WHITE PAPER

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POLYMER THICKENED LUBRICANT

Introduction by Guest Writer, Professor Emeritus Bo Jacobson

AXEL CHRISTIERNSSON

POLYMER THICKENED LUBRICATING GREASE

PROFESSOR BO JACOBSON RECEIVING THE TRIBOLOGY GOLD MEDAL IN 1997 IN RECOGNITION OF HIS POWERFUL COMBINATION OF ACADEMIC AND APPLIED CAPABILITIES, ESPECIALLY IN THE FIELD OF LUBRICANT PROPERTIES AND BEHAVIOUR UNDER HEAVILY LOADED CONDITIONS.

When I started to work at SKF Engineering & Research Centre 1987, one of the first problems which surfaced was the uncertainty in prediction of the re-lubrication intervals needed for grease lubricated applications at low temperatures. The standard greases during the preceding decades had mostly had problems with too short re-lubrication intervals due to bad behavior at high temperatures.

There had not been any problems with the old types of greases at low temperatures, because they had a course thickener structure which gave enough base oil bleeding also at rather low temperatures. To make the greases work at higher temperatures new thickener types were introduced. Those thickeners had finer geometrical structures and higher melting points, so they could be used in greases at higher temperatures without losing their consistency or melting. The problem was that the greases were optimized to work well at the highest possible temperature, and no-one thought that there could be any problems in low temperature applications, because all the old greases had worked perfectly well at low temperatures. About 20 years ago some slowly-rotating large grease lubricated roller bearings started to get early failures due to dry running despite the fact that the bearings were totally filled with lubricating grease. The grease, or rather the base oil, did not seem to be able to flow back fast enough to the lubricated surfaces between the roller passages. When the temperature was low, the base oil viscosity was too high for the surface tension to be able to spread the oil over the surface quickly enough to avoid dry running.

These grease lubrication problems made SKF Engineering & Research Centre start a basic grease research program in January 1988 to investigate the grease lubrication mechanisms at relatively low temperatures. By studying the basic mechanisms for the spreading of grease base oil over the lubricated surface, it was early obvious that the grease properties needed to be quite different from the grease properties of standard lubricating greases.

For standard greases the base oil bleeding was strongly dependent on the temperature. At high temperatures enough base oil was bleeding out from the grease to give almost fully flooded lubrication, but at room temperature and lower temperatures the oil bleeding was so low that all lubricated contacts were being heavily starved. The starvation led to lubricant film thicknesses one order of magnitude smaller than calculated or even less. These thin lubricant films led to early bearing failure.

The low bleeding rate at low temperatures was caused by two phenomena. One was that the base oil viscosity increased very much at low temperatures and thus decreased the oil mobility in the bulk of the grease. The other phenomenon was that the surface energies (surface tensions) of the oil and of the thickener soap changed in relation to each other when the temperature decreased. This gave extremely low or no oil bleeding at low temperatures. In experiments we even saw that oil which had been bleeding out from the grease at high temperature was absorbed back again leaving the lubricated surface dry when the temperature was decreased.

The idea then came up to develop a grease which should have a more constant bleeding rate independent of temperature, and the grease should also be able to bleed out much more base oil to allow the re-lubrication intervals to become much longer. For this purpose we choose to test synthetic base oils, which had a more constant viscosity independent of the temperature. A research program was also started in 1991 together with YKI (The Surface Chemistry Institute in Stockholm) to find polymers or mixtures of different polymers, which could work as thickeners in the new grease. This led to the first working grease being ready for tests in January 1994.

In April 1994 we had the first grease lubrication course at SKF ERC and in November 1994 we had the first GRIT (GRease lubrication In Tribology) meeting in Luleå to start a European research

SLOWLY ROTATING LARGE GREASE LUBRICATED ROLLER BEARINGS

program on grease lubrication. In June 1995 the final proposal for COST 516 was delivered. There three areas of research were specified: Grease lubrication, renewable lubricants and friction and wear.

Since then the COST 516 research program has been finished and a follow-up program COST 532 has also just finished with a final meeting in Ljubljana in June 2007.

