WHITE PAPER

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H_2O, FRIEND OR FOE?

Lubricating greases for wet conditions

Laboratory methods for testing water stability

AXEL

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LUBRICATING GREASES FOR WET CONDITIONS

Water can be a necessary and integral part of the thickener structure of certain greases. On the other hand, water is often considered to be a lubricant's worst enemy. Statistics show that bearing failures, where the principal default mechanism has been identified as a "lubrication problem", are in fact more likely to be associated with the lack of lubrication or even more likely with contamination rather than being due to the quality of the lubricant itself. In many applications, the service life of vital and expensive components is drastically reduced due to contaminants, solid or liquid, and where water is often the primary villain.

In the real world, it is often difficult, if not impossible, to avoid the ingress of water into bearings and other types of machine elements. Agricultural machinery, heavy construction vehicles working in the forest, fishing boats in heavy seas, drilling equipment on offshore oil platforms, industrial machines in steel or paper and pulp mills, bottling plants in breweries, and many many more, are all examples of applications where contact with water is quite simply unavoidable. Fresh water, dirty industrial water, salt sea water, metal working emulsions, sugar solutions, high pressure steam, ice and snow; water comes in many phases, types and forms. The ability of a lubricating grease to withstand, reject or absorb "water" can therefore be vital to optimal performance in many areas. Throughout the years, many different types of greases have been developed to combat the threats associated with water.

In the "beginning" (i.e. before the industrial revolution), lubricating greases were often based on simple calcium soaps. These so-called "axle greases", (not AXEL greases!), were manufactured by saponifying different types of natural fatty acids, like tallow, lanolin and lard, with lime. In order to stabilise such calcium soaps, a small yet important amount of water had to be introduced into the formulation and without which the thickener structure would easily break down. The bad news is that this relatively small amount of water limits the use of such greases at higher temperatures. The melting point of a hydrated calcium soap is somewhere in the region of 100°C but already at temperatures of about 50°C, the water starts to evaporate and the structure deteriorates rapidly. Before the advent of the steam engine, this was normally not a big issue since lubrication demands on axles and other simpler machine elements of the time did not include performance at elevated temperatures. Such hydrated calcium greases, albeit in slightly more modern versions, can still be found on the market today and their primary property and advantage is, in fact, excellent water stability. For non-demanding applications and where the temperatures are moderate, these greases can still perform satisfactorily. Examples include propeller shafts on outboard motors and in shipyards during launching procedures. Another example of grease where water is used as an integral part of the formulation is in bentone thickened products. These inorganically thickened greases rely on small microscopic clay "platelets" which are kept in an ordered structure and where water is used as a vital part of the gelling and coupling system. This water becomes chemically bonded to the clay and therefore does not evaporate should the application run hot. Here, the exact amount of water is critical. Without water, no gelling; too much water, no gelling.

In the latter part of the 19th century, a number of different discoveries, inventions and events for ever changed the demands placed on lubricants. In parallel to the availability of a "new" and exciting raw material, petroleum, engineers were designing new and more complicated machines and also using a new source of energy, steam. To meet the need for reduced friction at ever higher temperatures, grease formulators started to experiment with different types of soaps as gellants for mineral oil. One of the first types of high temperature grease for the new-fangled steam locomotives was based on a sodium soap. This raised the upper temperature limit significantly since the melting point of such a soap was in excess of 150°C and, in addition, mineral oil could tolerate much higher temperatures for a much longer time than any of its predecessors from animal or vegetable sources. This, of course, came at a price. We use sodium soaps at home for many different domestic purposes including personal hygiene and these obviously need to be water soluble in order for them to perform their tasks. These new greases had therefore a very big downside in that they could not be used in the presence of water. Efforts were made to modify these products by the inclusion of additional soaps. These were often compromise solutions where the relation between high temperature performance, mechanical stability and water resistance had to be balanced very carefully indeed. One example here was a sodium potassium-based grease developed by AXEL and SKF for "Jakob", the first commercial Volvo car produced in Gothenburg in the late 1920s. In the technical information provided for that product, it was stated that "Small amounts of water can be absorbed by the grease and a rust protective emulsion is formed. With larger quantities of water it becomes so soft that it might leak out of the bearing housing."

