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No Middle Option, or why little has changed over the past 70 years

G.M. Gow

Axel Christiernsson International AB, PO Box 2100, SE 449 11 Nol, Sweden

Presenting author, E-mail: graham.gow@axelch.com

From an historical perspective, our story begins in the early 1940´s. On March 3, 1942, Clarence E. Earle was granted U.S. Patent No. 2,274,675 for his invention called "Lubricant Containing Lithium Salts." This is the first time in patent literature where claims were made concerning greases based on simple lithium soaps. And the soaps described in that particular patent are, in principle, exactly the same types typically used to produce lithium-soap-based greases today.

Today, more than 70% of all lubricating greases produced globally are still based on lithium soaps, the technology originally patented by Clarence E. Earle in the early 1940's. And more than 70 years on, we are still trying to "polish the paradigm" by incorporating all sorts of different additive systems instead of focussing on the real issue, the fact that such soaps are not very efficient at delivering effective lubricating films. In the laboratory books of Axel Christiernsson AB, the first documented trials with this type of lithium soap thickener date back to 1948, which by coincidence happens to be the same year as the author was born. So it is perhaps time for something new !

NLGI - 2012 Annual Production Survey

Total Grease Production For Calendar Years 2012, 2011, 2010, 2009

GRAND TOTAL FOR ALL COUNTRIES

All data is reported in Pounds (@ 2.2046 Lbs./ Kg)

	Pounds of Lubricating Grease				Percentage of Total Lubricating Grease			
Grease Production By Type Of Thickener:	2012	2011	2010	2009	2012	2011	2010	2009
Aluminum Soap:								
a. Conventional (Dropping Point below 350F or 180C)	**3,174,910**	5,606,587	4,061,755	3,271,712	**0.13%**	0.22%	0.16%	0.15%
b. Complex (Dropping Point above 350F or 180C)	**79,493,906**	81,677,422	78,493,361	77,834,720	**3.22%**	3.19%	3.13%	3.54%
Total Aluminum Soap	**82,668,816**	87,284,009	82,555,116	81,106,432	**3.34%**	3.41%	3.29%	3.69%
Calcium Soap:								
a. Hydrated	**117,533,445**	108,102,141	100,971,127	[illegible]	[illegible]	4.22%	4.02%	5.52%
b. Anhydrous	**57,566,172**	78,503,421	90,464,779	[illegible]	[illegible]	[illegible]	3.60%	2.52%
c. Calcium Sulfonate	**45,521,409**	46,882,667	34,714,850	[illegible]	[illegible]	[illegible]	1.38%	1.28%
d. Complex (Dropping Point above 350F or 180C)	**16,800,255**	30,480,131	31,318,134	[illegible]	[illegible]	[illegible]	1.25%	1.35%
Total Calcium Soap	**237,421,281**	263,968,360	257,468,890	[illegible]	**9.60%**	[illegible]	[illegible]	10.67%
Lithium Soap:								
a. Conventional (Dropping Point below 400F or 210C)	**1,428,110,734**	1,459,738,997	1,460,150,772	[illegible]	**57.77%**	[illegible]	[illegible]	58.46%
b. Complex (Dropping Point above 400F or 210C)	**467,239,569**	472,489,205	444,490,412	[illegible]	**18.90%**	[illegible]	[illegible]	17.16%
Total Lithium Soap	**1,895,350,303**	1,932,228,202	1,904,641,184	[illegible]	**76.67%**	[illegible]	[illegible]	75.61%
Sodium Soap:	**11,563,309**	22,961,226	15,660,856	[illegible]	**0.47%**	[illegible]	0.62%	1.03%
Other Metallic Soap:	**37,923,401**	43,624,189	38,865,661	[illegible]	[illegible]	[illegible]	1.55%	1.40%
Polyurea (Including Complexes):	**128,302,795**	128,354,272	132,162,581	[illegible]	[illegible]	[illegible]	5.26%	4.37%
Organophilic Clay Thickeners:	**45,568,833**	45,837,745	44,095,625	36,244,499	**1.84%**	1.79%	1.76%	1.65%
Other Non-soap Thickeners -All Non-soap thickeners except clay	**33,269,232**	35,589,648	35,359,363	35,096,999	**1.35%**	1.39%	1.41%	1.59%
Grand Total of Lubricating Greases:	**2,472,067,970**	2,559,847,651	2,510,809,276	2,200,951,304	**100.00%**	100.00%	100.00%	100.00%
Sub-total Utilizing Conventional base Fluid	**1,857,946,788**	1,699,181,686	1,631,791,265		**92.32%**	91.35%	93.07%	
Sub-total Utilizing Synthetic base Fluid	**83,976,318**	75,095,126	64,238,000		**4.17%**	4.04%	3.66%	
Sub-total Utilizing Semi-Synthetic base Fluid	**59,508,407**	72,117,292	48,341,828		**2.96%**	3.88%	2.76%	
Sub-total Utilizing Bio-based Fluid	**10,986,141**	13,672,250	8,831,703		**0.55%**	0.74%	0.50%	
Total Reported by Base Fluid Type:	**2,012,417,654**	1,860,066,354	1,753,202,796		**100.00%**	100.00%	100.00%	

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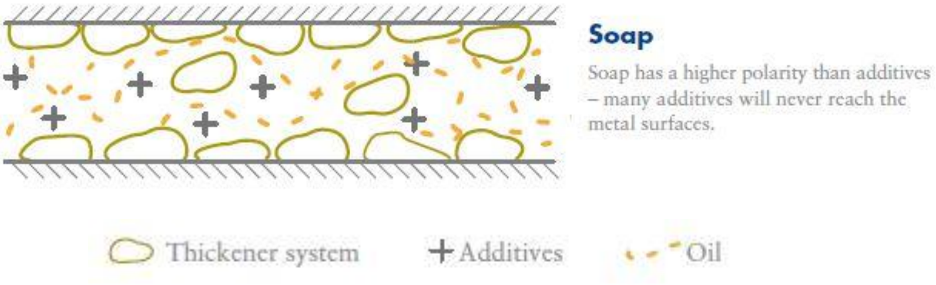
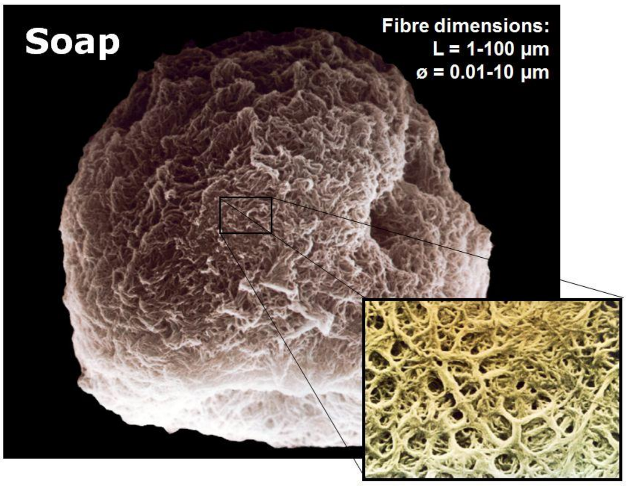
Source : NLGI Grease Production Survey Report 2012 [1]

In conventional types of lubricating greases, the soap is the most polar component in the matrix structure and clearly wins in competition for the metal surfaces. In machine elements like bearings or gears, the soap tends to cover the surfaces with a thin, perhaps mono-molecular layer, preventing any other materials (the additives, for instance) from doing their job (i.e. reacting with the metal). Instead, to let the active materials reach the surfaces, there are two, and quite "opposite", solutions: either attach the active materials to the soap structure, or replace the soap with a non-polar thickener. Sorry to say, but today´s simple lithium soaps are simply a poor "middle" option.



