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Grease Compatibility – Relevance and Determination

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Abstract

Switching from one grease to another, be it from one thickener type to another, or from one supplier to another, is no simple undertaking. Different greases can interact when mixed, even at very low levels, in ways that are detrimental to proper lubrication. This paper investigates the phenomena of grease compatibility touching on the causes of incompatibility, how to determine and communicate grease compatibility, and preventative measures that should be taken when switching from one type of grease to another.

It is critically important for both the grease manufacturer and the grease user to understand the importance of grease compatibility when making decisions on grease usage. There are several methods in use today to guide the user in making the best decision for their application.

This paper will use real-world examples to illustrate the effects of grease incompatibility.

Introduction

There are a number of reasons for converting the grease fill in an application or a piece of equipment: Change of supplier, the current product being unknown or no longer available, a change in operating conditions requiring different grease properties, a desire to reduce the number of greases in use on site, or the decision to upgrade to a higher performance or lower cost product.

In any case, whether the product change is on purpose or unintentionally, almost immediately the issue of grease compatibility comes up. While it is preferred to fully clean out all old grease, and then replace with a full charge of the new product, this may not always be feasible, or even technically impossible to do. On the other hand mixing greases without taking the proper precautions with respect to potential incompatibilities can damage the greased components, finally leading to premature equipment failure. In case comingling greases of different origins in the application is unavoidable, it can become vitally important to know about potential performance impacts, which may affect lubrication or equipment life and function over time.

For maintenance professionals, a grease conversion does not have to be a major source of concern though. Knowing about effects of grease incompatibility, and generating related data as outlined in the following, will facilitate application specific risk assessments in case, comingling two greases cannot be avoided. Thus the user can make an informed decision about any actions to be taken before or during conversion to an alternative product, such as equipment cleaning, flushing or purging, increased feed rates, or performance monitoring. This in turn will help perform a successful grease conversion, while ensuring valuable equipment performance and life.

Miscibility and Compatibility

Two greases are incompatible when a mixture of the greases performs worse in service, or has poorer physical properties than either of the constituent greases. An example is shown in *Figure 1* below. The most common indications of grease incompatibility include

- Grease leakage caused by excessive softening.
- Reduced grease flow caused by excessive hardening.
- Oil or grease leakage caused by deterioration of mechanical stability.

It is important to not confuse miscibility and compatibility. As shown in the following pictures (Mixtures of PAO and Ester based LiX greases A and B respectively at different ratios), two greases may mix very well forming homogenous mixtures, but the properties of mixtures can still be inferior to either of the constituents. While miscibility is a prerequisite for compatibility, it is not necessarily sufficient on its own for establishing thus.

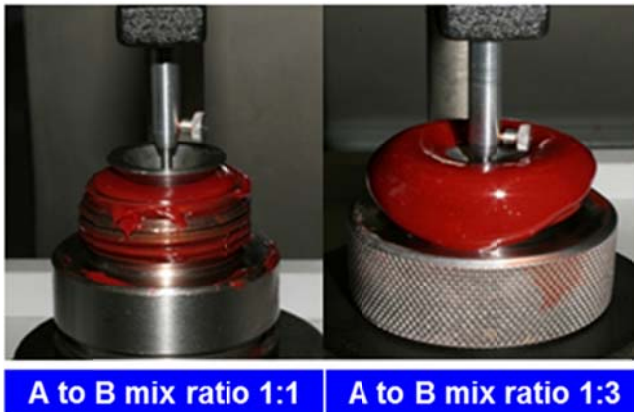


Figure 1: Effect of Grease incompatibility – Extreme softening

Causes for Grease Incompatibility

Lubricating greases are a combination of base oils, additives and thickener. When comingling two different greases these three components can interact with each other, leading to detrimental effects on performance. Consequently grease incompatibility is the result of chemical interactions between any combination of the thickener, base oils or additives.

Figure 2 below represents some general industry knowledge about potential incompatibilities of base oils and thickeners commonly used for lubricating greases.

Compatibility of Grease Thickeners	Li	LiX	PU	CaSu	Ca	CaX	AlX	C	Na
Lithium (Li)									
Lithium Complex (LiX)									
Polyurea (PU)									
Calcium Sulfonate (CaSu)									
Calcium (Ca)									
Calcium Complex (CaX)									
Aluminium Complex (AlX)									
Clay (C)									
Sodium (Na)									
Key	Compatible			Potentially incompatible			Incompatible		
Source	NLGI Lubricating Grease Guide, 5 th Edition, 2006								

Compatibility of Base Oils	API	MO	HC	PAO	AN	LEs	PEs	PAG
Mineral Oils (MO)	1,2							
High VI Mineral Oils (HC)	3							
Poly- α -Olefine (PAO)	4							
Alkylated Naphtalene (AN)	5							
Linear Ester (LEs)	5							
Polyolester (PEs)	5							
Polyglycol (PAG)	5							
		Compatible		Potentially incompatible		Incompatible		

Figure 2: Industry accepted grease compatibility charts

The information contained therein can provide some general guidance and help rule out some combinations from start. However grease compatibility can usually not be predicted with certainty from this foreknowledge of grease compositions, also this information may not be readily available. Uncommonly, even greases composed of the same type of base oils and thickener, although normally compatible when mixed, can be incompatible because of incompatible additive treatments. Last but not least, even within the groups of thickeners or base oils shown in the tables chemical compositions sometimes may vary widely and thus cause incompatibilities even within the same groups.

Therefore evaluating grease compatibility on a case-by-case basis can provide insight into these effects, and thus help ensure the performance of the grease mixtures in application is not inferior to the constituent greases, or deteriorating over time.

Evaluating Grease Compatibility

Evaluating compatibility of two greases from different origins typically would include three stages.

Paper check: The first assessment is based on comparing base oil characteristics, including ISO VG, and thickener type, including NLGI Grade. ExxonMobil typically does not recommend mixing greases differing by more than one ISO VG or NLGI Grade, unless explicitly required for the change.

Basic Laboratory Testing: Predefined mixes and constituent greases are evaluated for basic properties, such as consistency, dropping point, and mechanical or storage stability

Advanced Laboratory Testing: Predefined mixes and constituent greases are evaluated for application specific properties, such as wear protection, water resistance, low and high temperature performance, and many others.

Compatibility Testing

Equipment problems caused by grease incompatibility usually occur over time, but they can also manifest themselves very quickly. Thus compatibility testing in the laboratory can help generate data on potential impact on grease performance at best and worst case scenario levels.

Laboratory testing for grease compatibility typically consists of comparing the properties of grease mixtures and the constituent greases in industry standard tests. The blends of two greases made can represent the potential scenarios during the conversion process. Compatibility rating is based on the deviations from predefined reference limits, established from the constituent greases. To minimize test costs and workload compatibility testing is often conducted in two stages. First basic compatibility ("Miscibility") is established with some basic tests, and then in case basic testing was passed successfully, application specific performance testing will follow to ensure performance of the mixes is suitable for the application ("Performance Retention").