In the aftermath of the Second World War, lithium-based greases became the industrial standard. This giant step forward, following the patents of Clarence E. Earle, gave the grease formulator, for the very first time, the possibility of developing a truly multi-purpose grease. These are still by far the most common types of greases used all over the world today. Here, water is often used during the saponification process as a "facilitator" and water is also formed as a by-product of the reaction of the fatty acids and lithium hydroxide, the latter often in mono-hydrate form. This process water is, however, evaporated off when the temperature is raised to the peak level and a conventional lithium grease in its delivery state should contain only residual traces of water. Products based on this technology are excellent lubricants, have good high temperature performance (dropping points in excess of 180°C), exhibit enhanced mechanical stability and are "reasonable" in water resistance. Lithium soaps are partially hydrophilic and these modern universal greases have the tendency to absorb any and all water with which they come in contact. This does not cause major problems if the amounts are kept to a minimum and many present-day greases have in their specification that they must stay in grade even when mixed with up to 10% water (see explanation in the green section). At higher levels however, the products begin to soften and they eventually lose their structure and will leak out from the point of application. As before, efforts have been made to rectify these problems by introducing additional soaps and "mixed base lithium" greases are widely available on the market. The most common types are lithium-calcium hybrids produced either by the co-crystallisation of lithium and calcium 12-hydroxy-stearate or by "baking" calcium carbonate into the thickener matrix. Special high-performance greases for steel mill applications (cold rolling mills) or for heavy off-road vehicles are examples of these kinds of development programmes.

On the fringe of this mainstream process, some interesting developments took place using other different and specialised technologies. One such side-stream led to an invention relating to formulations and production methods for lubricating greases based on an anhydrous calcium soap. In contrast to the older types of calcium soaps, the 12-hydroxy stearate version does not need water as a structure stabiliser and this enhances performance both in regard to the upper temperature limit and to the inherent solubility issue. These greases are characterised by their exceptional water resistance, good adhesive qualities and improved low temperature properties. This technology has been further modified and improved throughout the years using more qualified production methods and by incorporating modern polymers into the grease formulations. In addition, by varying the type of base fluid used, many different versions are now available including super water resistant greases based on polymer dispersions, foodgrade qualities for wet conditions and even readily biodegradable greases for sensitive aquatic ecosystems. Suitable applications can be found in marine environments, in water sewage plants, in forestry, agricultural and construction vehicles and even in industrial

LABORATORY METHODS FOR TESTING WATER STABILITY

Since there are many different ways water can have a detrimental effect on lubrication, it is difficult to design any single laboratory test method to evaluate the general ability of a lubricating grease to withstand such conditions. In the existing branch standards (ISO, ASTM, DIN, IP etc) there are a number of procedures available, all of which operate under different test parameters and, as a consequence of this, measure different properties and abilities of the particular grease in question. It is therefore very important to select the most appropriate test for the actual application(s) and to be able to interpret the results accordingly. A read-across between these different methods is not possible since a good result in any one of the tests does not guarantee a good result in another. In certain tests, adhesion is the determining factor; in others, cohesion can be just as important. Greases can be tailored to perform well in the individual tests but it is difficult to formulate a product for general compliance. Examples of such methods are highlighted here in the green section.

WATER RESISTANCE

DIN 51807 is, as the test designation might imply, a method claimed to determine the ability of a grease to "resist" water. This is, however, a purely static test which simply evaluates how well the grease sticks to a glass plate submerged in hot water. A thin layer of the test grease is applied to the glass plate which is then put into a test tube containing hot (90°C) water and left to stand for three hours. After the completion of the test, both the grease and the water are inspected for any detrimental effects. After a visual inspection, the results are given on a scale from 0–3, where 0 means that there has been no change in the equipment where water washout and corrosion are problematic.

