WHITE PAPER

Lubrisense™

2005 02

Thickeners in the Grease Matrix
Market and Product Trends

AXEL

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Thickeners in the Grease Matrix

The Grease Matrix

A modern grease consists of a physical matrix containing a fluid base oil, a thickener which provides its gelled structure and, in most cases, additives which offer a range of additional benefits.

Typically, a grease might contain 85% base fluid, 10% thickener and 5% additives.

The multiphase grease structure gives the product a suitable consistency which enables the grease to remain in place under the conditions of use. This ensures effective lubrication, provides a sealing capability and enables the grease to position functional additives close to the working surfaces of the equipment.

Depending on the shear conditions at the moving surfaces, the grease will deform and flow to provide lubrication and then regain its structured consistency as the shear decreases.

Thickeners

Developments in thickeners have been fundamental to the advances in grease technology. The contribution of thickeners has been so central to developments that many greases are often classified by the type of thickener used to give the structured matrix and consistency.

The two principal groups of thickeners are metal soaps and inorganics, soap based greases being by far the most widespread.

Calcium Soaps

The earliest greases were made by reacting lime with vegetable oils, or animal fats, in the presence of water, to produce a calcium soap of the natural fatty acid. The resulting thickened oil was adequate for simple lubrication tasks such as cartwheel and waterwheel shafts and bearings. These simple calcium greases were only found to be inadequate when the development of the steam engine led to higher operational temperatures. The melting point of a calcium grease is around 100ºC and higher running temperatures proved to be too challenging at that time.

Nevertheless, calcium greases of this type are still in use today for less demanding applications and their manufacture is very similar to the processes used over one hundred years ago.

Calcium soap is produced with a small residual water content which acts as a stabiliser for the soap matrix and thus provides the required structure of the thickener. In some operating conditions, when the temperature is constantly

MARKET AND PRODUCT TRENDS – BACKGROUND AND FUTURE PERSPECTIVES

LITHIUM DOMINANCE

In the industrialised world, approximately 70% of the grease consumed today is based on thickeners using lithium technology. The patented inventions of Clarence Earle in the 1940's have been developed into the traditional and complex soap thickeners which are currently in use.

In practice, the improvement of lithium greases has centred on the search for additives to extend the capabilities of the basic products.

However, the reality is that much of the grease in current use is based on a concept which is 60 years old!

Sales of grease comprise just a few percent of the total lubricants market. Lubricating oil attracts much greater attention, both in terms of research and commercial focus.

The attractions of innovation have declined over recent decades. For example, polyurea grease was originally developed over 40 years ago and sulphonate complex grease has been available for many years, but neither category has achieved a particularly significant market share.

above 50ºC, water evaporation may result in the complete breakdown of consistency in the grease and it will revert to a fluid state.

Conventional calcium greases have good adhesive properties and they are extremely water resistant. At relatively low cost, their use today continues in cool, wet conditions such as in marine applications, propeller housings and water pumps.

Sodium Soap

Sodium soaps, which are very similar to domestic soap used for washing, were found to have higher melting points than calcium soaps. Greases based on sodium soaps were fundamental in the lubrication of steam engines and the early machinery of the industrial revolution. Sodium grease has an operating capability up to temperatures of approximately 110ºC and it became the foremost high temperature grease at the beginning of the 20th century.

Unfortunately sodium greases have three significant weaknesses. They are water soluble like washing soap and also suffer from hardening in storage.

Furthermore, due to the large fibre size of traditional sodium soaps, they do not contribute lubricity to the grease. This inadequacy results in poorer load carrying capabilities and means that a base oil of higher viscosity is needed to provide heavy duty properties.

The use of sodium grease is declining rapidly, but occasional applications are still found in enclosed gears and couplings.

Aluminium Soap

Greases based on aluminium thickeners were developed at the same time as sodium greases as engineers searched for improved lubrication for steam engines.

Aluminium thickeners and, in particular aluminium stearate, seemed to offer a grease with both water tolerance and a higher temperature capability. Unfortunately, aluminium thickened greases have a major weakness in that they are extremely sensitive to shear. They are easily broken down mechanically, losing both their consistency and lubricating capability.

Aluminium stearate grease can still find applications in low shear simple plain bearings and as a chassis grease but has generally been replaced by more modern products.