ASTM D6185 Compatibility Testing

This standard provides a protocol for evaluating the compatibility of lubricating greases in two stages:

- **Primary Testing:** Dropping point, mechanical stability, and storage stability at elevated temperatures
- **Secondary Testing:** For mixtures passing all primary tests, application specific non-mandatory testing schemes are suggested when circumstances indicate the need for additional testing.

Pass, borderline or fail ratings for all tests are somewhat depending on the property evaluated, but in general are referred to lower or upper values of the constituent greases. Final compatibility ratings then are based on the single property ratings.

Compatibility Testing – Opportunities to improve ASTM D6185

While ASTM D6185 provides some good insight into grease compatibility and compatibility testing including sample preparation, in some cases interpreting test results generated as suggested in this standard can become somewhat challenging.

ASTM D6185 pass requirements do not account for test precision, making a pass potentially impossible when properties of both greases are numerically close or even identical. This is not unlikely to occur when greases of similar performance, e. g. same NLGI consistency class are mixed, as represented graphically in the following *Figure 3*. It is evident, that a pass becomes the more difficult, the smaller the difference between the fresh grease properties are.

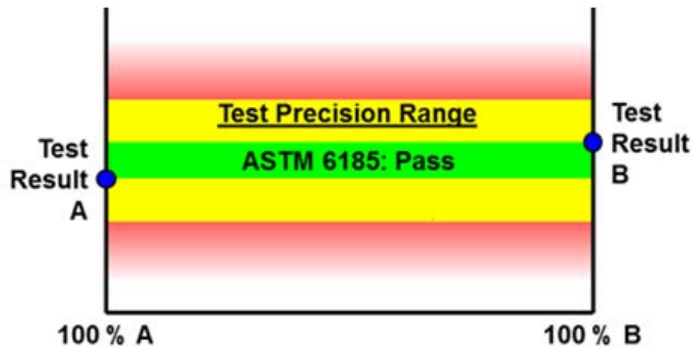


Figure 3: ASTM 6185 results for two greases of differing penetration

To overcome this, testing pass requirements should account for test precision, as expressed by test repeatability and reproducibility.

Moreover ASTM D6185 does not account for properties combining linearly relative to mix ratios. Consequently if test results for the constituent greases are significantly different, incompatible greases may still pass requirements. This case, graphically represented in *Figure 4*, could occur e. g. when one or more properties are changed intentionally to address changes in operating conditions.

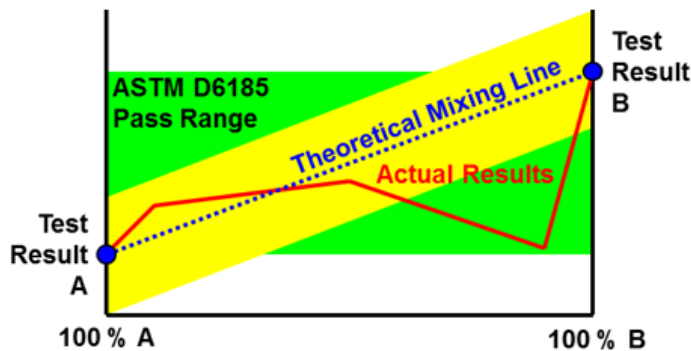


Figure 4: Improved interpretation of compatibility results.

While considering the test precision, compatibility testing pass/fail ratings for properties combining linearly are based on deviation of test results from the theoretical mixing line.

Summary

When conducting a grease conversion, it is of vital importance for equipment and grease life to know about potential incompatibilities between the greases, when mixed in the application. Compatibility testing can help developing conversion strategies including application specific risk assessments, and potential mitigating actions to minimize service interruptions.

Impact of EP Additives on Overbased Calcium Sulfonate Complex Greases

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Abstract

In real grease application cases, there will always be the need and demand to achieve higher performance levels. Though the inherent superiority in extreme pressure (EP) performance of calcium sulfonate complex grease is very obvious in both lab bench tests and real world applications, every now and then, there are complaints that the intrinsic EP performance offered by the base grease is not enough. This present paper reports the impact certain unique EP additive chemistries have on the EP performance of overbased calcium sulfonate complex greases. Further, the MTM test method is employed to comprehend the effect of various additives mixed with overbased calcium sulfonate grease on EHL, mixed and boundary lubrication regime.

Introduction

Calcium sulfonate complex grease, since its development and introduction from the simple calcium sulfonate grease more than 20 years ago, has gained significant commercial interest and popularity in recent years (1-9). It is the only grease thickener system which has enjoyed a more than 30% annual growth rate by a recent grease production survey (10), albeit from a relatively small base. Expiration of certain key calcium sulfonate complex grease patents, and improved availability of key raw materials, i.e. high TBN Newtonian calcium sulfonate suitable for grease making, may explain partially the trend. However, the real driving force for the popularity of this relatively new grease thickener technology is the fact that the thickener system can also provide several key intrinsically superior grease performance functionalities without any or with minimal use of grease performance additives. The thickener system for the calcium sulfonate complex grease probably can be considered as one of the most complex among all complex greases. It is believed that the main component of this thickener system, i.e. calcium sulfonate covered crystalline calcium carbonate in micelle form is the key to its inherent high load carrying or extreme pressure capability, excellent water resistance and rust inhibition performance. The pseudo particle nature of calcium sulfonate covered calcite micelle further explains its high temperature performance similar to most particle thickened greases like bentonite clay or fumed silica thickened greases.

Nevertheless, in real grease application cases, there will always be the need and demand to achieve higher performance levels. Though the inherent superiority in extreme pressure (EP) performance of calcium sulfonate complex grease is very obvious in both lab bench tests and real world applications, every now and then, there are complaints that the intrinsic EP performance offered by the base grease is not enough. This present paper reports the impact certain unique EP additive chemistries have on the EP performance of overbased calcium sulfonate complex greases. Further, the MTM test method is employed to explore the mechanism of such improvement.

Grease Samples and Additives

Three overbased calcium sulfonate complex base greases were obtained from three different regions. Base Grease A is from North America, Base Grease C is from Asia Pacific and Base Grease S is from Europe. Three different EP additives and two antiwear additives/friction reducers were used in this study. The identities of these base greases and additives are listed in Table 1.

Table 1. Base Greases and Additives

Grease A	Ca Sulfonate Complex Base Grease from North America
Grease C	Ca Sulfonate Complex Base Grease from Asia Pacific
Grease S	Ca Sulfonate Complex Base Grease from Europe.
Metal DTC	Mixed metal (Sb and Zn) dialkyl dithiocarbamate (liquid, 80% active ingredient) (11)
DMTD	2,5-dimercapto-1,3,4-thiadiazole (solid, 100% active ingredient) (12)
DMTD Dimer	1,3,4-thiadiazole-2(3H)-thione,5,5-dithiobis (solid, 100% active ingredient)(13)
MoDTP	Molybdenum dialkyl dithiophosphate (liquid, 75% active ingredient)(12)
MoDTC	Molybdenum dialkyl dithiocarbamate (solid, 100% active ingredient)(12)

Experimental Technique

In antiwear and EP performance evaluation, standard ASTM test methods and conditions were used. For four-ball wear test, ASTM D2266 test method was used. For four-ball EP test, ASTM D2596 test method was used. For Timken EP test, the Timken OK Load was measured according to ASTM D2509 test method.