One of the basic definitions of a lubricating grease has been established by the ASTM, "A solid to semi fluid product of a **thickening agent** in a liquid lubricant. Other ingredients imparting special properties may be included." ASTM D 288 (discontinued). [2] This means that grease is a **thickened** oil not a thick oil! A multi-phase system .... like a sponge full of water. This particular definition focusses on the contents of a lubricating grease, in which there are three major components, the base fluid (liquid lubricant), the soap (thickening agent) and the additives (other ingredients imparting special properties).



A sponge full of water

Lithium EP 2 is probably the most widespread type of grease in the world today. For economic reasons the base fluid is almost always mineral oil, aromatic, naphthenic, paraffinic or a mixtures thereof. Differentiation can perhaps be found in a slight modification of the soap structures or in the details of the production process (peak temperature, heating and cooling rates etc.), but the truth of the matter is that almost all base lithium greases (i.e. without additives) are very similar indeed, if not identical. Me too ! So it is in the third component where differences may be found, **may** be found. But even there, there is a limited choice. Due to the relatively low potential sales volumes, very few additive companies produce dedicated chemistries specifically for greases and this means that the grease formulator is often channelled into the realms of gear oil additivation. Or alternatively, into purchasing ready-made packages, claimed to provide all the properties required to meet varying specifications. So there are not too many options available. This has led to a commoditisation of the grease market where price becomes the most important criteria for choice.

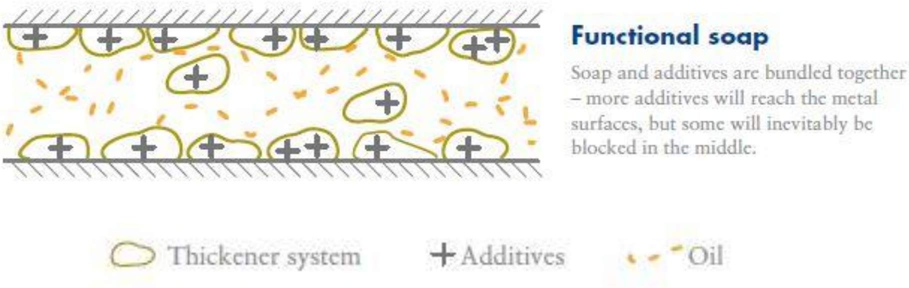
There are other definitions of lubricating grease which need to be considered. In the Choice and Application of Plastic Greases, Sinitsyn[3] claims that grease is "a lubricant which under certain loads exhibits the properties of a solid body, undergoes plastic strain and starts to flow like a fluid should the load reach the critical point and regains solid body properties after the removal of the stress". In rheological terms, grease is a therefore **non-Newtonian plastic solid** ! It does not move under the force of gravity, only when exposed to a higher level of shear.

A more interesting definition has however been proposed by Hamnelid[4] : grease is a dynamic energy saving shearable surface separator (DE + 4S). This is an attempt to describe the use of grease and how it works (= functionality). If we can develop products which keep (bearing) surfaces apart using a minimum of energy, we will have done a good job. If it works, who cares about what it contains or whether or not it has well defined rheological properties !

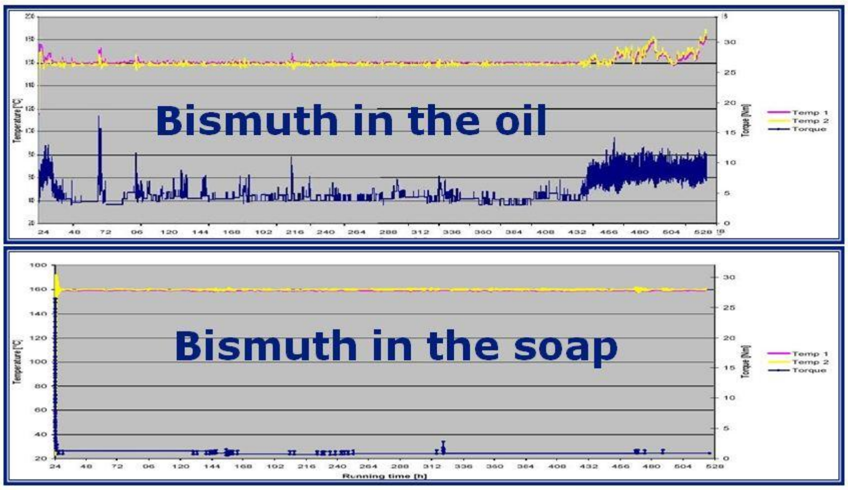
Comparing grease to a sponge full of water does give some interesting insights into the mechanisms of grease lubrication. How, for instance, do you pump a sponge full of water, how do you filter a sponge full of water; what happens to a sponge full of water if exposed to centrifugal forces ? However, the most important mechanism, how the "sponge" is able to deliver the lubricant into the contact zones between the moving surfaces and keeping them apart in an efficient fashion, is a subject of debate. For rolling bearings, this is well described by Lugt[5] where he claims that grease lubrication is a dynamic process which can roughly be divided into three phases, an initial churning phase, a bleeding phase and eventually a severe film breakdown. Using the sponge theory, the soap acts as a reservoir supplying fluid oil into the contacts. Oil separation (or oil "bleed") is therefore critical to the efficiency of the grease. Too high an oil bleed and the grease will dry out after a very short period of time. Too low an oil bleed will also cause dry running since the oil will stay in the bulk matrix and not be available for lubrication purposes. The heart of this debate is however related to the replenishment mechanisms, how the lubricant (whether it might be the whole grease or the fluid oil) gets back into the track once "ploughed" away by the moving parts. We are now well aware of the importance of filament formation in the track behind the rolling bodies and this has been well described by the author in previous presentations[13]. To create an efficient "deforce", we need to carefully study the different replenishment mechanisms. And today, there are much better alternatives to mineral oils, simple soap thickeners, and conventional additives.

Beginning with the most widespread solution, more efficient greases can be formulated using less conventional additives. One example worth mentioning is the use of bismuth based materials. The primary champion of this has been Otto Rohr[6] who is a many time presenter of papers at the NLGI. There are several types of bismuth additives available on the market today including naphthenates, octoates, carboxylates and dithiocarbamates. However, and as Fish and Ward[7] have highlighted, there are some antagonistic relationships to be straightened out. Bismuth and calcium, for example, are not a particularly suitable combination. But once this equation is solved, the rewards can be surprising. In developing a candidate grease for use in the new generation of hub units for heavy vehicles (THU), a proprietary bismuth additive system was introduced into a synthetic lithium complex grease (considered by many as the "best" lithium soap based alternative available today). This was in an attempt to reach an extremely low friction regime. In a test rig designed to simulate a fully loaded truck, after start-up running at a constant speed of 65 km/h, experiencing cornering from 0.1 up to 0.5g lateral acceleration, resulting in radial and lateral forces, the performance of 8 different candidates was evaluated by recording the bearing operating temperatures during the test. The highest bearing operating temperature when lubricated with .. (*the bismuth grease*) .. was below 100^{o}C and when lubricated with .. (*the other greases*) .. was greater than 160^{o}C. A temperature difference of 60 C^{o} !! Science friction ?? As a matter of curiosity, in the conclusion of the report[8], the following was stated. "It was found that laboratory grease tests do not always correlate with the functional test results. For example, .. (*the bismuth grease*) .. would not be considered superior in terms of laboratory testing, yet it shows superior performance in the functional testing." Superior is hardly the right word. It showed a paradigm shift. This is now the first fill grease for this particular application. Functionality was chosen instead of the "original specification".

