affecting the composition. One of the few chemical analyses that can be used for investigation of the untreated product is Infra-red (IR) Spectrometry, especially with the introduction of the more sensitive Fourier Transformation evaluation of the received signal. The test is normally qualitative although quantitative measurements are possible. Conventional salt crystal windows (in a detachable cell) or the use of ATR (Attenuated Total Reflectance) are both feasible, ATR being better for very dark or opaque samples.

The resulting spectrum can be compared to a known reference or references, analysed by comparison of peaks known to be typical for certain compounds. The principal for IR spectrometry is the stretching, bending or vibrating response of molecular bonds at different energies. Different types of functional groups having a unique response pattern. This shows clearly the physical response, although the test is normally considered to be a chemical measurement (detecting type of compounds present in a sample). The limits between the physical and chemical tests are sometime very diffuse!

When investigating a complex mixture of many different compounds, as for instance a mineral oil, the responses normally overlap and make the interpretation of individual compounds very difficult. This is widely accepted and does not diminish the use of the test at all, something worth considering when judging rheology for determination of physical properties of lubricating greases. The use of IR spectrophotometry is an excellent qualitative test, with only a very small quantity of sample required, short test time and simple cleaning of the test cells.

Atomic Adsorption Spectrometry, Inductive Coupled Plasma Spectrometry and different types of X-ray techniques are used for investigation of composition and reaction products for fresh and used lubricating

greases. All these techniques are labour and competence intensive. The equipment is often expensive and the methods are therefore seldom found in outright grease laboratories, although they are frequently used in oil laboratories.

Chemistry is important in formulating greases and for understanding the process reactions, for instance during saponification. Additive chemistry is of course also important and must be known by lubricating grease developers, but the true knowledge and research is covered by additive suppliers worldwide. A close co-operation between lubricating grease manufacturers and additive suppliers is necessary in order to develop novel lubricating greases with improved flow properties. The chemistry of lubricating fluids is another field, and this is covered by the fluid suppliers. For the lubricating grease developer, it is necessary to have a broad knowledge about all these areas of chemistry, but the developed product must fulfil demands that are more or less only of physical character. A multi-disciplinary approach is therefore necessary.

Physical characteristics

Lubricating greases are thickened lubricating fluids, not thick (in the meaning of high viscous) lubricating fluids! Alternatively, more accurately lubricating greases are diluted thickeners. This can be justified since it is known that the thickener can contribute to a great deal in **DE4S** actions. Soap-thickened oil can have a lower friction coefficient compared to the base oil included!

Ideally, the thickener improves the lubricating properties, by building a thicker film at the lubricated surfaces than can be achieved with the included fluid alone. At the same time, it is necessary to have lubricating grease that can replenish itself into the contact area through microscopic flow behaviour.

The film thickness is directly dependent on the viscosity and the resistance to flow at actual shear rates, dependant on pressure and temperature. The film thickness in a lubricated contact is determined by the lubricants viscosity in the inlet region of the contact at atmospheric pressure, as well as the value of the pressure-viscosity coefficient to describe the viscosity variation in the Hertzian pressure region.

To measure the rheological properties at very high pressures (up to 1 GPa) and at very high shear rates ($\dot{\gamma} > 10^9 \text{ s}^{-1}$) are challenges that demand a lot from the materials when constructing an appropriate rheometer. In recent years, several attempts have been made to build rheometers for this purpose. The technique is well under way and it is hoped to be available soon to provide information to elucidate the behaviour of lubricants in a normal lubrication contact.

It is assumed that lubricants will be transformed to a "glassy" state in highly loaded contacts, the easier they reach this glassy state the higher the friction will be. The formation of pressure spikes, which will be transduced into the lubricated metal surface, invoking possible minor cracks which in turn will create wear, is dependant to a great deal on the transformation progress of the lubricant. Simply explained, the

transformation to (and back from) the glassy state will effect the dampening of the pressure spike, where, of course, a higher dampening effect is favourable.

Recently, evidence has been found evidence of very peculiar behaviour for fluids when present in layers of a few molecules in thickness. The thinner the layer, the more "sluggish" the movement of the fluid molecules will be, not at all represented by its bulk properties. The illustrative example with a billiard ball separated by a drop of water from a surface shows a quick transport of water splashing from the contact when letting the ball go. The last two to four molecules of water layer in the contact would need extremely high forces to be squeezed out of the contact. The same seems to be true for all types of fluids. At the same time, the molecules of a confined fluid can slide over each other and in-between the phase borders, giving the fluid a lubricating effect, see for details the very recent article by Granik [10].