Rolling and sliding friction experiments were conducted using Mini Traction Machine (MTM). MTM consists of a rotating $\frac{1}{2}$ " diameter 52100 steel ball pressed against an independently rotating 52100 steel disc immersed in the grease. The operating conditions are set by independently controlling the rotational velocities of the shafts that drives the ball and the disc, in order to obtain a particular combination of rolling speed and slide to roll ratio, as well as by controlling the contact force and the oil bath temperature.

All experiments were conducted at two temperature 40°C (low temperature) and 140°C (high temperature). All experiments were carried out at 0.5 slide to roll ratio corresponding to 50% rolling-sliding contact conditions. Slide-roll ratio is defined as the ratio of sliding speed to ub-ud mean speed, where ub and ud are speed of ball and disc respectively. These experiments were carried out at contact pressure of 1.5 GPa. Mean speed for each Stribeck curve were started at 1000 mm/s and decreasing in steps of 100 mm/s to 100 mm/s and finally decreased from 100 mm/s in steps of 10 mm/s to 10 mm/s.

A comparison of the performance of each grease samples can be made by integrating the area under each Stribeck curve. The value of this integral, $TC.\log(u)$, is known as the Stribeck Friction Coefficient (SFC). Lower values of SFC indicate that less energy will be absorbed by the lubricant under mixed and EHL regimes. Lower values would therefore be expected to correlate with better performance in reducing frictional losses.

Results and Discussion- Rolling – Sliding Friction using Mini Traction Machine

Rolling-Sliding Friction of Overbased Calcium Sulfonate Grease

The frictional properties of overbased calcium sulfonate Greases A, C & S were evaluated using Mini Traction Machine (MTM) as show in Figure 1. Typical Stribeck curves were generated through continuous rubbing test at 50% slide-roll ratio where friction is measured over a range of entrainment speeds at low and high temperature of 40°C and 140°C. As the test time progresses, it can be seen that friction increases when entrainment speed decreases for all three grease samples at 40°C and 140°C. Moreover, all overbased calcium sulfonate grease samples demonstrated noticeably different Stribeck curves. At 140°C overbased calcium sulfonate Grease S shows dramatic increase in the friction compared to Greases A and C as well as Grease S at 40°C at intermediate entrainment speed. Interestingly, at lower speed and at 140°C, all three grease samples demonstrated reduction in friction. At lower speed and higher temperature, Stribeck curve operates under boundary lubrication regime where an increased number of asperities contact would occur which leads to higher possibilities of wear and friction. However, reduction in friction in the boundary lubrication regime indicates the formation of a friction reducing film by overbased calcium sulfonate grease.

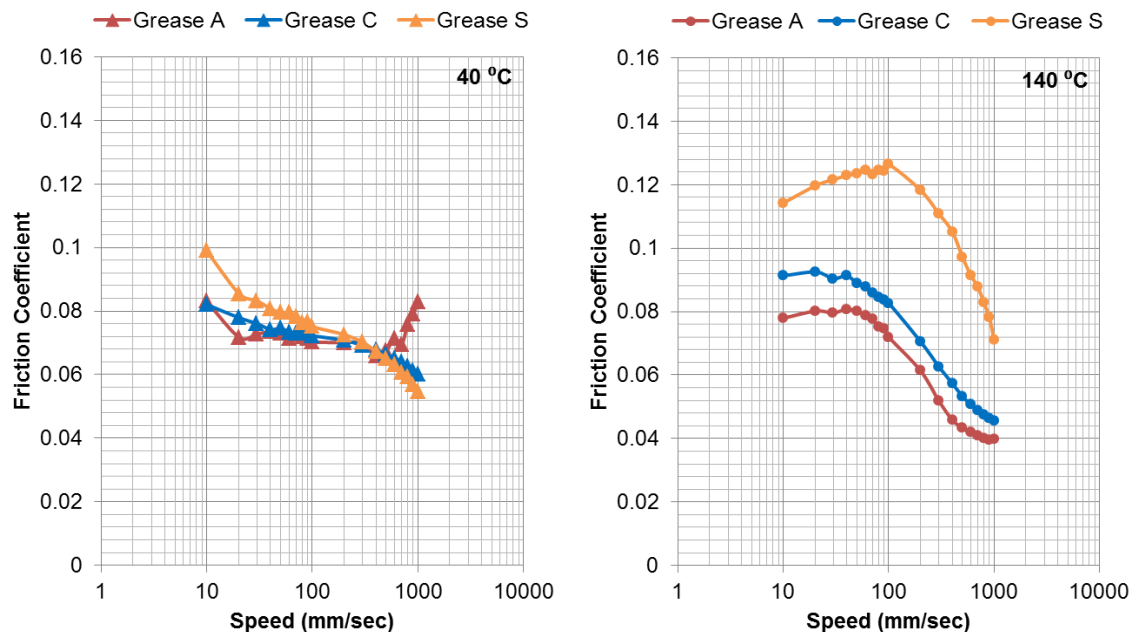


Figure 1 Stribeck curve (speed vs. friction) obtained at 40°C and 140°C for 50% sliding-rolling condition at 1 GPa using calcium sulfonate greases A, C and S

Figure 7 shows Stribeck friction coefficient (SFC) for overbased calcium sulfonate Greases A, C & S at 40°C and 140°C. Comparison of SFC values at 40°C and 140°C indicates energy absorbed by the test samples in boundary, mixed and EHL lubrication regime as a function of temperature. Higher SFC values of Grease S at 140°C than at 40°C is indicative of higher energy absorption with increasing temperature which contributed to higher frictional energy losses during test. An analogous phenomenon was noticed with Grease C. Grease A, however, has a lower SFC value at 140°C than at 40°C indicating less energy absorption at 140°C thereby suggestive of less frictional energy losses with increasing temperature.

Effect of Metal Dithiocarbamate

Antimony dithiocarbamates in combination with ammonium or zinc dithiocarbamate was added to the grease samples and the rolling friction performance was measured. As shown in Figure 2, Stribeck curve at 40°C shows analogous friction behavior at all entrainment speeds for all three greases which indicates less influence of metal dithiocarbamate (DTC) addition to overbased calcium sulfonate grease on the rolling friction compared to grease by itself. However, at higher temperature, a significant increase in the rolling friction was noticed with Grease S mixed with metal DTC.

As shown in Figure 7, higher SFC values at 140°C for Grease S mixed with metal DTC indicates higher energy absorption for all boundary, mixed and EHL lubrication regime which contributed to higher frictional energy losses. Similar frictional performance was observed with Grease S without addition of metal DTC (Figure 2).