Continuing on the same theme, bismuth was then introduced as part of the thickener system instead of as a liquid additive in the oil. "Functional soaps", where the active components are connected to the thickener structure, are much more effective since the additives become more readily available for the metal surfaces. This has been reported by Mats Gullander[9] in a previous ELGI paper "To Bi, or not to Bi" and further improvements in both grease life and friction levels have been achieved.



This is the first of our two “opposite” options available to be able to deliver active materials to the metal surfaces. By simply moving exactly the same percentage of metallic bismuth from the additive system (i.e. dissolved in the base fluid) onto the soap structure, a much better performance can be observed. Friction levels drop even further.



Testing conditions: 30 kN@160°C

In the FAG FE8 bearing test rig, a clear improvement can be seen by moving the bismuth into the soap matrix. Using bismuth as a conventional “additive” (i.e. dissolved in the oil), vibrations are clearly visible and the system starts to fail after some 400 hours. Using bismuth as an integral part of the thickener structure instead, there is smooth running for the whole of the test period. Products using this technology have been developed for applications within the automotive, paper & pulp and steel industries as well as a very interesting prototype for wind power which has shown excellent results in the Ripple test[10].

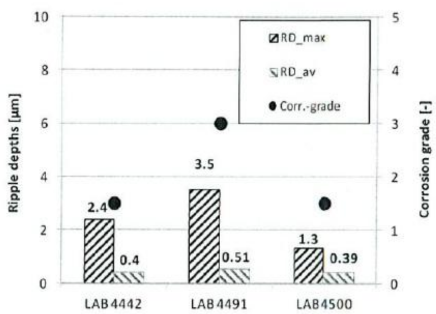


Fig. 5: Results of the ripple test

According to the IME the following recommendation for the classification of the results is proposed:

RD_{max}	< 10 µm	
RD_{av}	< 3 µm	⇒ good ripple protection
Corrosion ≤ 2		

There are other types of functional soaps available today where calcium sulphonate complex is the most widespread. Such products have performed well under harsh conditions, heavy loads, hot & wet, in the steel and paper industries as well as in marine applications. A special adaptation of this type of product is “Alassca complex” which is a novel lithium-calcium grease where the sulphonate has been replaced by a better alternative. This was first presented in an NLGI paper in 1995[11]. This type of product has been developed with a special focus on the lubrication of open gears. Traditional products contain substantial amounts of black solid particles like graphite or MoS_2 and these can cause problems with vibrations and housekeeping. For many years, it has been assumed that these particles are absolutely necessary to be able to keep the mating surfaces apart but this “myth” has been clearly challenged by Stemplinger[12]. In his work using the FZG back-to-back test rig, he has demonstrated that graphite causes wear on the gear surfaces, and the more graphite, the worse it gets.

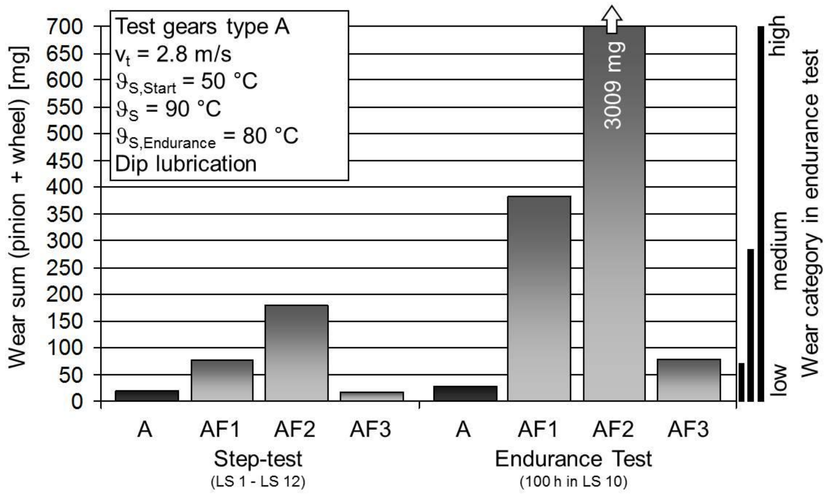


Fig 2 : Wear behaviour – influence of amount and type of solid lubricant[12]

A : *Aluminium complex base grease*

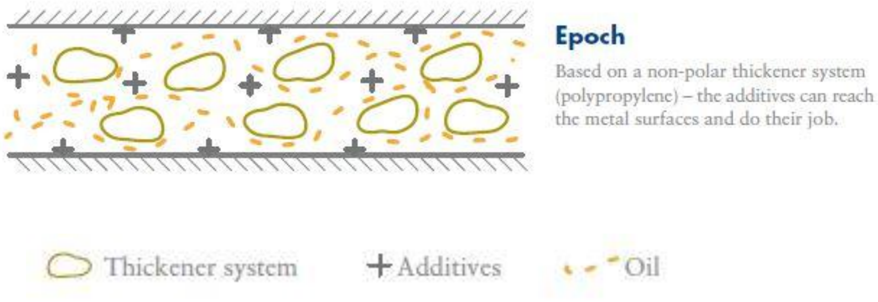
AF 1 : *Base grease + 4.2% graphite*

AF 2 : *Base grease + 11.1% graphite*

AF 3 *Base grease + 4.2% molybdenum disulphide*

Alassca complex greases have performed successfully in open gear applications in the mining and cement industries as well as in traction motor gears on railway locomotives (even in Norway under frozen Arctic conditions). Even as semi-fluid gear greases, they meet the specifications for most open gear applications, high adhesion to the surfaces, good pumpability, excellent corrosion inhibition, extremely high load carrying capacity (4-ball weld load > 7500N), FZG test > stage 12). Everything except the expected content of solids ! The advantages of excluding the solid particles are attractive to the end user, if they can be convinced that a product which is not black will actually do the job. This is the dilemma of any new technology. The current specifications describe the “old” best practice products and, in many cases reject a new and improved product. New products need new specifications. There is no build-up of solids in the gear teeth, reducing vibration and noise and for the ambitious maintenance engineer, the surfaces are visible and can be monitored using, for instance, a stroboscope. And the fact that the greases are not black has even some cosmetic advantages like in the wind power industry where it not seen to be environmentally attractive to see black oil running from the turning gears down on to the ground.

Going to the other extreme, the second "opposite" implies replacing the soap with a non-ionic thickener. Compared to conventional soap thickened greases like lithium EP 2, modern polymer-based greases offer many advantages such as extended re-lubrication intervals while at the same time reducing both friction and wear. Tests under laboratory conditions, and in practice, indicate a potential improvement in grease life somewhere in the region of 10 to 20 times. In addition, by carefully designing the replenishment mechanisms of such polymer greases, additive response can be greatly improved and significant friction and wear reduction achieved.



By reducing the polarity of the thickener system, both the base fluid and the additives now have much better access to the metal surfaces and are able to do their job in a much more efficient way. Yet another, and perhaps even more important, advantage with a polymer system is that the filament forming properties of the grease can be designed to be fit for purpose. In a roller bearing, for instance, any given roller is separated from the raceway by what is left behind by the previous roller. This is extremely important for replenishment, for friction and wear and for bearing life. This has been described in detail a previous NLGI paper "Ecclesiastes 3:1"[13].

An actual "buzzword" in modern society is sustainability ("the capacity to endure") and, in this context, the choice of an effective lubricating greases can make a considerable contribution. For lubricating greases, there are three key issues to consider, long life, low friction and the use of renewable primary produce. And, in addition, by contributing to the optimisation of these factors, we are not only increasing our capacity to endure, there is also a substantial financial reward. The long life issue has been covered in previous articles, so low friction will be the main focus for this paper.