The most common micro-structural theory is that the soap thickeners are forming a three-dimensional network structure built up by soap fibres. This picture is probably based on the images found by using a Sweep Electron Microscope (SEM) for investigation of the thickener and is a possible reason for the sponge theory.

The problem is that to make it possible to get an image in such a device, the fluid part has to be removed and a conductive film must cover the residual thickener. To get a reproduction of the solid thickener, and, at least in earlier equipment, subject it to bombardment of electrons in a high vacuum environment and let the reflections and/or adsorption of electrons be detected for creation of an image.

This process can be considered as seriously damaging the form and shape of the thickener, which is indicated by the actual SEM images from a specific thickener composition but derived from lubricating greases using different types of lubricating fluids. Every type of fluid used gives a specific shape and form of the thickener fibres. If a solvent is used to flush out the lubricating fluid, its solubility strength and polarity can be assumed to make an impact on the form and shape of the thickener structure.

The expected three-dimensional structure is destroyed when using the technique described above. To see a three-dimensional structure, another technique is commonly used, where a supercritical fluid replaces the fluid part of the lubricating grease. This creates an aerogel, which can be imaged by the SEM technology. However, the incompatibility between thickener and the supercritical fluid will remain and the "true structure" is still possibly unknown.

Tunnelling Electron Microscope (TEM) techniques show the surface of a sample down to the atomic scale. Different types of light microscopy, where particles can be identified as clusters and agglomerates of several molecules, no evidence is found of fibres or a network structure as discovered by the SEM techniques. This might be considered as a possibility of the thickener forming the solid body properties by other means than the commonly accepted idea of a fibre network structure.

The most commonly presented idea of how lubrication occurs in a contact is that the soap structure acts like a sponge, keeping the oil loosely bonded by weak forces, and letting the oil bleed out when sheared, miraculously "sucking" back the oil again when coming out on the other side of the contact.

When using lubricating greases that are subjected to very high centrifugal acceleration forces, it becomes evident that the density of the thickener is important for the degree of separation. The smaller the difference between thickener and fluid, the less the separation will be, even at extreme conditions.

A more scientific and continuously more and more detailed investigation by several institutes, notably Luleå Technical University and Imperial College in London, have shown a much more plausible and logic process taking place. By the use of a ball and disc apparatus, where the disc can be of specially coated glass or sapphire, when investigating the lubrication contact area, the thickener is not only found to get into the contact area but also remarkably increase the film thickness. Several articles have been published on this matter [11,12,13].

The difficulty to comprehend the complexity of greases was once described by Gow [14] in the metaphorical phrase; "*Grease is an elusive butterfly*". This has shown to be even more of a truth than first thought, the shape of the lubrication point area (for the ball point contact) of lubricating greases looks very much like a butterfly. For lubricating oils, the shape resembles a horseshoe.

Temperature influence

The soap thickener has very poor heat transfer properties, and can very well act as an insulator when considering the bulk of the grease. This can be easily demonstrated by putting a piece of lithium complex thickened lubricating grease, based on mineral oil, on a heating plate at around 200°C - 300°C. The oil that separates from the bulk of the grease will immediately oxidise and form coke, while the bulk of the grease will be undisturbed, this can be checked by lifting the lump of grease with a spatula and look at the surface in contact with the heating plate). This will not be the case for so called high temperature greases based on silica and/or bentonite clays. The structural forces, in such lubricating greases, are too weak to prevent severe oil separation at high temperatures, leaving a residue of coke and "sand". Still, even for greases with a thermally stable structure, oxidation is sometimes a problem and the choice of both the type of lubricating fluid and the appropriate antioxidant is important. On the other hand, at low temperatures, the structure can improve mobility of the lubricant.

For fluid lubricants, the lowest possible temperature of application is determined by the measurement of the Pour Point (PP) temperature, the temperature at which the fluid will solidify and cannot flow (under normal gravitational or small-imposed forces). Since lubricating greases have at least a two-phase system (thickener and fluid), the mobility along or within phase borders can extend the application temperature down to 20°C below the Pour Point of the included fluid. The use of polymers, different mixtures of lubricating fluids (with different PP) and different additives, makes the lubricating phase system enormously complex, with no

proven model to describe the actual mechanisms for flow within the bulk or at surface layers. What is known about the mobility (or lack of mobility), is normally derived by practical tests (e.g. tests in pilot rigs of centralised lubricating systems) or from use in real life applications.