Percent friction reduction of overbased calcium sulfonate grease due to addition of metal dithiocarbamates was calculated, as shown in Figure 8. Grease S mixed with metal DTC displays an improvement in the reduction of friction at 40°C. This frictional benefit is completely lost at 140°C where frictional losses increased by 4%. SFC values and frictional increases at 140°C for Grease S indicate that addition of metal DTC does not contribute to the friction improvement of Grease S. On the contrary, at

140°C, Grease sample C mixed with metal DTC shows 26% friction reduction compared to base grease itself. Similarly, Grease A mixed with metal DTC shows reduced friction at both temperatures. SFC values and percent friction reduction in tandem indicate that metal DTC shows synergistic effect to reduce frictional losses at higher temperature with Greases A and C, while it shows antagonistic effect with Grease S.

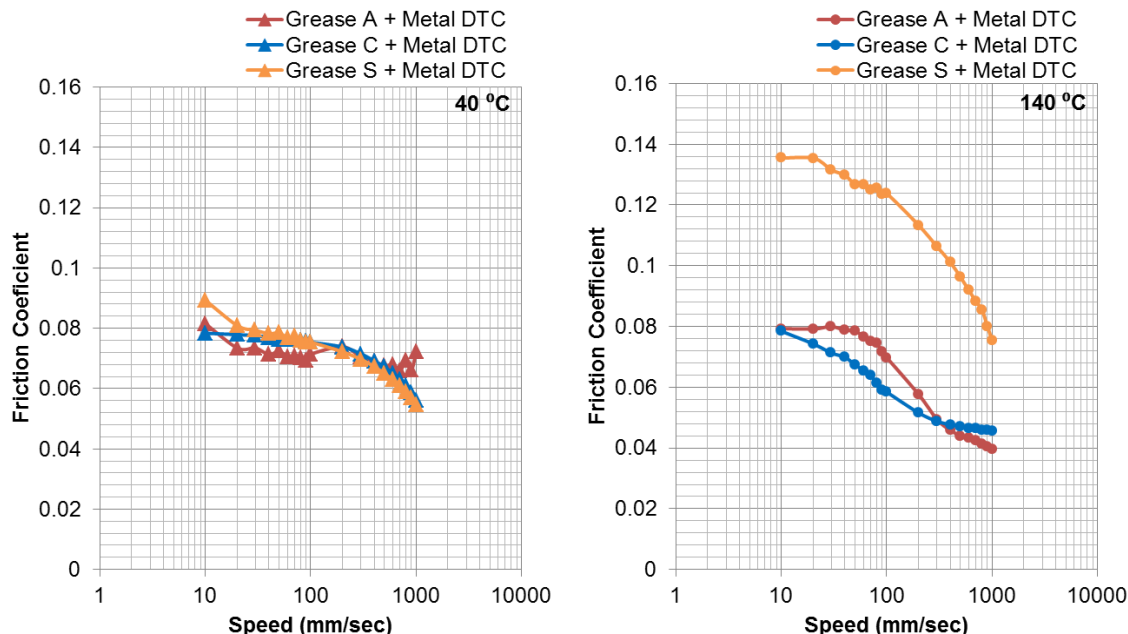


Figure 2 Stribeck curve (speed vs. friction) obtained at 40°C and 140°C for 50% sliding-rolling condition at 1 GPa using calcium sulfonate Greases A, C and S mixed with Mixed metal (Sb and Zn) dialkyl dithiocarbamate (liquid, 80% active ingredient)

Effect of DMTD

2,5-dimercapto-1,3,4-thiadiazole (DMTD) was evaluated for its rolling friction performance in overbased calcium sulfonate grease. As shown in Figure 3, Greases C and S mixed with DMTD exhibit typical Stribeck curve where rolling friction increased as entrainment speed reduced at 40°C and 140°C. However, Grease A mixed with DMTD shows contrasting friction performance at 40°C and 140°C. At 40°C, reduction in the friction is noticed with reduction in the entrainment speed indicative of formation of friction reduction film at lower temperature in mixed and boundary lubrication regime. At 140°C, Grease A mixed with DMTD shows increase in the friction at lower entrainment speed at higher temperature.

As shown in Figure 7, all greases mixed with DMTD exhibit lower SFC values with increased temperature. Percent friction reduction results, as shown in Figure 8, indicate that Greases C and S mixed with DMTD can reduce frictional energy losses by 23% and 73% respectively at 140°C. Only Grease A mixed with DMTD shows an increase in the friction compared to base grease at 40°C and a slight increase in friction at 140°C

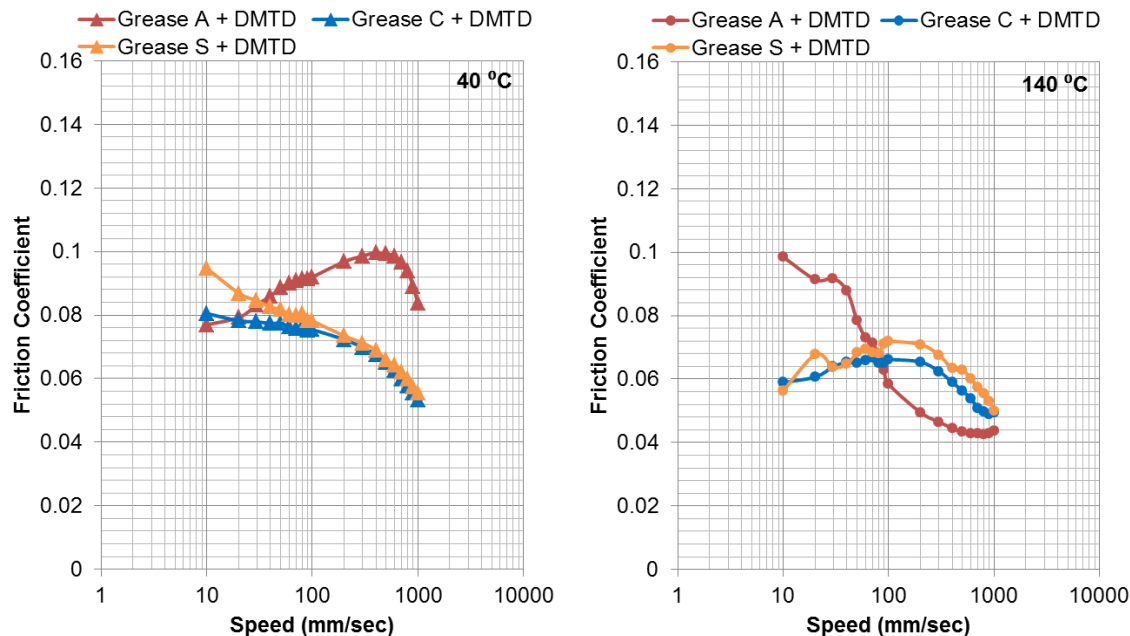


Figure 3 Stribeck curve (speed vs. friction) obtained at 40⁰C and 140⁰C for 50% sliding-rolling condition at 1 GPa using calcium sulfonate greases A, C and S mixed with 2,5-dimercapto-1,3,4-thiadiazole

SFC values and percent friction reduction results indicates that DMTD interacts synergistically with all overbased calcium sulfonate greases at higher temperature which contributes to lower frictional losses and improved rolling friction performance of overbased calcium sulfonate grease.