Lithium Soap – A Major Step Forward

In the first half of the 20th century, mechanical engineers had a relatively limited choice of grease types to cater for an increasingly challenging set of lubrication needs. Traditional calcium, sodium and aluminium greases were asked to cover all of the requirements.

Catalysed principally by developments in the aircraft industry during the late 1930's, the

'UNIVERSAL' GREASE?

Fundamental innovation has perhaps been diverted by the search for a truly multi-purpose grease based on lithium technology.

During the 1970's and 1980's, the formulator's target was one single grease which would be capable of superior performance in a wide range of applications, temperatures and environments and there is no doubt that the new greases offered benefits; – in industrial maintenance, the use of a single multi-purpose grease reduced any confusion and prevented the risk of damage due to the wrong choice of grease.

Unfortunately, the new multi-purpose greases were simply too expensive for many basic applications.

At the same time, the market was actually fragmenting as more demanding applications required much more technical capability than even a lithium multi-purpose grease could offer. Thus the focus for more basic uses was centred on considerably less costly, but nevertheless effective greases.

The increased technical challenges were emerging from machinery and automotive manufacturers; original equipment producers were specifying greases with extended service life, longer relubrication intervals and a greater performance capability.

introduction of lithium based greases came as a very significant step forward, (with patents issued to Clarence Earle in 1942-43). For the first time, lubrication engineers had access to a grease which could be classified as truly multipurpose.

Early lithium soaps were made from simple stearic acid, derived principally from beef tallow. Today, almost all lithium greases are based on the castor oil derivative, 12-hydroxy stearic acid (according to the Clarence Earle patents). The capabilities of lithium grease include excellent mechanical stability, good water resistance and reasonably good high temperature performance, up to 120ºC. This combination of benefits did not previously exist in the 1940's. During the second half of the 20th century, lithium greases replaced the earlier greases in the great majority of applications.

The only real disadvantage with lithium 12-hydroxy stearate grease is pumpability at low temperatures; this can present a difficulty in centralised lubrication systems at temperatures below -10ºC. Lithium soaps are very elastic and this property can affect mobility in long supply pipes.

Anhydrous Calcium Soap

A more recent development in calcium grease is the use of a soap that is not stabilised by water. This allows an upper operating temperature of 110°C, similar to sodium or even lithium greases. In addition to the temperature benefit, anhydrous calcium greases offer the advantages of traditional calcium greases, excellent adhesion, low temperature lubricity and water resistance.

Anhydrous calcium thickeners are normally based on 12-hydroxy stearic acid, just like their lithium counterparts and the resulting grease offers excellent mechanical stability. These greases are used widely in Europe for applications such as marine, agriculture, forestry and construction equipment.

Complex Greases

The availability of a range of soaps, based on different metals encouraged grease formulators to investigate the effect of mixtures in the final grease. Little benefit was found from this mixed-based approach, although compromise mixtures such as lithium-calcium have found some special applications.

A much more rewarding approach over the past thirty years has led to a range of so-called complex soaps. Derivatives of a single metal reacted with a combination of different types of acids can be crystallised into the same fibrous thickener structure.

The principle advantage of complex greases is their ability to withstand high operating temperatures.

The lubricant was required to offer a service life similar to the machinery components in which it was performing.

ENVIRONMENTAL CHALLENGES

During the past decade, the environmental aspects of grease production and application have significantly increased the technical challenges faced by the lubrication technologist.

The increasing legislative pressure on the oil and chemical industries continues to catalyse changes in raw materials and manufacturing processes. Protecting the health of production operators and reducing waste emissions are becoming key factors in future developments in grease production.

For example, in the manufacture of polyurea grease, producers can now avoid the use of toxic amines and iso-cyanates by using pre-reacted raw materials, made by speciality chemical companies under highly controlled conditions. Similarly, manufacturers of aluminium complex grease now avoid the emission of isopropyl alcohol by using suitable chemical precursors.

The environmental impact and ecotoxicology of the product are increasingly important in grease applications.

When it comes to loss lubrication, the fate of the disappearing grease can no longer be ignored. Account must be taken of biodegradability and the toxicity of the grease and its biological impact on animal and plant life.

Aluminium Complex

Aluminium complex greases have dropping points above 240ºC, are highly water resistant and offer good lubricating properties at high temperatures. Furthermore, a low thickener concentration can provide the required grease consistency and this leads to excellent pumpability. This combination of properties has made aluminium complex grease popular as a steel mill lubricant.

