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The Chemistry and Physics of Grease

The Advantages of Grease: Grease and oil have different performance characteristics and the benefits of grease are unique compared to oil. The basic components of grease (base fluid, thickener system and various additives) are held together in a structured matrix. Grease is not simply a highly viscous oil but a complex, physical, multi-phase system. It can demonstrate the properties of a solid or a liquid, depending on the conditions to which it is subjected.

Multi-phase structure: The structure of grease enables the lubricant to remain solid until shear between component surfaces reaches such a level that the grease starts to flow and becomes mobile. The rheological properties and corresponding lubricating abilities can be enhanced by properly formulating the grease to respond appropriately to combined effects of shear, strain and temperature. The gel structure provides grease with its main physical characteristic, a rigidity commonly referred to as consistency.

In a lubrication application, one of the main benefits of consistency is that the grease stays in place, where it is intended. The mass of grease acts as a lubricant reservoir and minimizes problems related to leakage. It also makes it easier for the equipment design engineer to select mechanical seals.

In practice, the gel structure offers additional capabilities, e.g. it stops external contaminants, whether liquid or solid, from penetrating through to the metal surfaces. In effect, this permits extended maintenance intervals. If lubricating oil is contaminated by the smallest amount of water, the lubricating film may fail completely. Grease, on the other hand, remains effective in the presence of a variety of contaminants even at higher concentrations.

Thickeners: Compared with a fluid base oil, the thickener system within a grease provides viscosity and elasticity benefits, which will result in higher temperature performance and better load carrying capabilities. In most grease applications, the thickener acts as an active component at the interface between the equipment surfaces. Protective effects are enhanced by selecting a thickener with the right chemical polarity, resulting in strong attraction to the metal surface of the machine component.

A multi-phase system comprising of a thickener and base oil can also improve performance at low temperatures since the thickener system can counteract any tendency of the fluid lubricant to crystallise as operating temperatures fall. The solid structure of grease offers considerable advantages in many applications. In fact the grease technologist has many more possibilities and a whole range of benefits for the end user at his disposal that would simply not be available using lubricating oils.

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Additive solubility in oil and grease: Fluid oil formulations are limited by the need for any additive or component in the lubricant to be dissolved or, at least, very reliably suspended in the base oil. Phase separation of the components can result in harmful effects such as sediment formation.

The need for an additive to be soluble in a liquid base oil may well prevent it from performing as expected. For example, an anticorrosion additive, which is properly dissolved in the base oil, may not be present in sufficient concentrations at the metal surfaces. Additive solubility is however not a necessity in grease formulations. The solid matrix structure and the consistency of the grease allow much more flexibility in formulation.

Indeed, even completely insoluble solids or liquids can be suspended in the multi-phase grease matrix to deliver the required functionality at the metal surface; classic examples in grease technology are the use of solids such as molybdenum disulphide, graphite and zinc oxide.

In a similar way, selecting corrosion inhibitors is not constrained by the need for solubility since careful formulation can enhance the delivery of an insoluble liquid additive to the metal surface where it is needed to perform its task.

The benefits of positioning the additive optimally at the metal surfaces become more important when it comes to additives which reduce the effects of extreme pressure and wear.

Extreme pressure additives are required to function in acute situations when the lubricant film has been severely reduced in thickness by high loads, elevated temperatures or low speeds. This type of additive must be positioned in the grease matrix to react immediately with the metal surfaces in order to prevent seizing.

An anti-wear additive offers similar protection under less severe conditions, but again, it must still be available at the interface to coat the metal surface by physical adsorption. The multi-phase structure of grease allows great flexibility in the choice of soluble or insoluble active components. Soluble additives, such as certain antioxidants, can of course be selected for their specific solubility in either the base fluid or the thickener system and the additives are thus appropriately positioned to neutralise the chemical intermediates that promote oxidation.

Benefits of grease: The major advantages of grease over lubricating oil focus on four basic capabilities:

- as a lubricant, involving the properties of the base oil, the thickener and any functional additive,
- as a sealant, to protect the working surfaces from the effects of contamination by gases, liquids or solids,
- as a matrix, to provide a carrier for a wide range of beneficial additives and to improve specific performance capabilities of the grease,
- as a corrosion inhibitor, both directly as a sealant and indirectly as a matrix for corrosion inhibiting additives,

The benefits to the user are significant. They include reduced wear, extended relubrication and service intervals, less vibration and noise and lower energy consumption, all of which have the potential of contributing to a considerable reduction in total maintenance costs.