Effect of DMTD Dimer

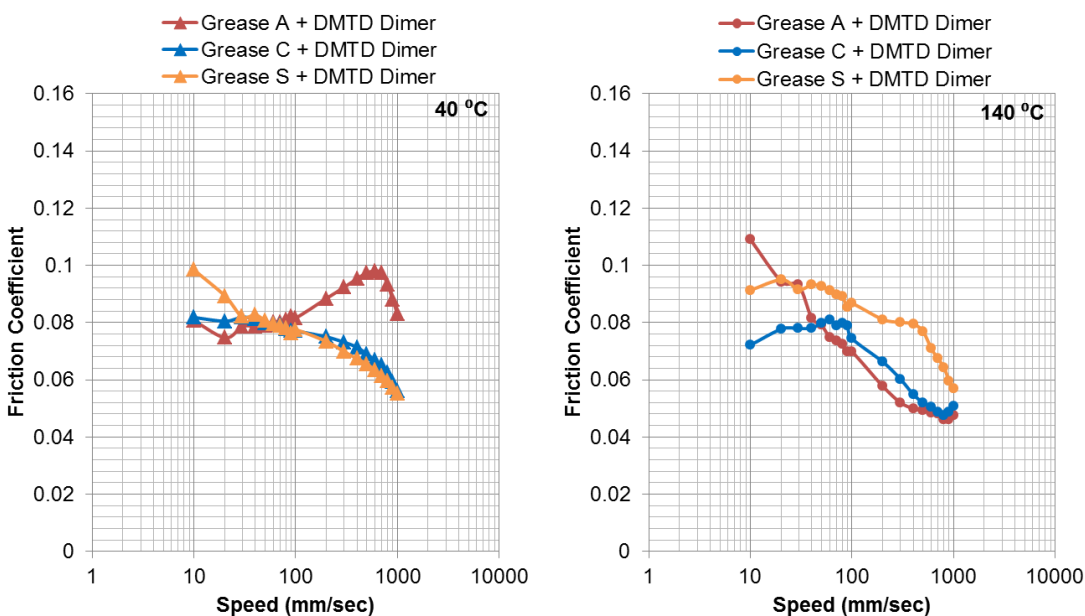


Figure 4 Stribeck curve (speed vs. friction) obtained at 40⁰C and 140⁰C for 50% sliding-rolling condition at 1 GPa using calcium sulfonate greases A, C and S mixed with 5,5-dithiobis(1,3,4-thiadiazole)

5,5-dithiobis(1,3,4-thiadiazole) (DMTD Dimer) was evaluated for its rolling friction performance in overbased calcium sulfonate grease. As shown in Figure 4, Greases C and S mixed with DMTD Dimer exhibit typical Stribeck curves where rolling friction increased as entrainment speed reduced at 40°C and 140°C. However, Grease A mixed with DMTD Dimer shows contrasting friction performance at 40°C and 140°C. At 40°C, reduction in the friction is noticed with reduction in the entrainment speed, indicative of formation of friction reduction film at lower temperature in mixed and boundary lubrication regime. At 140°C, Grease A mixed with DMTD Dimer shows increase in the friction at lower entrainment speed.

As shown in Figure 7, higher SFC values at 140°C for Grease S mixed with DMTD Dimer indicates higher energy absorption for all boundary, mixed and EHL lubrication regime which contributed to higher frictional energy losses. Similar frictional performance was observed with Grease S without addition of metal DTC (Figure 2). While Greases A and C mixed with DMTD Dimer exhibit lower SFC values with increased temperature.

Figure 8 shows percent friction reduction of overbased calcium sulfonate Greases A, C & S mixed with DMTD Dimer at 40°C and 140°C compared to overbased calcium sulfonate grease by itself. Grease S mixed with DMTD Dimer shows 34% friction reduction at 140°C, while Grease C mixed with DMTD Dimer shows 11% reduction in friction compared at 140°C. Only Grease A mixed with DMTD Dimer shows increase in the friction compared to base grease at 40°C and a slightly lower increase in friction at 140°C.

SFC values and percent friction reduction in tandem indicate that DMTD dimer shows synergistic effect to reduce frictional losses at higher temperature with Greases A and C, while it shows antagonistic effect with Grease S.

Effect of DMTD Dimer & MoDTC

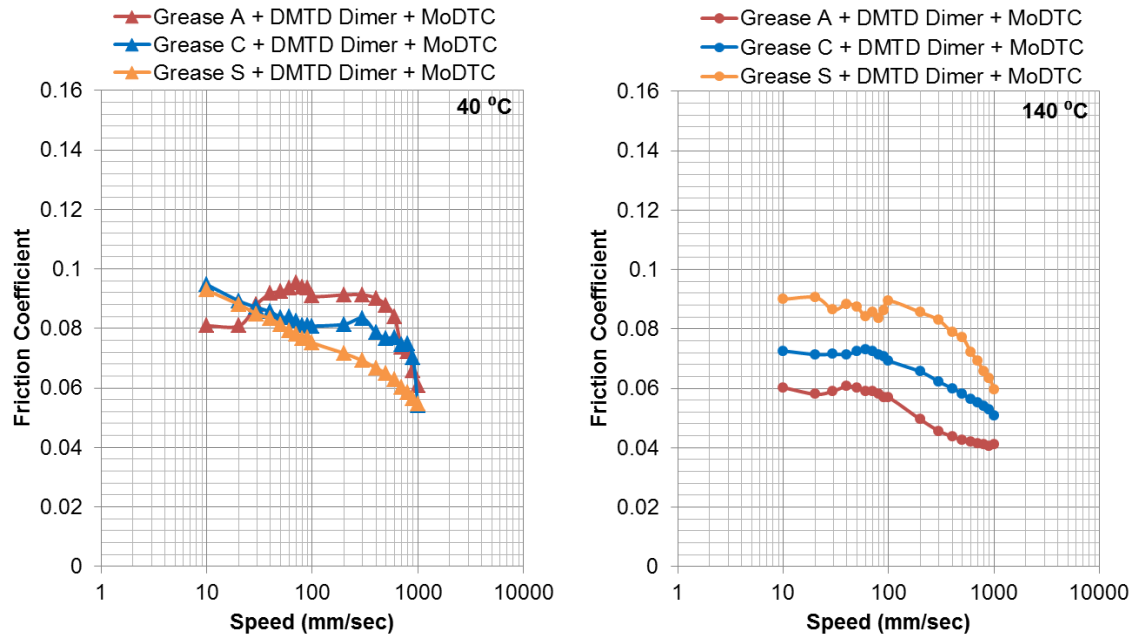


Figure 5 Stribeck curve (speed vs. friction) obtained at 40°C and 140°C for 50% sliding-rolling condition at 1 GPa using calcium sulfonate Greases A, C and S mixed with 5,5-dithiobis(1,3,4-thiadiazole) and Molybdenum dialkyl dithiocarbamate

A combination of 2 mass% 5,5-dithiobis(1,3,4-thiadiazole) (DMTD Dimer) and 1 mass% molybdenum dialkyl dithiocarbamate was evaluated for its rolling friction performance in overbased calcium sulfonate grease. Figure 5 shows that addition of molybdenum dialkyl dithiocarbamate (MoDTC) along with DMTD Dimer in Grease A significantly reduces rolling friction at 140°C.