The cooperation between SKF ERC and Axel Christernsson regarding the new polymer thickened grease started with a visit by Graham Gow to SKF ERC 1995-08-23 and it was followed up by a meeting in Nol 1996-06-24. The grease development then was taken over by Axel Christiernsson and now ten years later the first production unit for polymer thickened grease is started at AC.

It has thus taken close to 20 years from the recognition of the grease lubrication problem at low temperatures until a grease manufacturing facility is available to solve the problems.

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A PATENTED POLYMER SOLUTION

Most modern multipurpose EP2s, whatever thickener system they may contain, have been optimised to operate at ever increasing temperatures and this is detrimental to their lubricating ability under normal “ambient” conditions. A typical NLGI 2 grade lithium grease will bleed perhaps up to 10% of its base oil within a short period of time and then “dry up”, with starvation as a consequence. Especially with greases intended for high temperature applications, like some polyureas or calcium sulphonate complexes, this deficiency can happen very quickly indeed and problems with dry running have been experienced with these kinds of products in the lower “ambient” temperature ranges.

When operating under higher temperatures however, these materials exhibit excellent performance. This increasing demand for greases with optimised performance in bearing tests at ever higher temperatures has created a trend towards super-stable products both in terms of mechanical stability and reduced oil separation. The Swedish bearing manufacturer, SKF, was quick to identify this problem and highly qualified scientists at their Engineering & Research Centre in the Netherlands, in cooperation with the Swedish Institute of Surface Chemistry (YKI), were able to develop a new type of polymeric thickener system, which, under the microscope, closely resembled the fibrous structure of a lithium soap (a synthetic “sponge”). Based on a mixture of different polypropylenes, this provided improved oil separation at lower temperatures and gave the products a rheology less dependent on temperature. This was eventually patented and, in an effort to upscale and commercialise this innovative technology, Axel Christiernsson was invited to join the project and become a full partner in the development process.

In a continuation of the research work, Axel Christiernsson’s development engineers found that by optimising the crystalline-amorphous balance in the system, i.e. by adding an additional component, a rubber, the working concept could be further improved. This resulted in yet another “joint” patent (AXEL/SKF) where the principal claim is for a non-ionic thickener system, where it is possible to carefully control the level of oil separation. Laboratory tests and field trial experience have shown that this new material has a number of unique properties which make it superior to many conventional soap-thickened products. Advantages include an extremely long service life, improved low and ambient temperature performance, resistance to water and aggressive chemicals, enhanced additive response etc. In laboratory test rigs, for instance, the service life was extended more than eight times compared to that of an equivalent lithium soap thickened grease and this magnitude of improvement has been verified in field trials.