Once again, current specifications can be a hinder to improvement. For instance, many OEMs stipulate a minimum viscosity requirement for the base fluid. This however, assumes that it is only the base oil which is present in the lubricant film. But today, we know better. By blindly following the viscosity recommendations, a far too robust regime is achieved and the film thickness too high. By calculating with the rheology of the grease instead, it is possible to get closer to the optimal conditions, reducing the level of unnecessary excess hydrodynamic lubrication. And the amount of internal friction in the lubricant itself.

As one example, in a recent energy savings project at Volvo Powertrain in Skövde, Sweden[14], comparisons have been made between using conventional types of lubricating greases (lithium complex multi-purpose products) with new and modern materials (synthetic fluids, polymer thickeners, etc.). The results were stunning. In one single paint shop, where 25 fans circulate and evacuate the air, energy savings were calculated to be in the region of 200,000 kWh per year and, at a cost of 1 SEK/kWh, this translates into economic savings of about 30,000 USD ... in one single paint shop. And these were only the energy savings. So what does that mean for the whole plant? And what does that mean on a much wider (national or global) scale? A very large number ! So, how has this been achieved ? The grease recommended by the OEM and, of course (?) the lubricant supplier was a high quality state-of-the-art lithium complex EP 2. Calculating with the advice from the bearing supplier, the grease should have a base oil viscosity around 200 mm^2/s at 40^oC. The grease chosen meets Volvo Specification 97720 and this is a flagship product used by them as factory fill in passenger cars and recommended for aftermarket sales. A slightly stiffer (NLGI 2.5) version is preferred for heavy vehicles. By using a lubricating grease with a base oil viscosity of 210 mm^2/s at 40°C in the flue fans, the film thickness becomes robust and excessive. Full film lubrication is achieved and this is not the most advantageous regime for roller bearings. This can cause the rollers in the bearing to slide and wobble on the lubricant. Normally this leads to extensive wear in terms of smearing and flaking of the raceway. All of this was confirmed by the practical problems experienced in the actual flue gas fan bearings. A more thorough film thickness calculation needed to be made on fully formulated grease, taking both the base oil and the thickener system into consideration in order to determine the required viscosity level for optimal lubrication. Unfortunately, when looking at already available film thickness calculation methods commonly used today to establish the required base oil viscosity, they are only valid for Newtonian behaviour, i.e. for liquids. However, by developing the methods further and adding a new parameter to the calculation, the elastic modulus, the thickener systems´ contribution can be established giving a more accurate lubricating film thickness estimate and thus securing proper lubrication. Aiming for low friction in the EHL regime, calculations were made on fully formulated greases. The conclusion was to reduce the base oil viscosity by a factor of 4-5, giving the roller bodies a slight metal to metal contact and thus the rollers and the rotating ring the same linear speed. There is also an additional advantage in that there will be less "dynamic viscosity" to shear, thereby keeping the bearing temperature at a lower level, which gives a better control over the viscosity and a smoother roller bearing operation. The new product chosen was still based on a lithium complex thickener but the base oil was changed to a polyalphaolefin with a viscosity of 46 mm^2/s at 40°C. By choosing a synthetic base oil, the viscosity index (VI) increases keeping the viscosity more stable in relation to fluctuating temperatures as in the case of the flue gas fan. A field trail was started with this optimized lubricating grease and focus was put on monitoring the roller bearing temperature and the degree of vibration. Vibration monitoring was used to establish re-lubrication intervals and determining when maintenance stops need to be carried out. The first thing observed, once the lubricant had stabilized, was a significant reduction of the roller bearing temperature. The temperature dropped some 20 to 30 C°, the exact magnitude depending on the degree of utilization and the flue gas temperature. A lot of unnecessary friction was thus removed. A rapid drop in the vibrations was also noticed and the fan unit operated much more smoothly. The remaining vibrations basically originated from particle deposition on the fan blades. The reduction of friction and lowering of vibrations is also expected to lead to a decrease of bearing wear which, in turn, should considerably extend the life of the bearing. At the planned maintenance stop, one month later, nothing indicated that the fan was in any need of overhauling. Bearing temperatures stayed at the lower level and vibrations had not significantly increased. It was decided to continue to run the flue gas fan and, at the same time, closely monitor vibration levels until they increased to levels that normally called for replacement actions. After six months of operation, still running smoothly, the fan was shut down, just to be on the safe side, and all the rotating parts were examined. Nothing negative was observed, apart from some minor polishing of the outer ring raceway. The roller bearings were in very good shape and could be re-used. Since Volvo Powertrain is continuously working with optimizing lubricants and lubricating routines, they have recently introduced polymer grease technology instead. By applying this type of product, Volvo Powertrain has succeeded in reducing the bearing temperature of the flue gas fan by an additional 10 C°, down to an operating temperature of 60°C and this trail continued until mid-2012. An attempt was made to simulate the conditions in the laboratory using an SKF R2F test rig and the corresponding calculation models for friction. It is always difficult to make any absolute measurements of friction levels and/or energy savings so a comparative test was run, comparing the originally specified grease with the new polymer product. The calculations only include parameters that effect the "Total frictional moment" (M) and information is available in SKF product catalogue. Without getting into the details of the calculation, we can conclude that by changing from the conventional lithium complex grease to the new technology, energy savings are in the order of **36 %**. This was under laboratory condition and, of course, in the real world, in the paint shop at Volvo Powertrain, the conditions were not so ideal. However, well documented measurements on the energy savings accomplished were in the region of **10%**, still a remarkably high number. And, according to SKF Kappa calculations, the tribo-film in these two tests is far too robust; the optimum kinematic viscosity for the conditions in this test should be about 8 mm^2/s for the base oil, at operating temperatures. The viscosity of the base fluid in the commercially available polymer grease used in the trials is 46 mm^2/s at 40°C. So there is still more to do. The base oil viscosity has been reduced from 210 to 46 and now perhaps 8 mm^2/s at 40°C. To be continued ….

Over and above this, a more recent development has been to incorporate nano-particles into such polymer-based greases. Laboratory tests indicate that friction levels can be reduced, even further. Earlier attempts to introduce nano-particles into conventional soap greases did not show any increased performance. Our theory is that they "disappear" into the soap structures and never interact with each other or the metal surfaces. This is different in polymer thickened products. A series of greases were formulated using the commercial polymer grease as mentioned above. To this was added both a so-called friction modifier and nano-particles. Tests made in the SRV rig have shown a much lower friction (50%) and better wear characteristics compared to the polymer product on its own. Comparing like with like, the coefficient of friction at 120°C drops from a level of 0.12 to 0.06, a significant step in the right direction. And the wear measurements as illustrated by a profiler are also very encouraging.

In conclusion, the implementation of modern tribology offers substantial savings in both wear, energy, and not least money. At the recent World Tribology Congress in Turin, Peter Jost told delegates that "new materials and new technologies are cascading upon the world but their tribological benefits are often not recognised by potential users". In conclusion, he claimed that "applied research in tribology is a good investment. It saves energy, benefits the environment and adds people to the workforce". This is however, nothing new. Already in 1987, the STU (Swedish National Committee for Technical Development) claimed that domestic industry could make substantial savings and this could be done by simply utilising already existing lubricant technologies. By reducing energy losses, friction and wear, the life of machine components could be extended significantly, down-time reduced. Calculations at the time showed a big number : 500,000,000 EUR .. per year. Needless to say, this did not happen. Commoditisation triumphed over sustainability in a mature market like lubricants. We seemingly can't afford to save money !