The thickener keeps a major part of the lubricating fluid more or less in a fixed position. The exact mechanisms, or the exact proportions, are not very well known but a great part of the fluid is kept within the structure by pure steric hindrance and weak van der Waal forces. A minor part is possibly bonded, to keep the soap structure, by hydrogen bonds or in the case of heteromolecules by ionic bonds, more strongly to the soap structure. Another small part can move freely within the bulk. The last part is not necessarily composed by a fixed type of molecule but can vary depending on process and composition, something that can be found out by investigation of the separated oil. The amount of oil bleed, separation of the fluid component from the bulk, is determined by type of thickener, amount of thickener, the solvency parameter of the lubricating fluid and even the manufacturing process.

The separation speed is increased by pressure differences and at increased temperature (increased mobility of the molecules), from moderate separation at storage to excessive separation in high temperature applications and/or transportation in (inappropriate) centralised lubricating systems.

The thermal stability of lubricating greases is commonly determined by the Dropping Point (DP), the temperature where a drop falls from a standardised cup. The Dropping Point is not defined as a specific physical occurrence, independent of it being a melting point, softening point or separation point. The value is accepted as the maximum temperature that a lubricating grease can be exposed to before irreversible destruction of the thickener structure occurs. For safety reason, the upper application temperature is set at 15 - 20°C below the DP. Since the test is made under static conditions, the relevance for dynamic situations as in practical service is doubtful. Other tests, dynamic tests, are available but lack determined precision as required by national and/or international standards.

Much more investigation to find a way of really measuring and monitoring the physical structure in lubricating greases is needed, before any conclusions about the physical shape and form of the structure can be correlated to the chemical and physical behaviours of lubricating greases. Since these abilities and properties are most important for actual service behaviour of lubricating grease, such research must be given a high priority by manufacturers and customers, preferably involving universities or other institutes with experience of microscopy techniques.

Current Lubricating Grease Testing

The chapters of this book are focused on a detailed investigation (from theoretical, experimental and numerical simulation viewpoints) of the rheology and rheometry of lubricating greases in simple flows, which are easily modelled with available commercial rheometers. Perhaps, one of the possible consequences of

the presented work will be its contribution in establishing a general test procedure for the greases in simple shear flows.

Rheology is practised and well established in many other business areas, with products not unlike lubricating greases, at least from a consistency viewpoint. Molecular weight distribution, texture, ability to be spread and even taste can be estimated or measured by the use of now classical rheological tests.

The continuum mechanics, which is the part of physics that includes rheology (the science of flowing), can be overwhelming when looking at the theoretical part. *"Graeca sunt; non leagatur"*, seems to be many peoples reaction within the lubricating grease business. Even if the theories behind rheological responses and material behaviour are difficult to comprehend, it is the practical application and use of rheology that should be focused upon by the lubricating grease business. To make it possible though, a basic understanding of the rheology concepts and rheometry techniques must be achieved. It is the aim of this book to describe the possibilities available and to create interest into the potentials of rheology.

To continue using empirical tests would be to comply with *"Mundus vult decipi, ergo decipatur"*, although no party within the lubricating business can betray another without betraying itself. The use of precise and reliable methods to describe and control lubricating greases will be a benefit for all parties within the business. "Magic" has to be abandoned as a description of lubricating grease properties, and "art" as a description for the manufacturing, to be replaced by the use of know-why and know-how. Rheology can provide a key to both.

Lubricating greases must fulfil many different demands, some even contradictory to each other. The major difference between a lubricating grease and other lubricants is the consistency, the property provided by the thickener, making lubricating grease act as a solid or semisolid body at low stresses. The consistency is the most important property of lubricating grease, sometimes even more important than the actual lubricating ability, making it possible to use lubricating greases in applications where fluids cannot be used.

Since the very beginning of using lubricating greases, it was the consistency, the ability to stay in place (the resistance to flow under normal gravitation and temperature) that has made lubricating greases preferable to fluid lubricants. Lubricating greases are even today sometimes referred to as consistency greases, although this description originally was used for conventional Calcium soap thickened types of greases.

In modern times, fluid greases or slightly thickened oils have been developed to make the use of centralised lubrication possible. Centralised lubrication was from the very beginning developed for use with fluids, mainly mineral oils, and when modified for grease lubrication, often a compromise must be made between pumpability and application criteria. This is true for many systems used for automotive applications, while systems used in the industrial area are more designed for pumping greases with higher consistency. Block greases have today almost disappeared from the market. Block greases are "cheese hard" moulded blocks of high concentrate soap in oil, most commonly Sodium soaps, used for slumping lubrication via mechanical and thermal break-down of the structure. In some applications, a low stress for creating steady state flow is desirable and, on the other hand, a quick and full recovery of the structure (consistency) after removal of the

stress is just as important. This creates a delicate balance in the choice of the consistency of lubricating grease for a given application. Lubricating greases are materials able to exhibit both the fluid and solid rheological behaviour, as a function of the level of applied stress.