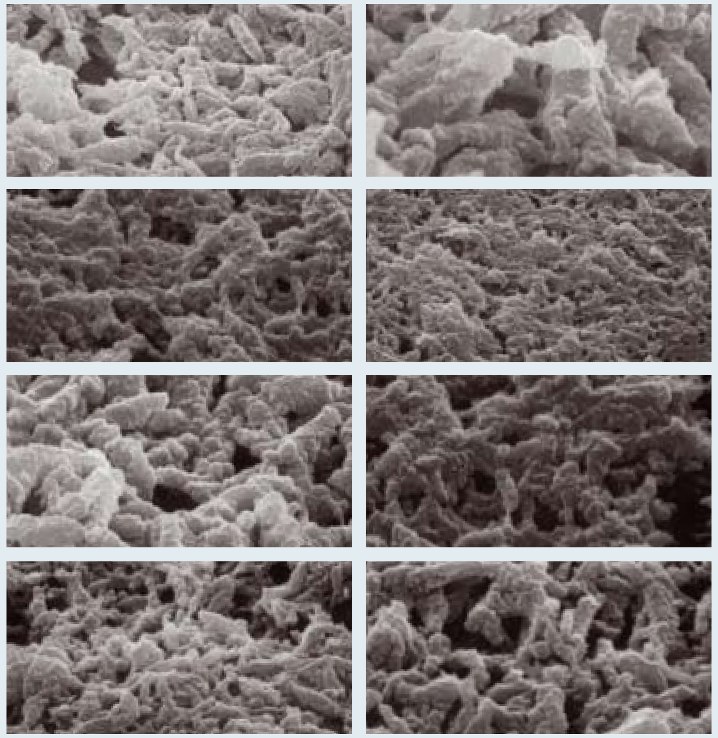
This additional patent describes a concept whereby a lubricating material can be produced by quenching a mixture of a given high molecular weight polypropylene and a rubber in an oily environment. The types of base fluids can be changed in both chemical and physical terms and the amount and type of polymer adjusted to suit the application. In addition, just as with conventional greases, the type and the amount of additive can be tailored to fit the requirements. Since the material is compatible with most present day greases, there is also the possibility of formulating “hybrid” versions. A number of given products from an upscaling exercise have been tested in both the laboratory and in a whole array of field trials with very promising results indeed. This means that there is a concept rather than a single product and that special lubricants can be developed to match customer and end-user expectations based on this novel technology. In addition, formulations from a whole series of pilot batches are available, ranging from simple mineral oil based products, through biodegradable alternatives like sunflower and cottonseed oils, to sophisticated synthetic versions for electrical contacts and foodgrade applications. Furthermore, a number of hybrid products have been developed where the dropping point of the finished grease has been elevated to meet certain customer demands. And to date, there are even more sophisticated prototypes in the pipeline.

POLYMERS IN LUBRICANTS

The use of so-called “polymers” in lubricants is by no means a new concept. One simplistic definition of a “polymer” can be a macromolecule built up by linearly linking a large number of a smaller unit. These types of materials have been used in lubricating oils and greases as viscosity modifiers, viscosity index improvers, adhesion agents and rheology modifiers for many many years. As early as 1937, Otto and Mueller-Cunradi claimed that the addition of a polymeric homologous compound, such as polyisobutylene, improved the properties of greases. Since then, a large number of different lubricating grease compositions, for use in lubricating bearing applications, and containing such polymers, have been developed and commercialised.

In addition, different polymeric thickeners or “consistency-imparters” have previously been used as a physical matrix in lubricating grease formulations. One such material is “Solid Oil”, developed by SKF specifically for bearing applications. According to this invention, Solid Oil is a polymer matrix saturated with lubricating oil which completely fills the internal space in a bearing, encapsulating the cage and rolling elements. Solid Oil uses the cage as a reinforcement element and rotates with it. By releasing the oil, Solid oil provides good lubrication for the rolling element and raceways during the operation. It is normally based on synthetic oil and, due to the melting point of the specific polymer used, the recommended maximum continuous operating temperature is 85 °C. Other examples are different types of synthetic gels which unfortunately often proved to exhibit instability in terms of both shear and thermal properties. Yet another type of “polymer” thickener is polyurea even though these greases are, more often than not, based on di- and/or tri-ureas and, by strict definition, perhaps not polymers as such. Typical properties of polyurea greases are enhanced high temperature performance, high film thickness, oxidation stability, water resistance and low noise. However, there are also some drawbacks that may cause problems, including low temperature properties, the tendency to age harden in storage and the fact that these greases are not always compatible with the most common soap-based greases. Perhaps even the toxicity of the raw materials and the relatively high price can be included here. All these polymeric thickeners have been developed during the last 70 years since different advantages of using polymers in lubricant technology were first identified. Many of the patents published are interesting and technologically advanced. There are however only a few polymers that have managed to take a central position in the lubricating grease market. This will probably change with the implementation of the REACh legislations, since the development of tailor-made polymers may have a cost benefit compared to components which need comprehensive testing for REACh registration.

The use of *polypropylene* as a thickener in lubricating grease formulations is, however, not so commonplace even though there are a number of patents describing this technology.



MACRO PHOTOS OF DIFFERENT POLYMER STRUCTURES

Compared to lithium based lubricating greases, which correspond to almost 60% of world production according to the NLGI Survey, the main technical arguments for using this new technology can be summarised as follows.