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14 AXEL Lubrisense™ White Paper 2012-12 www.axelch.com/downloads

A.S. Medzhibovskiy[1], A.A. Moykin[1], L.V. Zheleznyi[2], U.V. Veligorskaja[2]

[1] - "QUALITET GROUP" (Moscow, Russia), [2] – UkrNIINP "MASMA" (Kiev, Ukraine)

Overbased calcium oleo-greases: nanostructure and properties

Various branches of industry and transport are extensively applying high-temperature overbased greases based on calcium sulfonates. The composition of the simple overbased sulfonate greases thickener includes calcium carbonate and calcium sulfonate. The thickener for complex overbased sulfonate greases has a more complicated structure. Calcium sulphonate and carbonate are added with a number of inorganic and organic compounds, forming a grease of a new qualitative level. The term "overbased" is used to denote dispersions containing an excess of metal hydroxide above those needed to neutralize the dispersion agent - sulfonic acid.

Simple sulfonate greases are very sticky due to the high content of sulfonates required to thicken the base oil. Greases are having high protective properties and thermal stability. However, low volumetric-mechanical properties and insufficient antioxidant stability narrow the scope of application of these greases. Simple sulfonate greases are generally applied as a corrosion resistant coating, good in the marine vessels sector.

Complex overbased greases are characterized by high mechanical and colloid stability, good tribological characteristics, but they do require the improvement of protective and anti-oxidative properties using the appropriate additives.

World production of overbased calcium sulfonates, phenolates and salicylates, was growing steadily in recent decades, due to their wide application in motor oils and high-temperature greases. However, recently there has been a steady trend to replace the components made of petrochemical raw materials, with oleo-chemistry products, in the content of grease compositions. A tender interest in renewable agricultural feedstocks, particularly oils and greases for industrial purposes, is a response to the instability of the oil market and environmental problems associated with low biodegradability of synthetic petrochemicals.

The sulfonation process applied for production of calcium petroleum sulfonates is dangerous for the environment. Its waste utilization always requires significant expenses. Therefore, closing the sulphonation plant at the "Martinez Refinery" of the "Shell" Co., casts doubt on the prospects of the petroleum sulphonates supplies and predicts the future trend to replace surfactants of petroleum origin with oleo-chemical products.

In this regard, it is challenging to develop a new generation of overbased high-temperature greases, which thickener composition contains substances obtained from the recovered natural raw materials. We carry out researches aimed to develop a technology of manufacturing simple overbased greases with the thickener containing, in addition to calcium carbonate, calcium soaps of carboxylic acids. These greases have got the title of "oleo-greases".

This work presents the results of researches of the structure and properties of greases, produced with the use of stearic and oleic acids - the most accessible and unexpensive fatty acids, as well as animal and avian fat as an organic component of a thickener.

The technology of oleo-greases production includes the following stages:

• neutralization of acid or saponification of fat in the media of petroleum oil and hydrocarbon solvent;

• solubilization of the estimated quantities of calcium hydroxide and promoter in oil-soap dispersion;

• carbonation with formation of the grease overbased component;

• removal of hydrocarbon solvent and promoter from suspension of the grease overbased component in oil;

• thermo-mechanical treatment of the grease.

It is well known that specific properties of overbased greases are provided by the ultra-dispersed substances formed in the process of carbonation. However, so far is not developed a unified theory of this process in complex emulsions.

According to some researchers, elementary particles of the structural carcass of the sulfonate greases are the micelles and overbased over-micelle carbonate formations (inorganic component) and calcium sulfonate (organic component). According to the former surveys, calcium carbonate presents in the composition of sulfonate and salicylate overbased greases in two forms: calcite and vaterite. There are known its four modifications - one is amorphous and three are crystalline: calcite, vaterite and aragonite. Moreover, vaterite is a least stable polymorph of calcium carbonate, and it is very rare in nature.

To determine the form of existence of calcium carbonate in oleo-greases, there was applied a method of x-ray phase analysis. Diffractograms of oleo-greases on stearate and calcium oleate differ insignificantly. The dominant diffraction reflex of calcite crystalline form of $CaCO_3$ is a peak at 29,13°. Other diffraction peaks belong to the $Ca(OH)_2$. Mass content of $CaCO_3/Ca(OH)_2$) calculated using the program Match ! V.1.9a, makes for the grease on calcium oleate 53/47, and on calcium stearate 59/41. Diffraction reflexes typical for vaterite and aragonite, were not detected.

In order to find out the existence of different calcium carbonate polymorphs in oleo-greases, there is also applied a method of Fourier IR spectrometry, considered to be one of the most reliable among researchers and developers of overbased greases.

Of particular interest is the position of the peaks in the field of 850-880 cm^{-1}. This area in the spectrum corresponds to the different forms of calcium carbonate. Absorption band in the area of 858-862 cm^{-1} characterizes the amorphous calcium carbonate. Peak in the area of 880-885 cm^{-1} corresponds to the calcite form of calcium carbonate. Peak in the area of 875-877 cm^{-1} – faterite form.

In IR-spectra of oleo-greases on calcium stearate, in the field of 850-880 cm^{-1}, are observed the two bands with the frequencies of 872 and 860 cm^{-1}. The first of them doesn't fit into the above intervals. The IR spectrum of calcite powder, given for comparison, are observed bands with frequencies of 878 and 848 cm^{-1}, which also do not fit the proposed intervals for calcite.

Thus, the method of Fourier IR spectrometry can be used to identify calcium carbonate in grease, but it is doubtful for identification of its modifications.

At the same time, the results of x-ray phase analysis clearly show the existence of only two crystalline phases in oleo-greases: calcite and calcium hydroxide.

Thus, we can assume that the inorganic phase of the thickener is a composite of core-shell type. The core – is $Ca(OH)_2$, and the shell - is calcium carbonate in the form of calcite.

It is known that the pH environments play a key role in formation of various polyforms of calcium carbonate during the process of carbonation. Calcite is the dominant product for the high alkaline media.

In the process of carbonation in spirit-water phase, with the highest concentrations of $CA(OH)_{2,}$ is formed calcium carbonate in the form of calcite. On the surface of a positively charged carbonate core is formed a compensating layer of hydroxile anions. Increasing temperature and removing from the system of solvent, promoter and water, the hydroxile anions are gradually being replaced with oleophilic surfactants. Their saturation at the surface of calcite is low due to its low adsorption ability. But at the high concentration of calcite cores, they are able to form the over-micellar structures, i.e. elements of the grease structural carcass.

To study the external shape and spatial structure of oleo-greases, there was used a scanning electron microscopy. It delivers crisp, volumetric photo of the grease’ disperse phase.

As calcite polymorphic modification formed in the process of carbonation, is characterized by low adsorption capacity, the presence in the structure of oleo-greases different in size and shape of the aggregate formations, is explained by the tendency of colloidal particles ti aggregation, with formation of the structure of plastic systems thickener.

The structure of the grease on calcium stearate contains fibers typical for the calcium greases on stearic acid. Thus, dispersed phase of oleo-greases on fatty acids consists of two types of thickener: aggregate formations of calcium carbonate and fibers of calcium stearate.

In order to determine the upper temperature limit for oleo-greases application, we used a method of thermogravimetric analysis (TGA). On the curve of the mass loss from temperature, the initial horizontal area reflects a relative stability of oleo-greases up to 200°C. Vertical ledge on the curve starting at 400°C, indicates the intensive chemical decomposition of greases upon reaching this temperature.

Shape of TG curves indicates almost identical behavior of oleo-greases during the temperature increase. Influence of the nature of thickener’s components in this case does not play any significant role.