By definition, a pure fluid is mainly viscous and its viscosity determines the flow time. Pure fluids exhibit an immediate and total relaxation of the stress at the cessation of the motion and no recovery of the deformation at the cessation of the applied stress. A pure Newtonian fluid will show a linear relationship between applied stress τ and the responding shear rate $\dot{\gamma}$. The property of viscosity reflects the ability of lubricating grease to flow (even if the rheological behaviour is not a pure fluid like) under the applied shear stress. The viscosity function $\eta(\dot{\gamma})$ then gives the angle of inclination of the tangent at the flow curve $\sigma(\dot{\gamma})$, i.e. $\eta(\dot{\gamma}) = \sigma(\dot{\gamma}) / \dot{\gamma}$, which is a constant for a Newtonian fluid.

The determination of the steady viscosity is a classical test in rheometry, see for example [14]. A detailed presentation of the viscosity function of lubricating greases and its modelling is presented in the next chapter. A structured material with a yield shear stress σ_y , such as lubricating grease, will behave differently to a pure viscous fluid. At low stresses below the yield stress level σ_0 , no fluid behaviour can be observed within a reasonable time. Anyway, it is considered that even in this region of low stresses a flow characterised by a constant very high viscosity, the zero shear rate viscosity η_0 , exists within the material.

When the stress exceeds the yield stress level $s > s_y$, the material becomes fluid like; it will begin to flow fast and, for typical lubricating grease, the shear rate (i.e. strain rate) will increase more rapidly with increasing of the stress level. This is referred to as the shear thinning behaviour, respectively the viscosity decreasing with the increasing of the strain rate.

There are several test methods in use today, which try to describe and determine these rheological properties, consistency and viscosity, although most of them do this in a very empirical way.

The most commonly used test for determination of consistency or, as has been described above, the resistance to flow, is the cone penetration test. Worldwide, the cone penetration measurement is the most frequently used test method for the determination of lubricating greases most important property. The cone penetration value simply described as a measurement where a standardised cone falls freely for 5 seconds and thereafter the penetration depth is measured in tenth of millimetres, is used for both quality control in manufacturing and as a (very) rough tool in the selection of suitable products for use. Penetration is the basis of the NLGI classification, which is a linear scale of 30 units per grade separated by 15 units in between grades. The most frequently used grades vary from NLGI 3 (220 1/10 mm to 250 1/10 mm penetration depth) to NLGI 000 (445 1/10 mm to 475 1/10 mm penetration depth).

The adoption of this test is quite remarkable, considering the comments given by ASTM themselves in 1951; "Since the ratio of flow to pressure is not constant for either plastic solids or plastic liquids, a single numerical

value is inadequate to define the consistency of these materials. It is seldom true that two plastic materials, which give the same value under one set of tests, will be found alike under other testing conditions "

Later on in the same report, the committee established; "While the consistency of a plastic material cannot be defined by a single numerical value, it may be tentatively assumed that if the tests deal with a single class of materials and employ forces of the magnitude met in service, the results are helpful and significant".

Somehow, this very important conclusion was lost over the years. The current use of cone penetration as a tool to determine consistency of lubricating greases, and to some extent an approximate value of the yield stress, leaves a lot to be desired. Many have found the use of cone penetration insufficient for determination of yield stress level and some have suggested alternatives based on rheological measurements, (see chapter 2). The variation of area, depending on how deep the cone will sink into the sample of grease, implies a wide range of shear stresses. The time dependency is not considered at all, with the same experimental time for any type of product tested. The test is neither sensitive enough to distinguish between different types of thickeners used, nor in any variation in composition or as Lucretius put it: *De nihilo nihil*. This was also observed by the ASTM report, and expressed as "...two greases which vary widely in composition may behave quite differently, even though they have the same penetration ".

In reality, both the consistency and viscosity of lubricating greases are time dependent properties. The time dependency of lubricating grease's flow behaviour, its intrinsic (natural) time λ_1 , must always be considered in a complete rheological description of the material. The time dependency appears in the rheology of lubricating greases because they are not only viscous, but also elastic materials. In the general sense, lubricating greases are viscoelastic materials. In the simplest representation, viscosity is associated with the base oil and the elasticity with the internal structure built by the thickener. The property of elasticity also determines the existence of normal stresses during the shear motion of lubricating grease. The first normal stresses difference $N_1 = s_{11} - s_{22}$ are not zero, as is for a pure viscous fluid ("1" defines the direction of motion and "2" defines the normal direction to the motion, direction along the variation of velocity observed) [18]