And if the grease technologist is able to exploit the wide flexibility of formulation possibilities, the range of operating conditions in which a grease can offer optimum performance can be greatly expanded. These benefits can be maximised by carefully matching the choice of grease to three important factors: the machine components to be lubricated, the operating temperature and the surrounding environment.

The fundamental grease formulation: The science of lubrication focuses on optimizing the separation of contact surfaces on moving equipment. For several thousand years, both oil and grease have been the lubricants challenged with this task. Key elements are reduction of the wear, the frictional heat and the energy losses encountered in machinery throughout its working life and modern greases offer several significant advantages in many applications. Grease is, of course, a mixture of chemicals and inevitably, chemistry contributes fundamentally to the design and manufacture of the product. However, it is the understanding of tribology, the science of friction and abrasion, coupled with knowledge of the rheology of grease, the deformation characteristics of the lubricant, which drive innovation forward.

The development of the chemistry of grease formulations is closely linked to an understanding of the physics at the interfaces between the machinery and the grease. With this insight, it is possible to formulate greases that are capable of operating in increasingly demanding and wide ranging conditions.

There are three basic components that contribute to the multi-phase structure of lubricating grease; a base fluid, a thickener and very frequently, in modern grease, a group of additives.

The function of the thickener is to provide a physical matrix to hold the base fluid in a solid structure until operating conditions, such as load, shear and temperature, initiate viscoelastic flow in the grease. To achieve this matrix, a careful balance of solubility between the base fluid and the thickener is required.

Mineral Oils

A wide range of lubricant base fluids is used in grease technology. However, the largest segment consists of a variety of products derived from the refining of crude oil and downstream petroleum raw materials. These mineral oils can contain a very wide spectrum of chemical components, depending on the origin and composition of the crude oil as well as the refining processes to which they have been submitted.

There are three basic groups of mineral oils: aromatic, naphthenic and paraffinic. Historically, the first two have represented the principle volumes used in grease formulation, largely due to availability but also due to their solubility characteristics. However, concerns about the carcinogenic aspects of molecules containing aromatic and polyaromatic ring structures have led to their replacement by paraffinic oils as the mineral fluids of choice.

The oil components of grease must offer a range of appropriate properties in order to fulfill their roles in a wide range of applications. Viscosity and its temperature dependency are obviously key requirements, but loss of volatile components and oxidation stability can also be important selection criteria. In the latter case, the response of the base oil to antioxidants also needs to be taken into account.

Perhaps the most important factor in the choice of the oil phase is solubility. This criterion affects both the manufacturing process and the final matrix structure of the grease and is vital to the performance characteristics in any particular application.

The decline in the use of oils containing aromatic and polyaromatic components has reduced the range of solubility characteristics available to the grease technologist.

However naphthenic oils contain not only polyaromatics but also similar, less toxic, polycyclic compounds without a benzene ring structure. Using modern selective refining techniques, it is possible to remove only the unwanted components and produce oils with low toxicity. Thus these severely refined oils provide a range of beneficial solubility properties, similar to conventional types of naphthenic oils, but without the toxicity problems.

Modern base oils in lubricating greases are therefore often a blend of severely refined paraffinic and naphthenic oils, designed to provide the final product with the appropriate characteristics of mechanical stability, lubricity and dropping point.

Synthetic Fluids: Synthetic fluids can be tailored to provide properties that might be impossible to achieve using conventional mineral oil products. Typical examples are applications with a wider range of operating temperatures or where chemical resistance is required. Furthermore, compatibility with rubber or plastic components and seals, the lubrication of non-metallic surfaces and improved electrical properties are all areas where synthetic base fluids can make a contribution.

Environmental considerations, such as biodegradability, are increasingly becoming factors influencing the selection of synthetics. There are several groups of synthetic base fluids that find applications in grease and most of these are specifically designed products, rather than the oil distillate cuts that comprise the mineral oil range.

Polyalphaolefin (PAO): Polyalphaolefins are low molecular weight synthetic polymers, which provide advantages in oxidation stability coupled with good viscosity characteristics over a wide range of temperatures. Greases made from PAO exhibit excellent low temperature properties and can offer low friction and optimum energy saving performance.

Esters: Synthetic esters are produced from a variety of long-chain fatty acids, derived from petrochemical or renewable animal or vegetable sources. The acid is then reacted with a specific alcohol to give the chemical and physical properties required by the grease formulator.