The process of studies revealed that thickening ability of raw fats is different and therefore the content of thickener in greases varies widely. It depends on the nature of fatty acids, and also on composition of animal fats, technological conditions of their production, treatment, etc. However, all oleo-greases have a number of positive functional characteristics.

The table shows the results of oleo-grease tests.

The indicator of penetration of all greases corresponds to the 2nd class on the NLGI scale.

As shown in the data table, oleo-greases are characterized by positive volumetric-mechanical properties.

There are also conducted tests of oleo-grease operational properties: oxidation stability, mechanical stability, antiseize characteristics (welding load), water leachability. Quality characteristics of the commercial overbased sulfonate grease are given for comparison. The results show the identity in quality characteristics of oleo-greases with the commercial sulfonate grease.

Anti-wear and anti-friction properties of oleo-greases at different temperatures were defined in accordance with ASTM D 2266. Dependence of the wear spot diameter on the grease test temperature is shown on the illustration.

As follows from the greases test results in accordance with ASTM D 2266, anti-wear properties of oleo-greases are rather high in the whole range of the temperatures used. It should be noted that usually the composition of the complex sulfonate greases is added with a package of anti-wear, oxidation and anti-corrosion additives. And in the composition of oleo-greases the mentioned additives are absent. But these products are having high tribological characteristics without them.

As an indicator of greases' antifrictional properties was taken an average value of the friction coefficient (Coefficient of Friction f), measured within the last 10 minutes of the test of four-ball friction pair. The test conditions were equal with the conditions of the grease antiwear properties test according to ASTM D 2266.

The dependence of the friction coefficient on temperature is given in the figure.

According to the test results, friction coefficient of oleo-greases is quite low in the whole range of temperatures, and at 150°C (ASTM D 2266) - especially low (0,024) and matches the required level of antifriction grease.

Thus, summarizing test results, we can make the following conclusions:

• there have been developed compositions and synthesized simple overbased oleo-greases with balanced properties that are not inferior, and even superior in terms of quality of the commercial overbased sulfonate greases

• there have been settled a composition of oleo-grease thickener primary structures and identified the ultrafine substances formed in the process of carbonation. In oleo-greases, the inorganic component of the thickener is a composite of core-shell type, and the shell is presented exclusively by the calcite modification of calcium carbonate.

• there have been revealed a correlation between the structure of overbased thickener, the nature of surfactant and grease performance characteristics. As oleo-greases are prepared on the same base oil and do not contain functional additives, all of their positive properties are provided by the thickener system. The thickener, effectively thickening base oil and holding it in its carcass, in addition provides grease wit high performance parameters.

• volumetric-mechanical, anti-oxidation and tribological characteristics of oleo-grease are actually not inferior to the best representatives of overbased sulfonate greases containing multifunctional additive packages.

• technology of oleo-greases production is less expensive compared to classical, and greases themselves are environmentally safe, as they are made of the available raw ingredients from renewable sources.

Cost-Effective Formulating.
Sulfurized additives.

Larisa Marmerstein, Jim Vence
The Elco Corporation, 1000 Belt Line St, Cleveland Ohio, 44109, USA

Presenting author email: ***jvence@elcocorp.com***

Introduction – Need for additives in lubricating oils and grease.

Most lubricants are composed of base oil (or grease) and additives. These are chemical compounds that are necessary to improve various aspects of lubrication performance. Different chemistries are used to achieve different performance improvement. Additives are more expensive than base oils, but are used in small amounts, typically between 0.5 and 10%. It would not be correct to only look at the additive's cost per kilo, but % of that additive in the finished lubricant has to be taken into account. The least expensive additive may not be the most cost effective, because treat rate may be higher. And some additives, even more expensive, may have equivalent performances at lower treat level, which makes them more cost effective. When evaluating the effectiveness of an additive, emphasis should be placed on the Net Treat Cost.

Consequently, selecting the most cost effective additives becomes a major goal of the formulators and commercial managers.

Knowing how different chemistries affect different performances makes this task easier.

This presentation will talk about sulfurized chemistry, that is widely used in oil and grease industry to improve Extreme Pressure and Antiwear performance.

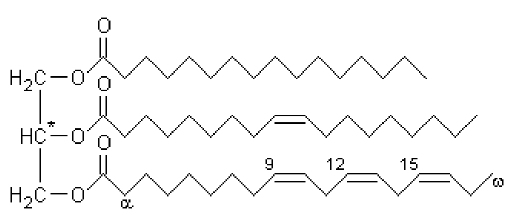
Sulfurized chemistry

Sulfurized chemicals used as lubricant additives are produced by reacting sulfur with organic compounds that contain double bonds in their structure. Sulfur reacts with double bonds, forming bridges consisting of anywhere between 1 and 5 sulfur atoms between the two molecules. The basic reaction may be described as follow:

$$\text{R-C=C-R} + S_8 \Rightarrow \begin{matrix}\text{R-C-C-R} \\ (S)_n \\ \text{R-C-C-R}\end{matrix}$$

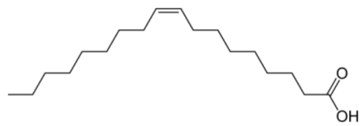
The common substrates used as donors for double bonds can be of natural or synthetic origin. These substances include:

1. Triglycerides derived from vegetable or animal sources. A triglyceride is an ester derived from glycerol and three fatty acids. There are many triglycerides - depending on the oil source some can be highly unsaturated, some less so. Here is an example of a structure of natural triglyceride:

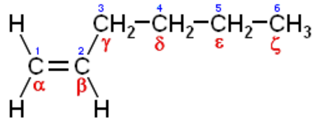


   Most of the natural triglycerides are complex triglycerides – having three different fatty acids attached to glycerol. Depending on the source, the chain length is between 10 and 24 carbon atoms, with up to 3 double bonds per chain. Only fatty acids that contain double bonds can react with sulfur.

2. Saponification reaction and subsequent esterification produce other substrates that are often used in a sulfurization process – free fatty acids and fatty esters. Here is an example of oleic acid structure



3. Olefins – synthetic hydrocarbons that contain a double bond, usualy at the beginning of the carbon chain (α-olefins)



Substrates and their combination, sulfur amount and sulfur type determine physical, chemical and performance characteristics of a sulfurized additive.

Viscosity is largely affected by the substrate being sulfurized:

1. Natural triglycerides are high molecular weight molecules with multiple unsaturation. When sulfurized, they yield high viscosity product.
2. Mono-esters, acids and olefins are low molecular weight substrates that typically have only one double bond per molecule. When sulfurized, the resulting product is low viscosity.
3. Higher sulfur content also results in higher viscosity.

Effect of % sulfur and its structure on the performance characteristics:

Generally natural triglycerides have limited sulfur carrying capabilities. Olefin can support higher oligomers of sulfur, which results in a different EP and AW performance, as shown in the Figure 1. 4 Ball weld test results improve, but wear protection decreases with higher sulfur.

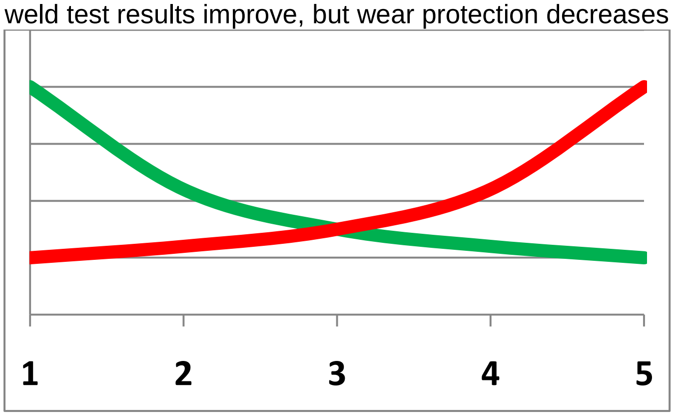


Figure 1. EP (red) and AW (green) performance vs. average number of sulfur atoms in sulfide bridges.