As shown in Figure 7, higher SFC values at 140°C for Grease S mixed with MoDTC along with DMTD Dimer indicates higher energy absorption for all boundary, mixed and EHL lubrication regime which contributed to higher frictional energy losses. Similar frictional performance was observed with Grease S without addition of metal DTC (Figure 2). While Greases A and C mixed with MoDTC and DMTD Dimer exhibit lower SFC values with increased temperature. A combination of MoDTC and DMTD Dimer appears to activate at higher temperature which resulted in reduced friction at all entrainment speeds. SFC values validate this observation. This is distinctly contrasting to the Stribeck curve generated by grease sample mixed with DMTD Dimers but without MoDTC.

Interestingly, addition of molybdenum dialkyl dithiocarbamate to Grease S mixed with DMTD Dimer reduced friction by 35% compared to base grease. Similarly, Grease A and Grease C mixed with molybdenum dialkyl dithiocarbamate and DMTD Dimer reduced friction at higher temperature by 24% and 14%, respectively.

SFC values and percent friction reduction results indicate that MoDTC and DMTD Dimer interact synergistically with all overbased calcium sulfonate greases at higher temperature which contributes to lower frictional energy losses and improved rolling friction performance of overbased calcium sulfonate grease.

Effect of DMTD Dimer & MoDTP

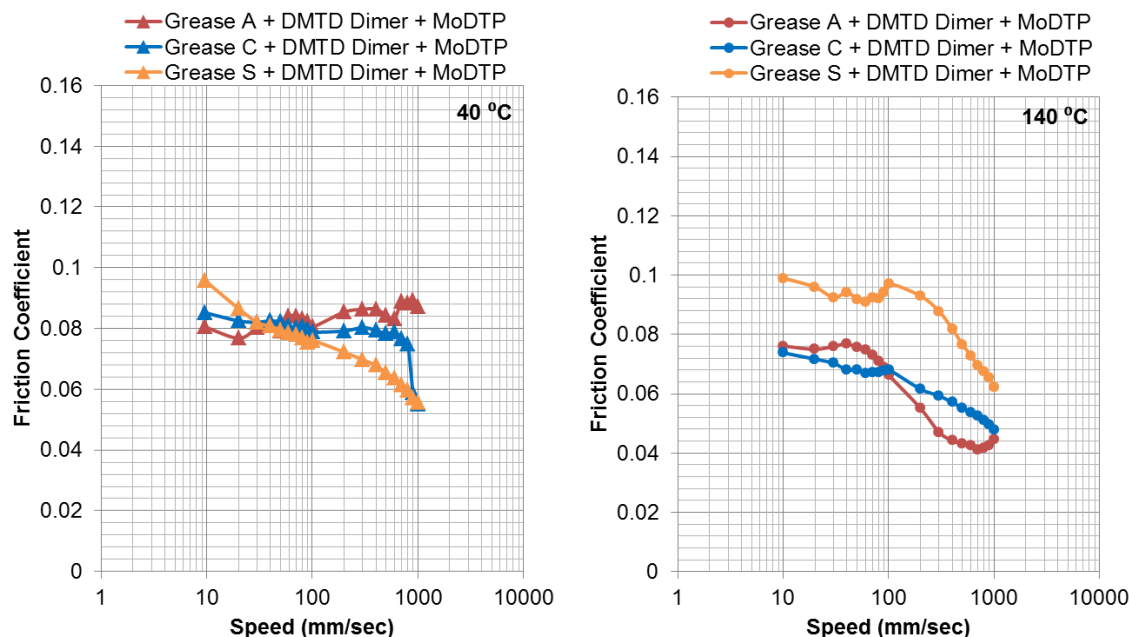


Figure 6 Stribeck curve (speed vs. friction) obtained at 40°C and 140°C for 50% sliding-rolling condition at 1 GPa using calcium sulfonate Greases A, C and S mixed with 5,5-dithiobis(1,3,4-thiadiazole) and Molybdenum dithiophosphate

A combination of 5,5-dithiobis(1,3,4-thiadiazole) (DMTD Dimer) and molybdenum dithiophosphate was evaluated for its rolling friction performance in overbased calcium sulfonate grease. Figure 6 show

that addition of molybdenum dithiophosphate (MoDTP) along with DMTD Dimer in Grease A significantly reduces rolling friction at 140°C.

As shown in Figure 7, higher SFC values at 140°C for Grease S mixed with MoDTP and DMTD Dimer indicate higher energy absorption for all boundary, mixed and EHL lubrication regime which contributed to higher frictional energy losses. Similar frictional performance was observed with Grease S without addition of metal DTC (Figure 2). While Greases A and C mixed with MoDTP and DMTD Dimer exhibit lower SFC values with increased temperature. This is distinctly contrasting to the Stribeck curve generated by grease sample mixed with DMTD Dimer but without MoDTP.

Interestingly, addition of MoDTP to Grease S mixed with DMTD Dimer reduced friction by 28% compared to base grease. Similarly, Grease A and Grease C mixed with MoDTP and DMTD Dimer reduced friction at higher temperature by 7% and 19%, respectively.

SFC values and percent friction reduction results indicate that MoDTP and DMTD Dimer interact synergistically with all overbased calcium sulfonate greases at higher temperature which contributes to lower frictional energy losses and improved rolling friction performance of overbased calcium sulfonate grease.