The Deborah number, defined as the ratio between the natural time of the material and the observation time of the process - $De = \lambda_1/t_0$, best describes this phenomenon. For example, the process (observation or experimental) time t_0 must be considered in any judgement of how a material will behave (sometimes, instead of Deborah number is used the Weissenberg number, it is defined in a similar way, see Chapter 6.1). Both material functions, the viscosity η and N_1 , are dependent on the Deborah number. If the observation time to an applied stress is very short, (fractions of a millisecond) even a fluid like water with a very small natural time $\lambda_1 \ll 1$ s, will appear to be a solid body, i.e. $t_0 \ll \lambda_1$ and $De \gg 1$ (for a pure solid $De \approx \frac{3}{4}$). Viscous behaviour can also be found for materials which are considered as solids (materials with high natural times $\lambda_1 \gg 1$) when the observation time is long enough (usually thousands or millions of years), i.e. $t_0 \gg \lambda_1$ and $De \ll 1$ (for a pure fluid $De \approx 0$).

This is in fact the background to the nomenclature, which is taken from the Bible (Judges 5:5), where Deborah says: "...and the mountains flowed before the eyes of the Lord". If a stress is applied and time is very long, all materials will flow!

By exact definition, no material can be found to behave as an ideal (pure) Hookean solid, neither is there an ideal (pure) Newtonian fluid. All materials therefore, are more or less viscoelastic. From a more practical point of view however, we normally consider those materials, which flow within a reasonable time as viscous. Those, which do not appear to show evident flow within a reasonable time, are considered as solids. Materials that can be both acting as solids and as fluids, also observed within a reasonable time frame, can then be considered to have viscoelastic properties.

In short, the rheological behaviour of lubricating greases can be summarised as follows.

Applying an external stress to the material can break the solid body appearance. If the shear stress is large enough, beyond the yield stress - $s > s_y$, the lubricating grease will first deform plastically and then flow as a fluid. Most types of grease show shear-thinning properties, i.e. the increase in strain rate (proportional to the velocity of flow) is a non-linear function of applied stress, after the initial solid and elasto-plastic regions are passed. The behaviour of lubricating greases shows viscoelastic properties. The viscosity function at zero shear rate has an asymptotic very high constant value. The same behaviour is observed at very high shear, with the remark that the asymptotic value is much lower. A part of the structure will be permanently destroyed at high shear by breaking not only the weaker bonds in the structure but also the stronger bonds as well and eventually making the thickener degrade. Over time, lubricating greases will become thinner whilst the thickening effect will be more reduced. This is normally referred to as the mechanical stability of lubricating grease.

These rheological properties of lubricating grease, viscosity shear thinning behaviour, yield shear stress and the time dependence (elasticity), are discussed in more details (mainly from experimental point of view) in the chapters 1 and 2 of the present book.

In the spirit of "tradition", the mechanical stability of lubricating grease is determined by using the cone penetration measurement to determine the change in consistency. The two most commonly used test methods are the prolonged worked penetration, where the grease sample is worked in a grease worker for up to a hundred thousand double strokes, and the Roll Stability test, where the grease is squeezed through a linear contact for a defined time period. Modifications of both tests are also used. One way to test grease mobility, or resistance to mobility, is the use of start and running torque. The test is often run at low temperatures to establish a low temperature application limit.

In addition, for this category of tests, rheological measurements are believed to be more accurate and easy to run.

Many types of equipment with documented test procedures have been developed over the years to make it possible to estimate service performance. These tests are commonly referred to as functional or OEM tests.

They are excellent for their intended purposes, but they normally have a fixed application and the results cannot be used for even related application areas, since the type of lubrication contact, speed and loads are all influencing the behaviour of the lubricating grease. This is also the very reason why so many types are available and no correlation can be found between the different tests, even though they at first glance seem to be of a similar type.

If construction engineers and lubrication manufacturers alike universally accepted the use of rheology, life for both would be a lot simpler. It is perfectly possible to measure and calculate the rheological parameters in any given application. In very much the same way, it is possible for lubricating grease manufacturers to develop products that fulfil these criteria, should they been known and measurable.

Progress in the use of rheology will only come about when both construction engineers are familiar with fluids and the correlating viscosity and, grease manufacturers referring to NLGI grades communicate with each other. Since the NLGI grade can never predict the service performance, there is no possible way for engineers to use the values. Rheology, and the scientifically derived values obtained by rheological measurements, provides a means by which both parties would be able to communicate with each other using a common language.

The present book is an attempt, and at the same time a challenge, to introduce rheology as the common language for specialists and scientists working in the area of lubricating greases.