What makes some sulfurized chemicals black and odorous, and some amber with a very mild odor?

The same substrates may be used to make conventional dark color and light color products, but different reaction parameters may result in different esthetic properties.

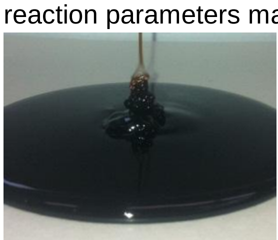


Figure 2. Dark color sulfurized product.

Figure 3. Light color sulfurized product.

Performance evaluation of these additives suggested that manufacturing parameters, in addition to substrate and sulfur content, have some effect on lubricant performance. To do this evaluation 4 Ball Ramp test was used.

Test parameters and equipment.

4 Ball Ramp Test was used to determine that manufacturing parameters, in addition to sulfur and substrate type, have effect on performance.
A state-of-the-art 4 Ball Tester used for evaluation has the following capabilities:

- A pneumatic loading cell that is capable of up to 800 kgf load
- Ability to collect data throughout the run in real time
    - Torque
    - Temperature of fluid
    - Wear
    - Coefficient of Friction
- Ability to change independent parameters during the test
    - Load
    - Temperature of fluid
    - Speed
- Different contact geometry available (e.g. disc-on-disc)

Figure 4. A picture of a 4 Ball tester.

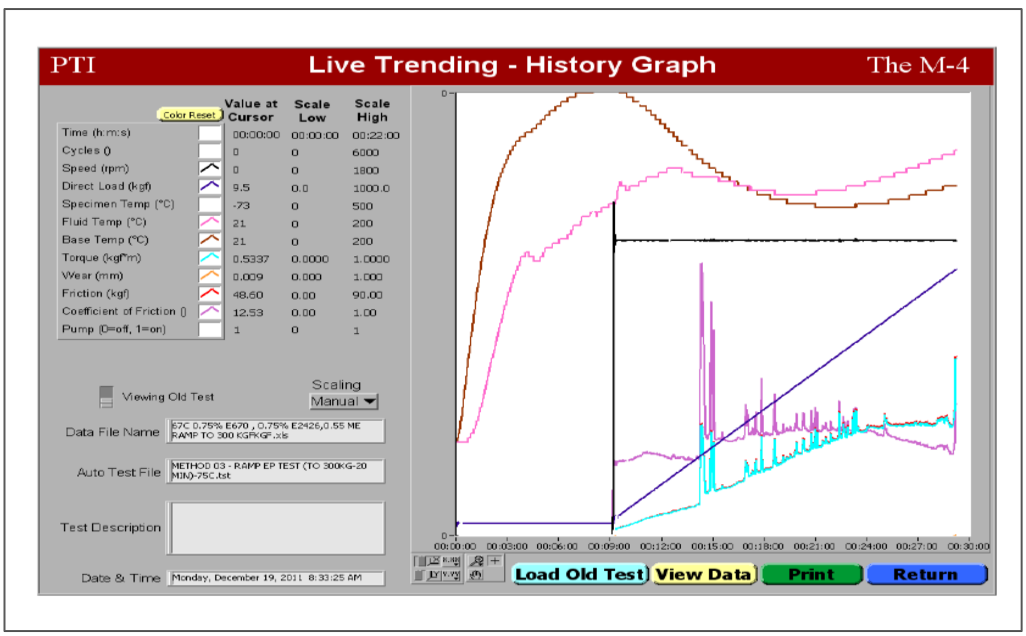


Figure 5. An example of the data collected during the test:
Figure 5 is a live trending graph of a Ramp Test. The test is set up like 4 Ball test, it is run at a constant speed and temperature, with the load increasing (ramping up) from 20 kgf to a higher load over 20 minute period. Torque increases linearly with load till the break in a lubricant film. At this point torque increases dramatically due to microwelds and excessive wear.
Figure 6 shows the Ramp Test results of the light color and dark color sulfurized products, both based on the same mixture of natural triglycerides and olefins. The torque increase in both chemistries is almost

identical, with a dark color chemistry having a few smaller spikes, like a shoulder before the failure. We believe the preliminary spikes are due to a small amounts of byproducts.

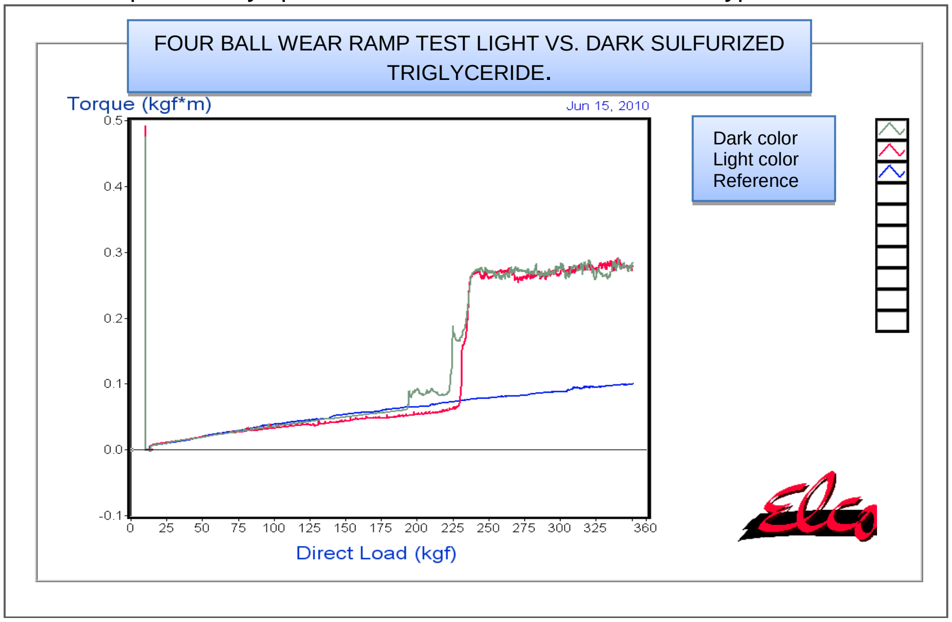


Figure 6. Comparison of light color and dark color sulfurized triglyceride.

Performance evaluation

Standard ASTM methods were used to evaluate various sulfurized chemistries in ISO 32 Group I Base oil. ASTM D4172 4 Ball Wear and ASTM D 2783 4 Ball Weld.

Additive	A	B	C	D
% sulfur	10	17	17	38
% active sulfur	<1	8	8	26
Substrate	Triglyceride	Mix of triglyceride and olefin	Mix of methyl ester and olefin	Olefin
Viscosity	High	High	Low	Low

Table 1. Chemical characteristics of the additives evaluated in ISO 32 Group I base oil

These additives were blended in oil at 5%. The chemical and performance characteristics of lubricating oils made with these sulfurized chemicals are summarized in Table 2:

Blend	1	2	3	4
Additive	A	B	C	D
% of additive in oil	5	5	5	5
% sulfur	0.5	0.85	0.85	1.6
4 Ball Weld	250	315	200	315
4 Ball Wear, mm	0.43	0.58	0.69	0.9

Table 2. Performance of additives in oil, at 5% treat rate.

Blend 3 (additive C) has a rather poor EP performance. It utilizes Methyl Ester as a substrate, which suggests, that sulfurized Methyl Ester by itself does not have very good load-carrying capabilities.