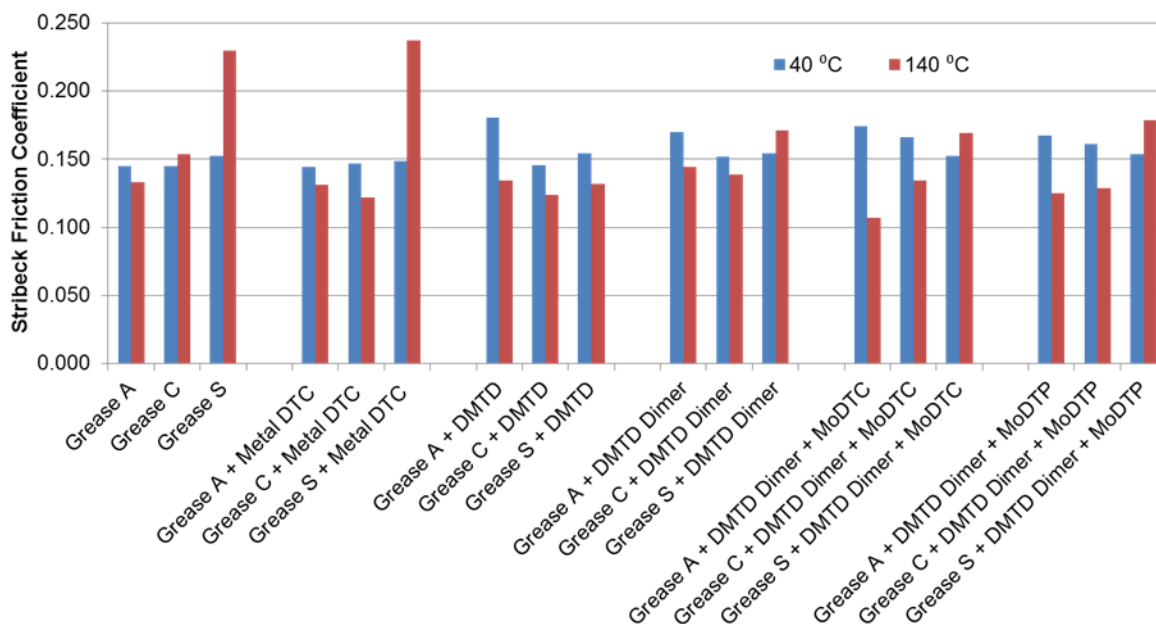


Figure 7 Stribeck Friction Coefficient (SFC) for overbased calcium sulfonate greases A, C & S mixed with different EP and AW additives at 40°C and 140°C

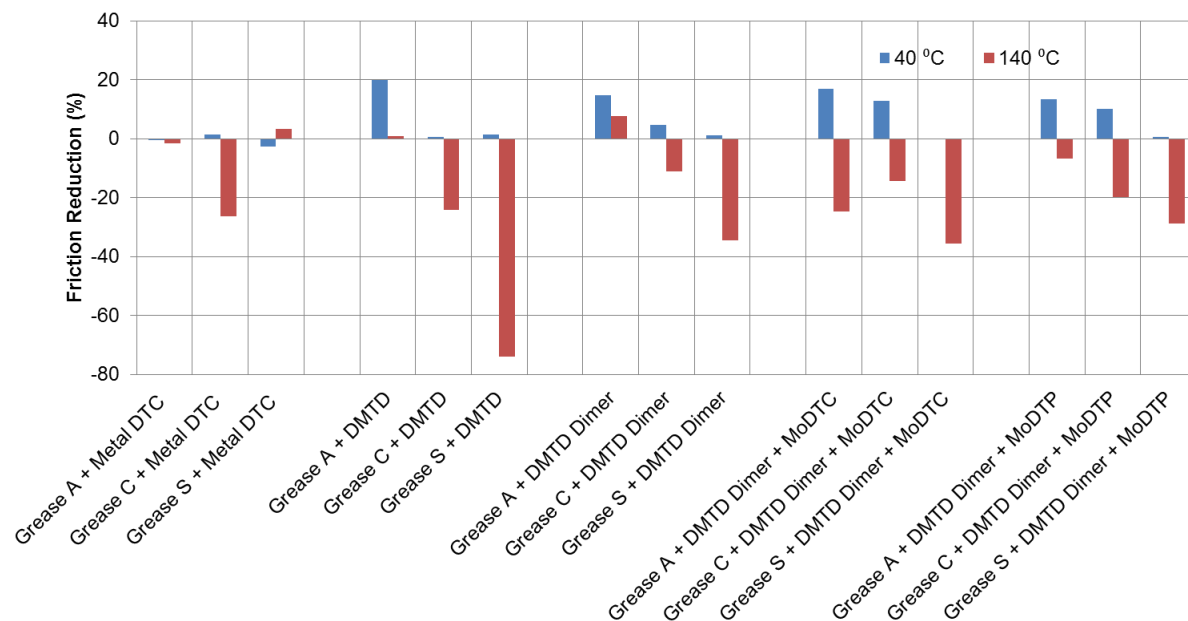


Figure 8 Percent friction reduction of overbased calcium sulfonate Greases A, C & S mixed with different EP and AW at 40°C and 140°C compared to overbased calcium sulfonate grease by itself

EP and AW Performance

Performance of Grease A, Grease C and Grease S treated and untreated are listed in Table 2.

Table 2. Summary of Four-Ball Wear, Four-Ball EP and Timken Test Data

Formulation	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Grease A	100	97	97	97	97	97	-	-	-	-	-	-	-	-	-	-	-	-
Grease C	-	-	-	-	-	-	100	97	97	97	97	97	-	-	-	-	-	-
Grease S	-	-	-	-	-	-	-	-	-	-	-	-	100	97	97	97	97	97
Metal DTC	-	3	-	-	-	-	-	3	-	-	-	-	-	3	-	-	-	-
DMTD	-	-	3	-	-	-	-	-	3	-	-	-	-	-	3	-	-	-
DMTD Dimer	-	-	-	3	2	2	-	-	-	3	2	2	-	-	-	3	2	2
DMTD Dimer + MoDTP	-	-	-	-	1	-	-	-	-	-	1	-	-	-	-	-	1	-
DMTD Dimer + MoDTC	-	-	-	-	-	1	-	-	-	-	-	1	-	-	-	-	-	1
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Four-Ball Wear Scar (mm)	0.41	0.40	0.45	0.45	0.42	0.38	0.56	0.72	0.64	0.67	0.69	0.50	0.56	0.62	0.62	0.67	0.66	0.54
Four-Ball Weld (kgf)	800+	N/T	N/T	N/T	N/T	800+	315	800	800+	800+	800	800+	800	N/T*	N/T	N/T	N/T	800+
Timken (lb)	50	100	N/T	N/T	N/T	70	N/T	N/T	N/T	N/T	N/T	N/T	30	60	N/T	N/T	N/T	60

*note: N/T, not tested due to limited amount of base grease available.

For Grease C, all additives used can increase four-ball weld point to 800 kgf or above 800 kgf , but only combination 2.0% DMTD Dimer and 1% MoDTC can have both high four-ball weld point and low four-ball wear scar diameter. Timken test data is not available for all greases due to limited amount of base grease available.

For Grease S, the base grease already has an 800 kgf weld point, therefore four-ball weld point after adding EP additives are not measured. As was true for Grease C, the combination of 2% DMTD Dimer and 1% MoDTC provided best antiwear performance with lowest wear scar diameter for Grease S. Timken improved from 30 to 60 lbs when 3% mixed metal dialkyl dithiocarbamate was used. Combination of 2% DMTD Dimer and 1% MoDTC provided best antiwear performance. In Grease S, it seems that combination of 2% DMTD Dimer and 1% MoDTC can provide best balanced performance in all three performance tests, four-ball wear, four-ball weld and Timken EP.

For Grease A, the base grease has a very high four-ball weld point of above 800 kgf. 3% mixed metal dithiocarbamate can improve Timken OK load from 50 lb/ to 100 lb/. Same as the other two calcium sulfonate complex base grease, combination of 2% DMTD Dimer and 1% MoDTC can provide best performance in both four-ball weld and four-ball wear. Though at this combination Timken OK load at 70 lbs is not as high as when 3% mixed Metal DTC is used, but considering the antiwear performance, overall, it is still the best balanced additive combination.