Their disadvantages centre on a tendency to harden under shear and their poorer mechanical stability in comparison to lithium greases. In this respect, they are similar to conventional aluminium stearate greases.

Calcium Complex

Developed at the same time as aluminium complex greases, calcium complexes found favour due to their load carrying and extreme pressure capabilities. Their high temperature performance was also found to be similar to aluminium complex greases with dropping points above 250ºC. Their extreme pressure capability is provided by integral components of the co-crystallised soap structure; calcium acetate, calcium sulphonate or similar calcium derivatives are crystallised into the thickener structure. In contrast to aluminium complexes, a very high soap content is required to provide a given grease consistency and this can detract from pumpability. Calcium complex greases also have a tendency to harden in storage.

More recent calcium sulphonate complexes also offer excellent water resistance, coupled with good high temperature performance and load carrying capacity. Their lubricating performance at more usual operating temperatures can be somewhat poorer however.

Lithium Complex – A Further Step Forward

Over the past decade, lithium complex greases have been finding increasing popularity. With dropping points above 300ºC, this type of grease can withstand peak operating temperatures of up to 240ºC for short periods of time. Continuous temperatures of 150ºC should not present a problem for grease formulated with mineral oils; service temperatures of up to and in some cases exceeding 200ºC are possible using synthetic base stocks.

This excellent high temperature performance results from a high melting point coupled with the very dense fibre structure of the soap matrix. Very small polar fibres strongly bind the base lubricant providing excellent protection against oxidation due to low heat transfer throughout the matrix.

According to the 2005 NLGI Grease Production Survey Report, 2004 statistics claim that Worldwide 15%, in Europe 10% and in North America >33% of the grease market is now held by lithium complex products.

An early consequence of legislative changes affected applications in the North Sea; for example the use of metallic additives in thread lubricants which is no longer acceptable. The European Union's Dangerous Preparations Directive requires full labelling of products to enable the end user to assess environmental risks. This will certainly have an impact on the choice of grease components for sensitive applications. Emerging issues such as 'REACH' and the new European Eco-label will be highlighted in more detail in coming editions of the AXEL White Papers

In the area of food applications, the NSF, the US public health and safety company, has prepared new guidelines for food-contact registration. All previously listed lubricants will have to seek re-registration and many previously approved greases may well lose their listing.

PRODUCT TRENDS

The development of today's large volume, commodity, lithium greases has relied on additive technology to ensure improvements in performance. However, the manufacturers of lube additives have tended to focus on the lubricating oil market, rather than the more specialised and smaller grease applications.

Environmental concerns associated with the use of lead as an extreme pressure agent have encouraged replacement by sulphur-phosphorus technology, often in combination with zinc compounds. But zinc itself is not completely acceptable from an environmental aspect and

Typical applications are in the steel and paper industries, where elevated temperatures are commonplace. In cars and trucks, the grease is used in hub units, where the temperatures generated in modern brake systems have increased significantly.

The excellent pumpability of lithium complex grease has led to its use in centralised lubrication systems on trucks and heavy equipment, particularly for cold climate applications.

Increasingly, lithium complex grease is regarded as the new generation, multipurpose grease with a wide temperature range, replacing traditional lithium products. This trend is enhanced by the broad compatibility of lithium complex with other grease types.

Inorganic and Other Thickeners

Solids which are essentially insoluble in the base oil can also be used as thickeners in grease formulations. Bentonite and hectorite clays, silica gel, polypropylene, polyethylene and polytetrafluoroethylene (PTFE) have all found applications.

Clays

Fine clays, particularly bentonite clays, were used in grease formulations from the beginning of the 20th century, primarily in an attempt to improve high temperature performance. The use of clay as the gelling agent results in a grease that does not melt or drop at high temperatures. However, the lack of a fibrous matrix structure does limit the stability of clay based greases. Furthermore, the deleterious effects of oxidation can still occur in the base oil at elevated temperatures. Oil oxidation and separation can result in a residue of abrasive clay being deposited on the machine surfaces.

However, clays still find applications for the gelling of highly viscous base fluids, such as bitumen, to produce compounds for use in open gear systems.

Silica Gel

The methyl derivative of silicon dioxide offers similar properties to a clay in grease formulations. These greases were originally developed for the lubrication of small mechanical devices operating at low temperatures, in aircraft, for example.