In a more interdisciplinary approach, a new type of grease was developed incorporating knowledge and capabilities from the corrosion inhibition industry. Through experimenting with different combinations of soaps, a very interesting material evolved combining the qualities of both traditional calcium stearate/acetate/borate soaps for lubrication purposes with a calcium sulphonate normally used for rust protection. A new generation of over-based calcium sulphonate complex grease was introduced in the late 1980s. In this type of "functional" soap, the active materials are attached to the soap structure rather than as additives in the base oil. Other types of functional soaps have followed including AXEL's "Alassca complex" for extremely heavy duty applications. These greases are extremely water resistant and mechanically stable and they stay in place much better than conventional lithium products. This, in turn, means that they act as an effective seal and serve to prevent both fluid and solid contaminants from getting into the bearings. An additional property for these types of products is that they have the ability to absorb much higher quantities of water

ASTM D 4049, WATER SPRAY OFF TEST APPARATUS

without losing their structure. Even with water quantities in excess of 20%, they still stay in grade. All the advantages with this new technology are best utilised in applications where it's hot, wet and heavy. Steel and paper mill equipment are prime examples of this but such products have also shown excellent performance even in the marine, offshore (thread compounds) and food-grade segments.

appearance of either the grease or the water and 3 means a dramatic change where the grease has been significantly dissolved and/or dispersed and the water discoloured by the formation of a milky-white oil-in-water emulsion. Where this ability to adhere to a glass plate under static conditions is relevant for any real-life application remains uncertain.

WATER WASHOUT

ISO 11009 is a more dynamic test method where the ability of a grease to stay in place in a bearing under washout conditions is evaluated. An SKF 6204/C3 bearing is filled with 4 g of the test grease and mounted into the specific equipment defined in the procedure. The bearing is then rotated at 600 rpm for 60 minutes. During the duration of the test, a jet of distilled water (5 ml/s) is directed at the bearing shield. The temperature of the water should be either 37.8°C or 79.41°C depending on the specific requirements and, in modified versions, different types of water and/or fluids can be used. After the test, the bearing is dried and the amount of grease remaining in the bearing calculated. The result is then given as a percentage of the original amount applied to the bearing. The AXEL version utilises a modified bearing housing made in aluminium to facilitate the weighing procedures. Repeatability and reproducibility are reasonable for stiffer greases (NLGI 1.5 and higher). Values below 10% washout are normally regarded as "acceptable" and below 5% as "good" but no major significance should be given to lesser differences between products.

WATER SPRAY OFF

ASTM D 4049 is designed to evaluate the ability of a grease to stay in place on an open metal plate directly exposed to a high pressure "shower" of water. Whether the result is influenced more by the effect of the water as such or by erosion from the physical pressure in itself remains a subject of debate. A stainless steel plate is

Yet another way to improve the water resistance of a lubricating grease is to limit the presence of hydrophilic materials like metal soaps. One opportunity of achieving this is to replace such thickeners with water insoluble polymers. Lubrisense White Paper 2007–07 highlighted a new and patented technology using polypropylene as the thickener system and these products exhibit exceptional water resistance. Trials in many different applications have demonstrated this property including bearings in extremely difficult conditions in the pickling bath of a steel mill, in submersible pumps in sewage plants, in the production of aluminium foil and in the winches of round-the-world sailing boats. In a recent trial, the relubrication interval for bearings flushed by metal-working emulsion has been extended by a factor of eight. Eight!

In addition to developing new types of thickener systems in an attempt to enhance the water stability of lubricating greases, different types of additives have become available which are claimed to improve performance, at least in the laboratory tests designed to demonstrate compliance. One particularly effective material is a so-called functional polymer which is introduced into the cooking phase during saponification. These functional groups, often based on materials like malaeic anhydride, are grafted onto the polymer molecules and they react in turn with the excess of metal hydroxides in the soap formulation. This serves to increase the ability to resist water spray off. Another type of polymer used in grease formulations swells in the presence of water and this means that the grease increases in consistency rather than getting softer and running out of the bearing. Whether or not this is only positive remains to be seen. Greases containing these types of materials have become common in many automotive applications especially for heavy duty vehicles working in wet and dirty environments, building sites, quarries etc. The use of “fillers” (i.e. different types and sizes of particles) can also improve the water stability of greases. This technology is utilised in, for instance, products for the offshore industry and for tunnel sealing compounds. An additional opportunity with the use of solid materials is to increase the density of the finished product so that it is heavier than water. This can serve to help prevent its wash-out. The possible ingress of water into a machine element causes many different problems which reduce the service life of the component in

coated with a 0.8 mm film of grease, weighed and then positioned at a given angle within the apparatus. The water in the tank is first heated to 38°C and then sprayed at a pressure of 276 kPa over the sample for 5 minutes. The sample plate is then dried and the amount of grease remaining calculated as a percentage of the original amount. This is a very harsh test method and values below 25% spray off are generally hard to achieve. Values below 10% are exceptional. To achieve such low values, the grease has to adhere firmly to the plate; otherwise it gets sprayed off very easily. In addition, it should be extremely cohesive so that the upper layers also remain in place by “sticking” to the underlying layers. This cohesive property may be excellent for this particular test compliance but, on the other hand, may not be desirable for other reasons (internal friction, starting torque etc). The results of this test should therefore be interpreted with due care.