Long Life:
This has been measured in the laboratory in the SKF R0F test rig on a multitude of different occasions and verified in field trials. A good quality conventional lithium EP 2 (tests run on different versions, both in-house and competitive) will last some 500-600 hours at 120°C in the R0F test rig. Curiously enough, non EP greases usually last somewhat longer. Equivalent versions (i.e. everything else equal, same consistency, same type of oil, same additive package etc.), using the polymer based thickener, last for 3,500-4,000 hours under the same conditions. As a matter of interest, we usually switch the machine off after 4,000 hours because we need the rig for other projects, so we are not quite sure of the true service life in many cases. But we do know that it is so much better than the lithium-based product. This long life expectation gives many benefits to the end-user including reduced lubricant consumption, extended relubrication intervals, reliability and dependability, reduced downtime, an improved environmental impact through less need for the depletion of finite resources and quite simply, “a good night’s sleep” for the maintenance manager.

Low temperature performance:
The patent provides for a “controlled” oil bleed at low and/or ambient temperatures. This does not only imply the amount of oil bleed but also the properties of the released oil. By varying certain parameters in the production process, the amount and the type of oil can be “controlled”, and even the amount of additives in the oil released. In this way the risk for starvation (dry running) and perhaps even false brinelling can be reduced or eliminated. In addition, the temperature dependence of the oil release can be modified, giving the product(s) exceptional low temperature properties where, once again, the emphasis is on functionality rather than specifications (starting and running torques may tell you that the bearing is rotating, but nothing about the state of lubrication). Under cold chamber conditions, some tests were run in the SKF R2F test rig. When the temperature fell below -20°C, all sorts of problems were experienced; the electronics didn’t work; the paint started to peel off the machine surfaces, but the lubrication just got better and better. Synthetic versions showed excellent functionality at extremely low test temperatures (< -40°C). Pumpability has been investigated at ambient and low temperatures, in different models of centralised lubrication systems and in small automatic lubricators, all with very satisfactory performance.

Resistance to water and aggressive chemicals:
The combination of high adhesion and low solubility in both water and different chemical media increases surface protection and corrosion resistance. This provides functionality under industrial conditions where process water, metal working emulsions, acids, bases and other types of chemicals in the surrounding environment rule out the use of conventional greases. The lubricant is therefore more stable under wash out conditions and this reduces the risk of leakage and any subsequent contamination and/or environmental impact.

Enhanced additive response:
The non-ionic thickener system allows the active components in the additives to reach the metal surfaces implying that the new technology is a better carrier of their functionality. Whereas soap-based thickeners will interfere with the additive reactions

QUICK QUENCH !

The production method for this novel lubricant technology is a highly controllable process which facilitates the “right, first time, every time” concept. The need for the “black art” of grease manufacturing can therefore be reduced or eliminated. In principle, this involves a melting and re-crystallisation process, although it is, in reality, much more complicated than it sounds ! The equipment necessary is relatively expensive and very unusual in the grease business but, once installed, allows design for purpose. Since there are no chemical reactions, and especially none involving naturally variable raw materials, there is the possibility of immediate reworking and/or adjustment. Recycling is even theoretically possible where the used products, in contrast to more conventional soap based products, can be re-melted and filtered. This, of course, is easier said than done since the used lubricants may well be contaminated with undesirable components but, in comparison to the current technology, the very possibility does exist. It is a modern process with significantly improved working conditions, and with no need to handle toxic raw materials as is necessary for polyureas.

As described in a previous edition of the Lubrisense™ White Papers (2006/05), cooling is often the bottleneck of many grease manufacturing process. This is partly due to the poor heat transfer properties of a soap mass, partly due to an operational decision to slow the process down in order to actively promote the formation of larger soap crystals or “fibres” (analogy with a sponge full of water). In complete contrast to this, these new polymeric materials must be cooled down as quickly as possible and this requires quite different equipment compared to conventional soap-based greases. The new patented concept requires the quenching of the polymer/rubber combination in an oily environment. Depending on the melting points of the individual components, the mixture is heated up to a given temperature for complete dispersion and homogenisation. At this stage of the process, the product is, of course, in liquid form. This fluid mass is then quenched and the polymer and the rubber are co-crystallised into a desirable and characteristic structure. From the fluid state, the material is immediately transformed into a relatively stiff concentrate. This can then be incorporated into a number of different lubricating materials exhibiting vastly different physical properties, all depending on the details of the finishing process.