When centralised lubrication systems in heavy vehicles were introduced, silica gel and clay based greases gained popularity due to their lack of elasticity and the resulting ease of pumpability. However, oil bleed, separation and the inherent instability of inorganic thickened formulations caused blockages in feeder lines and dosing modules. The use of these thickeners was abandoned in favour of other greases such as lithium complex. Silica gel greases still find applications in the lubrication of aluminium and some plastics.

compounds of bismuth have received increasing technical and commercial focus.

Most additive developments are of course driven by specific performance requirements. Ash-free additives offer a lower total metal content; water resistance has been improved by the combination of lithium and calcium soaps; the incorporation of functional polymers in thickener formulations to reduce water spray-off; and many more application or customer specific solutions have been offered.

The new generation of multi-purpose greases relies on 'complex' thickener technologies; the principle driving factor here has been the search for improved performance at higher temperatures. The market share of this type of lithium complex product has risen significantly in the USA and Europe, although principally at the expense of traditional lithium grease.

Other complexes, such as aluminium and calcium complexes and calcium sulphonate complexes, have achieved less significant market success.

In some grease formulations, particularly incorporating calcium sulphonate complex and polyurea based thickeners, enhanced high temperature performance has unfortunately been achieved at the expense of lubricating ability at ambient temperatures and, in some extreme cases, lack of oil separation and grease mobility have led to dry

PTFE

Inert base fluids, such as perfluoropolyethers, are used as lubricants in aggressive environments and require a PTFE thickener that is equally inert.

Applications for this type of grease include contact with aggressive solvents and strong acids and alkalis. Inert grease of this type is also used to lubricate pumps for oxygen and nitrous oxide in hospitals, where contact with other greases could pose a fire or explosion risk. Components containing sensitive or reactive plastics, rubbers, or ceramics can also be lubricated with this type of fluorinated grease. PTFE greases operate well under low pressure, such as in vacuum pumps and high speed bearings in vacuum environments (space).

Polyurea

This special polymer thickener system is normally a reaction product between different types of iso-cyanates and amines. Polyurea greases exhibit extremely good high temperature performance and have, in many cases, become the preferred choice for filled-for-life applications in both bearings and joints. On the other hand, drawbacks such as poorer performance at ambient temperatures and the toxic nature of raw materials have limited their development into a more multipurpose product. In 2004, they represented less than 5 % of the global market but, locally, in Japan, an impressive 21%. New developments in preformed polyurea powders can facilitate production for grease-makers in that the risks in the handling of toxic raw materials can be totally eliminated.

Polyethylene

Although not very common, polyethylene and other similar polymers and waxes are used in very specific applications. In circumstances where very high centrifugal force or very rapid acceleration prevail, a traditional matrix grease fails. Separation of the thickener and base fluid components occurs rapidly, immediately reducing lubricating ability. Polyethylene can be produced with a density very close to that of the chosen mineral base oil and separation does not occur. High speed flexible couplings are lubricated with this type of grease.

Polypropylene

Yet another new and innovative type of grease being introduced into the market is based on a polymer (polypropylene) thickener with an optimised crystalline-amorphous balance. This type of grease offers many advantages over standard multipurpose greases: Controlled oil bleed, extended service life, resistance to water and aggressive chemicals, enhanced additive response and not least a high film thickness in the track (efficient surface separator).

running and catastrophic bearing failure.

Synthetic base oils have certainly contributed to the enhancement of upper temperature performance, but their principle contribution has probably been in very low temperature applications. Greases based on synthetics are also making an increasing contribution towards extending service life and even where low friction under heavy load is required.

Many of these developments show grease rising to the challenges from original equipment manufacturers, who are stretching the limits of machine capability in difficult environments.

MARKET SEGMENTATION

In general terms, the grease market in the industrialised world can be said to fall into two categories. The commodity, relatively low technical challenge, low cost segment on the one hand, and the increasingly challenging, higher technology developments on the other.

The higher technology grease market is continuing to fragment as equipment design becomes more and more specialised and lubrication solutions become more and more application specific. Here is the real challenge for an ambitious lubrication technologist.

In the next issue of the White Papers we will address the important role of additives such as antioxidants, activators, antiwear additives and more, in the grease matrix. The issue will also include articles on how legislation influences the Grease Maker's work, ie. DPD and REACH. Mr. Laurie Hughes from Uniqema will be our guest writer in this section. As usual we encourage our readers to give us feed-back and requests for grease technology topics they want us to cover in future Lubrisense White Papers..

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