With the blends 1, 2 and 4 (additives A, B and D) Weld load increases but anti-wear performance decreases. This correlation supports the general trend depicted in Figure 1.

Table 2 represents the additives at the same % treat in oil. These additives have different % sulfur in them, so % sulfur in the finished lubricant is also different. Blends 1 and 4 were reformulated to have about the same sulfur content as 2 and 3 (table 4).

Additive	A	B	C	D
% of additive in oil	**9**	**5**	**5**	**2.5**
% sulfur	**0.9**	**0.85**	**0.85**	**0.8**
4 Ball Weld, ASTM	**315**	**315**	**200**	**315**
4 Ball Wear, mm	0.55	0.58	0.69	0.7

Table 4. Performance of additives in oil, blended so that % sulfur is the same for all formulations.

The same Extreme Pressure performance – 315 Weld – was achieved with three different additives, but economics of the three is different. 2.5% of sulfurized olefin with 38% sulfur, compare to 9% of sulfurized triglycerides with 10% sulfur.
In reality, just one performance characteristic (4 Ball Weld in this case) is not enough to assure the best lubricant. Other characteristics have to be considered, such as Wear, Corrosion Protection, Oxidation Stability, etc.
Careful balancing of EP, AW, lubricity and other properties allows a formulator to choose the right additive for the application.

Friction test

A few different substrates were evaluated in an in-house friction test.

- Disc-on-disc geometry
- 40 kg load
- 10 rpm
- Room temperature
- 1% additive in ISO 68 Group I base oil
- Torque over 10 minutes was recorded

Figure 7. A picture of Disc-on-disc test pieces.

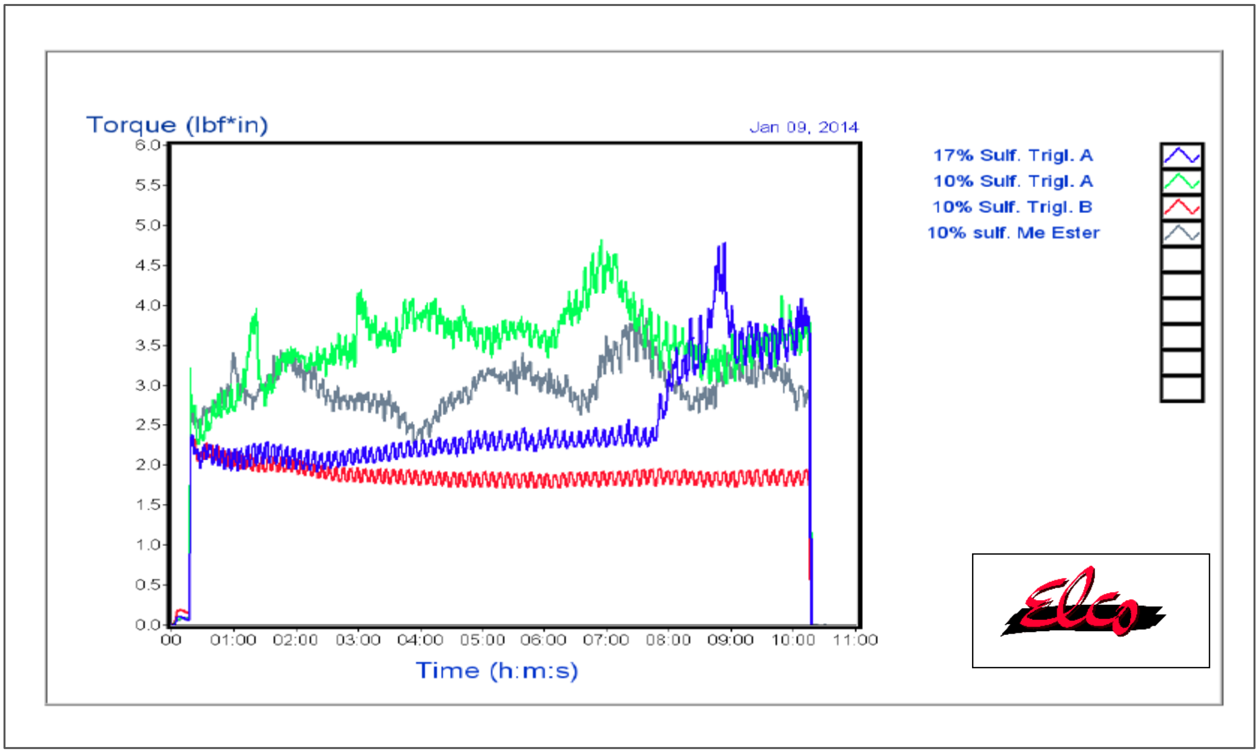


Figure 8. Results for Disc-on-disc friction test

A horizontal smooth line means that the lubricant stayed in place without deterioration, protecting metal surfaces and preventing metal-to-metal contact. Based on these results, only one sulfurized triglyceride (B) was able to perform for the duration of the test. The other triglyceride (A) did much better with an additional amount of sulfur (17% vs. 10%), but still failed toward the end of the test.

Formulating grease using sulfurized additives.

Lithium Soap grease was formulated with different sulfurized ingredients and its performance was evaluated using ASTM methods D2266 for 4 Ball Wear, D 2596 for 4 Ball Weld and D4048 for Copper Corrosion tests. Chemical properties and composition of the sulfurized additives are described in Table 5.

	A	B	C	D
	Mixture of triglycerides, sulfurized	Mixture of triglycerides and olefin, sulfurized	Mixture of triglycerides and olefin, sulfurized	Olefin, sulfurized
Total sulfur, %	9-10	11-12	17-18	37-38
Active sulfur, %	1-2	5-6	8-9	26-28

Table 5. Chemical properties and composition of the sulfurized additives

These additives were blended at 4 % into Lithium Soap, grade 2 grease using planetary mixer and milled using a three roll mill.

% sulfur in grease	No additive	0.36-0.4	0.44-0.5	0.68-0.72	1.48-1.52
4 Ball Weld, ASTM	160	200	250	315	400
4 Ball Weld (10 kgf increments)		200	220	260	330
4 Ball Wear	0.77	0.54	0.56	0.58	1.2
Copper Corrosion		1B	1B	3B	4C

Table 6. Performance of sulfurized additive mixed in Li Soap grease at 4%.

Data from Table 6 suggests that increasing total amount of sulfur and amount of active sulfur correlates with the increase in EP performance. AW performance as measured by 4 Ball Wear changed very little as long as sulfurized triglycerides were present in the lubricant. Wear performance decreased significantly when only sulfurized olefin with high sulfur % is used. Presence of active sulfur also causes copper corrosion and may require formulating with additional additives to protect yellow metal parts.

Conclusions

What should a grease formulator know?

The extreme pressure agent in your formulation typically provides the most important performance characteristic of your grease. Sulfurized chemistry is very effective in improving the Extreme Pressure, Anti-wear and lubricity performance of finished lubricants. There is a wide variety of these chemistries available – different viscosity, sulfur content, sulfur chain length, chemical composition and color. These physical and chemical properties affect performance characteristics in oil and grease. Knowing and understanding additive chemistry will help to formulate the most cost-efficient formulation.

Sulfurized components are generally the most cost-effective way to achieve EP. They have the potential, to deliver 4-ball weld points of 600 kgf or greater and Timken OK loads of 80 lbs. in combination with other additives, even without the use of antimony or solid lubricants.
Careful review of your customers' performance targets will prepare you to work with your additive supplier to select the correct type and concentration of sulfurized EP agent, or, to have one made to your exact specification keeping your treat rate and cost at a minimum.

India NLGI
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