The elimination of black art

by competing for the surface, the polymer system will let the additives win the race for some metal to react with. This provides improved functionality for EP/AW and corrosion inhibiting effects. In addition to this, the use of a non-ionic system allows the use of "different" additives compared to soap based thickeners. Since the polarity of the additives will not interfere with the binding forces of the polymer system, the "mayonnaise" effect can be avoided. The combination of these different effects contributes significantly to reducing the environmental impact.

Inert thickener system:
Polymer systems are in general more resistant to oxidation, degradation and centrifugal forces than soap based products. This leads, in turn, to longer life and resistance to different chemical media.
A polymer based product is also preferable for the lubrication of aluminium, copper and various alloys where the excess alkali of a soap-based system can cause staining and corrosion. For the lubrication of ceramics, polymers and elastomers, this new technology can be tailored to be fully compatible (in fact, in many cases, the same chemistry can be used!). Because of the inert nature of the materials, there is full compatibility with most existing greases and this allows problem free switch over and the possibility of developing "hybrid" products.
Due to the non-toxic nature of polypropylene (used in Tupperware®) and the other components, these thickeners are extremely suitable for foodgrade and even environmental applications. The development of a heavy duty lubricant using this new technology and based on sunflower oil has been published in a previous edition of the Lubrisense™ White Papers (2006/04).

Flexibility for customised solutions:
In general, the concept can be used to thicken most types of oils. For very unusual types of fluids, (worst case scenario) it has been possible to produce "GLS" (grease like substances) and these can, more often than not, be modified into functional prototypes by other means. Potential customers can therefore be offered "bespoke" products based on their own in-house product technology. They can take advantage of work already done for fluid oil applications by being able to thicken the particular oil/additive combination used in, for instance, their high quality gear oils. This, in turn, offers the opportunity of rapid and exclusive product development programmes.

High film thickness in the track:
The technology provides film thicknesses often too high in magnitude to be measured in existing equipment. The products offer an excellent "deforce" by quite simply keeping the surfaces apart in a very effective way. They are **D**ynamic Energy **S**aving **S**hearable **S**urface **S**eparators (D + 4S = Deforce). This reduces wear and increases load carrying capacity. Because of the thick film, vibration and noise can be eliminated and there are indications that "quiet running" versions can be developed. Running temperatures are significantly lower and friction under heavy loads can be reduced. And, compared to lithium thickened greases, the total energy losses in the machine can be minimised. Lower friction and lower energy losses contribute to functionality and lesser environmental impact.

"REACh free":
The thickener system is based on polymer technology and, in addition, there are no chemical reactions in the production process. Since polymers are generally exempt from the REACh regulations, this eliminates the need for expensive HSE testing compared to in-situ reacted soaps.

In conclusion, this new polymer based technology concept has been found to offer considerable advantages over the current generation of lithium thickened lubricating greases. This conclusion is based on the proven functionality of the products in real life situations and not only on the basis of fulfilling a given specification. In contrast, most of these products do not meet the specification provided by the current supplier.

The great majority of greases on the market today have changed little since the days of the early 1940´s when Clarence E. Earle filed his patents on lithium soaps. From what started as a modest development project to solve a particular problem in a particular bearing, a whole new range of products has emerged, using a new and innovative concept. These new polymer thickened greases offer a functionality which is widely superior to equivalent lithium based products. It took Clarence Earle's lithium-12-hydroxy stearate thickened greases 40 years to become the industrial standard.
Why wait so long this time round?