The large range of esters available generally offers good thermal stability, lubricity and, in some cases, excellent biodegradability. Ester based greases offer enhanced physical performance at low temperatures, combined with low evaporation losses at high temperatures, and this makes them useful in a wide range of applications and environments. Esters tend to swell elastomers, and this can cause problems with certain types of seals. However, this property can be used to advantage in, for example, a blend of small amounts of ester in polyalphaolefin. A grease based on this blend will show an equivalent compatibility towards rubber seals when compared to a mineral oil grease.

A synthetic grease, when properly formulated, can therefore replace a mineral oil grease without the need to change seals.

Polyglycols: Polyglycol chemistry offers a very wide range of polymeric structures, providing a great diversity of properties in both the liquid and solid state, together with a complete range of solubilities from water to less polar compounds such as mineral oils. In grease, a correctly selected polyglycol offers excellent performance opportunities, including a wide temperature range, specific rheological properties, exceptional thermal stability and good compatibility with plastics and rubbers.

Some polyglycols offer advantages at high temperatures, where their degradation products evaporate completely, leaving no harmful residue. Unfortunately, most polyglycol greases are incompatible with mineral oil based products and relubrication with the wrong product can be extremely problematic.

Polyethers: In their chemical structure, polyethers provide a particularly inert polymerised backbone, and this property is further enhanced in the fluorinated polyether derivatives.

Perfluoropolyethers: Perfluoropolyethers are inert to almost all types of chemicals, leading to their use in application areas where such exposure is expected. Typical examples are the lubrication of bearings in contact with strong acids and alkalis, with aggressive solvents, or indeed, with oxygen. These fluoroethers also have a very low tendency to evaporate and can be used in high vacuum equipment. The fact that they do not react with oxygen is also very beneficial in high temperature applications. However, at extremely high operating temperatures above 300°C, the fluoroether structure can break down, forming toxic by-products.

The Thickener

The history of the development of grease is closely linked to the invention of various thickeners that can be used to hold the base lubricant in a gelled matrix.

Metal soaps have been dominant in the progress of thickener development. Domestic soap, used for hygiene and washing purposes, is the sodium derivative of a vegetable or animal fatty acid. Traditionally, this has been made by reacting animal fat or vegetable oil with sodium hydroxide dissolved in water. In use, the long soap molecule combines water solubility at one end, with fat and dirt solubility at the other, thus enabling the cleaning process to occur.

However, 'soaps' can be made from a whole range of metals other than sodium, and each derivative has its own specific properties. This is related to the character of the metal used to neutralise the fatty acid, along with the chemical structure and length of the carbon chain in the fatty acid itself.

Metal soaps: Sodium soaps, similar to domestic soap, were widely used in grease formulations during the early stages of the industrial revolution and, indeed, some of these types of product are still used today. However, greases based on such thickeners have several inherent weaknesses, not least water sensitivity. A sodium soap is therefore unable to provide a stable and long-lasting matrix structure for the grease.

One of the earliest groups of soap thickeners used successfully in the manufacture of grease was based on calcium. The widespread availability of calcium hydroxide derived from limestone encouraged the use of this material in soap compositions.

Metal soaps based on aluminium and barium have also found a variety of applications. However, it is the range of soaps based on lithium that have been predominant in the development of modern thickener systems.

Advanced soaps: Of more recent importance are mixed base greases, involving combinations of different metal soaps to modify the matrix structure and thereby optimize the contributions made by each component. In so called complex greases, combinations of metal salts and soaps are co-crystallised into the grease matrix structure during the manufacturing process.

Development of technology: The driving forces in the search for improved thickeners are many and varied, but in general, the principle motivation is the desire to improve the capabilities of grease across an increasingly wide range of operating conditions. Improved performance at high or low temperatures and, in some cases, capability at both extremes, remains an ongoing challenge.

The key to providing a grease matrix that is stable, both over time and under the operating shear within machine components, can be found in the thickener system. The thickeners themselves also contribute significantly to the extreme pressure and antiwear characteristics of grease and additionally, thickeners provide a grease gel capable of carrying additives which, in turn, extends performance in these areas.

Water resistance, surface adhesion and tackiness, dropping point and compatibility with other greases are all properties where the selection of the right thickener is important. Increasingly, for centralised lubrication systems, pumpability is becoming an additional prerequisite.

And finally as with all other grease components, human toxicology, ecotoxicology and biodegradability of the thickener have become important issues.

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