MECHANICAL STABILITY IN THE PRESENCE OF WATER

The mechanical stability of a grease under dynamic conditions is key to the product’s ability to perform efficiently as a lubricant and as a seal. Many lubricating greases are thickened using metal soaps and these soaps have the ability to absorb water. The performance of a grease in the presence of considerable quantities of water is therefore of vital importance. The universal standard methods for mechanical stability include both 100,000 stroke prolonged cone penetration (ISO 2137/ASTM D 217) and roll stability (ASTM D 1403) and these tests can therefore be repeated using samples “contaminated” with water. The water content normally used is 10% but higher levels have also been adopted. This water is mixed thoroughly into the sample before being worked. In both these tests, the consistency is measured before and after question. In addition to reducing the efficiency of the lubricant, the risk for rust becomes imminent. Most modern lubricating greases therefore include different types of corrosion inhibitors to minimise the detrimental effect of this threat from water. The chemistry of these materials varies according to the particular type of water involved. Greases for marine applications require one type of inhibition, greases for sugar mills another.

In conclusion, grease technicians have made considerable advances in formulating products with improved functionality in wet conditions. Whether water is regarded as a friend or a foe now depends on perspective. Water is often a necessary component in the manufacturing process of lubricating greases whereas excess water can be a limiting factor in lubricity and service life. Without water, certain types of greases will lose their consistency and leak out of the bearings. With the ingress of water certain types of greases will lose their consistency and leak out of the bearings.

Can't live with it; can't live without it!

the application of mechanical stress and the difference in cone penetration between 60 and 100,000 strokes reported. A particularly differentiating method is to adopt a more severe modification of the roll stability test (50 hours at 80°C) and using higher concentrations of water. If the grease remains a "grease" after this harsh treatment, it is most certainly a suitable product for wet conditions.

EMCOR WATER WASHOUT

Yet another detrimental effect of water in lubricating grease is, of course, its adverse effect in terms of corrosion. There are two mechanisms required to combat this process, mechanical stability under dynamic conditions, to keep the water away from the bearing surfaces, and corrosion inhibition to ensure that the surfaces are protected should the presence of water be difficult or impossible to prevent. One test method to evaluate both mechanisms simultaneously is the ISO 11007 modified Emcor test using the washout procedure. The test bearing (SKF 1306K) is filled with 10 g of the sample grease. This is then mounted on an axel and positioned in the specified equipment. The bearing is then exposed to a given alternating sequence of running (80 rpm) and standstill for a period of 164 hours. In contrast to the standard Emcor test where the bearing housing is simply filled with 20 ml of water, the washout version involves flushing the bearing with in total 3000 ml of water (300 times more water than sample!). At the end of the test sequence, the inside of the outer ring is inspected for corrosion and the result compared to a given template and reported on a scale from 0–5 where 0 is no corrosion (not one single spot detectable with the human eye) and 5 is severe rust. In addition, the "water" used in this test can be tailored to the application, from distilled water to synthetic sea water and even industrial fluids from individual end user applications.

NEXT ISSUE

In the next issue of the Lubrisense™ white papers, we will continue on the theme of "friend or foe", but change focus from water to solid particles. Different types of particles can be used to enhance lubricating grease formulations by providing specific properties or advantages. On the other hand, deleterious particles existing as contaminants in greases can drastically reduce the service life of bearings and grease cleanliness has therefore become a new parameter in many OEM specifications. In Part 1, dealing with the positive effect of particles, guest writers Dr. Karin Persson from YKI, the Swedish Institute for Surface Chemistry and Mehdi Fathi-Najafi, previously Senior Development Engineer at AXEL, currently with Nynas AB, will present some of their latest findings. As usual, we encourage reader contribution, feedback and proposals for future editions of the White Papers.

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