THE PROOF OF THE PIE

The main driving force to develop new types of lubricants is, or should be, functionality and this can only be demonstrated outside of the laboratory in real life conditions. Developing products to meet yesterday's specifications does not create a major drive forward nor a paradigm shift of any kind. We therefore need to see beyond the present test methods and acceptance criteria into a world where functionality is put in the front seat. We must also understand that there is not a direct customer demand for something new since we cannot expect people to ask for something they do not know exists. Anyway, the proof of the pie is in the eating and the results from field and beta site trials using the new polymer lubricants have been generally extremely positive, including a number of exceptional performances

One interesting trial was conducted on the winches of round-the-world sailing boats. There were major problems with the lubrication of these since they are expected to perform in extreme weather conditions with corrosion and wear as a result. "Normal" greases were found to be too stiff, or rather too stable, and did not lubricate in a satisfactory manner. Trials were made with fluid lubricants but these could not provide the corrosion and wear protection needed for proper functionality. Molybdenum disulphide containing oils and pastes were used but these all leaked out and caused staining on the deck and sides of these highly visible yachts. The solution to the problem was a softer (but still solid) polymer based lubricant using state-of-the-art zinc free additive technology.
This resulted in excellent functionality. In addition, the new product was easy to apply, easy to clean and provided much better corrosion protection and a longer life.

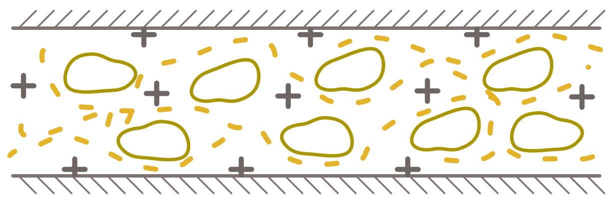

Novel lubricant technology in practice

THE EPOCH DIFFERENCE

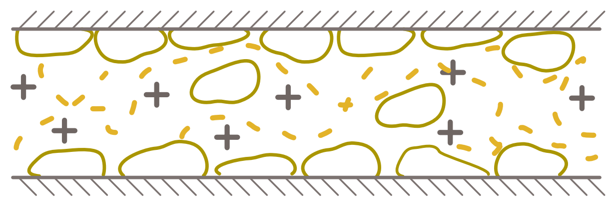
Which component wins the race to react with a metal surface? In a soap-based grease, the soap will mostly win over the additives because of its higher polarity. The same goes for a functional soap, even if the situation is improved by having the additives bundled together with the soap.

Epoch works the other way around. Since the polypropylene and other components included are non-polar, the additives will easily reach the metal surfaces. This makes it possible to use a lower dosage of additives for the same effect, and thereby improve the lubricating performance. Or you can use the same amount of additives and improve the required functionality, for example, resistance to corrosion. In addition, the inert character of Epoch allows it to work with most oils and additives, which is not the case with soap-based thickener systems.

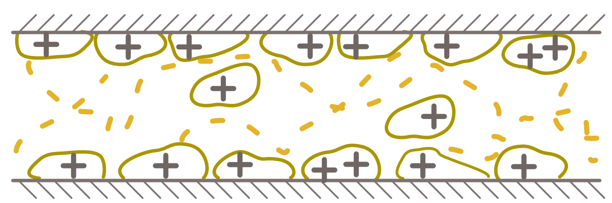
Epoch
Based on a non-polar thickener system (polypropylene) – the additives can reach the metal surfaces and do their job.



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



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



Thickener system + Additives Oil

The next issue of the Lubrisense™ White Papers will focus on greases specially formulated to stay in place under wet conditions. Water is often considered to be enemy number one when it comes to lubrication in general and, in the great majority of cases, greases perform better than fluid oils in such environments. Products designed for optimal functionality in the presence of water need specific properties in order to survive. These include adhesion, cohesion, mechanical stability and enhanced corrosion inhibition. This can be achieved by the choice of thickener system or by the addition of polymers and other types of additives. In order to develop and test greases for such applications, a number of test methods have been adopted and these will be described and compared.

We encourage reader contribution, feedback and proposals for topics in future editions of the White Papers.

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