Conclusions

Though each calcium sulfonate complex base grease has its unique characteristic in terms of friction-reducing, antiwear and EP performance, it is obvious in all three base greases evaluated that the base greases without any antiwear and EP additives can perform pretty well. On the other hand, it is shown that further improvements are also possible. Of the three different EP additives evaluated, it is shown that use of EP additive alone can further improve either four-ball weld point or Timken OK Load. But use of EP additive alone normally will also increase the four-ball wear scar slightly. This phenomenon probably can be explained in terms of competition of additive for surface adsorption or the balance between EP additive and antiwear additive surface coverage. In other words, higher the EP additive surface coverage, better the EP performance. Since both EP and antiwear additives, possibly others like rust inhibitors, are competing for the same metal surfaces in relative motion, higher EP additive surface coverage also means the lower the antiwear additive surface coverage. So when better EP performance is achieved, wear often suffers.

Overall comparison of all three overbased calcium sulfonate grease with different EP additive indicates that higher temperature plays crucial role to help reduce frictional energy losses for all grease samples. In particular, Grease S demonstrated the lowest frictional energy losses at lower and higher temperature. Antiwear performance of all grease samples exhibit synergistic as well as antagonistic interaction on addition of EP additives. For example, addition of metal DTC to three grease samples exhibit synergistic as well as antagonistic interaction. Metal DTC in Grease A exhibit small improvement of wear protection and reduced frictional energy losses. Metal DTC in Greases C and S exhibit increased wear and flip-flopping frictional reduction. On the other hand, addition of DMTD to all grease samples demonstrated antagonistic interaction to reduced wear, but synergistic interaction to reduced frictional energy losses with Greases C and S. Addition of DMTD Dimer to all grease samples exhibit analogous performance to DMTD but comparatively lower friction reduction than DMTD. Out of all EP additives, combination of DMTD Dimer and MoDTC exhibit improved wear protection and reduced frictional energy losses for all three grease samples. While combination of DMTD Dimer with MoDTP exhibit reduced frictional losses but increased wear.

The complicated impact of additives on grease performance probably can be best understood when understanding that each additive has a primary function, and such primary function will mainly manifest itself only in a particular lubrication regime relevant to its primary functionality. On the other hand, it is also possible for certain additives to be multifunctional. In this study, the test results suggested that the three EP additives can only improve the EP performance of the grease treated, with no obvious capability in improving antiwear or reducing friction. In order to have a more balanced performance in all three lubrication regimes, additives effective in boundary layer lubrication regime and/or mixed lubrication regime must also be considered.

In this study, it also showed that combination of EP additive with antiwear or friction modifier can achieve more balanced performance. It is obvious from the performance test data, combination of DMTD Dimer with MoDTP will only improve EP and friction reducing performance, and no obvious antiwear improvement can be seen. Whereas, the combination of DMTD Dimer with MoDTC has demonstrated an overall balanced performance in all three lubrication regimes.

Therefore, the key for grease formulators is to try to find a right balance between all types of additives used, especially combination of additives that would be effective in all three lubrication regimes. In this present study, it is found that EP additive DMTD Dimer in combination with antiwear additive molybdenum dialkyl dithiocarbamate is a balanced combination which can provide both improved EP performance and antiwear performance in all three calcium sulfonate complex greases tested. Due to the multifunctional capability of MoDTC in both friction reducing and antiwear, this particular combination can also provide benefit in friction reduction, especially at higher temperature. Additional work is planned to expand our study and possibly identify other synergistic combination of additives which gives the best EP, antiwear and friction reducing performance with the calcium sulfonate complex grease thickener system.

References:

- (1) McMillen, R.L., *Process for Preparing Lubricating Grease*, US Patent 3,376,222, April 2, 1968.
- (2) McMillen, R.L., *Non-Newtonian Colloidal Disperse System*, US Patent 3,492,231, January 27, 1970.
- (3) Hunt, M.W., *Method for Preparing Highly Basic Grease and Rust Inhibiting Compositions*, U.S. Patent 3,816,310, June 11, 1974.
- (4) Zhang, R., Wenzler, A.P. and Holloway M.D., *Bearing Cleaning Composition and Method of Use*, U.S. Patent 7,241,723, July 10, 2007.
- (5) Muir, R. and Blokhuis, W., *High Performance Calcium Borate modified Overbased Calcium Sulfonate Complex Greases*, US Patent 4,560,489, December 24, 1985.
- (6) Barnes, J.F., *Calcium Sulfonate Grease and Method of Manufacture*, US Patent 5,126,062, June 30, 1992.
- (7) Mackwood, W. and Muir, R., *Calcium Sulfonate Greases...One Decade Later*, NLGI Spokesman, Volume 63, No.5, pp24-37, 1998.
- (8) Denis, R., Sivik, M., *Calcium Sulfonate Grease-Making Processes*, Presented at 75th Annual NLGI Meeting, June 7, 2008, Williamsburg, Virginia.
- (9) Mackwood, W., Muir, R. and Dunn, W., *Calcium Sulfonate Complex Grease The Next Generation Food Machinery Grease*, Presented at 69th Annual NLGI Meeting, October 29, 2002, San Diego, California.
- (10) NLGI Grease Production Survey Report, June 1, 2012.
- (11) Hiza, R.J., Aguilar, G.A., Donnelly, S.G., Cheng, F.S. and Tepper, R.J., *Lubricating greases containing antimony dithiocarbamates*, US Patent No. 7,772,170 (2010).
- (12) Vanderbilt Chemicals, LLC. Product Brochure 2013.
- (13) Karol, T., Ronald J. Tepper, R.J., *Bis-1,3,4-Thiadiazole Compounds and Lubricating Compositions Containing Same*, US Patent No. 5,849,925 (1998).

The case for Nano solid based Lubricants – 10 year after

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Preface- Company Overview

The super performance of nanosized solid based lubricants has been promised for the past 10 years, with impressive graphs and academic papers to back it up.

Today, 10 years after the foundation of NanoMaterials Ltd (NML or the Company), is a good time to reflect and provide an assessment as to the level of performance of nano solid based lubricants. NML is based on technology licensed from Weizmann Institute of Science (WIS), and was the first in the world to achieve industrial scale production of closed-caged nanoparticles of WS_2 and commercial products based on this material.

The IP of the company is composed of more than 80 granted patents covering a wide spectrum of methods, materials, and applications. The variety of morphologies (closed-caged onions and nanotubes) is protected. The variety of possible layered materials: disulfides as well as other chalcogenides of transition metals (tungsten, molybdenum, vanadium and titanium to name but few) are covered by our patents. In addition, technological innovations and know how developed by the Company are being patented on an ongoing basis.

In this paper the recent data mostly from commercial customers, third party research institutes and strategic partners will be presented, showing the actual benefits from using nanosized solid based lubricants. We shall also show the challenges the company faced, as well as the economic case to use these lubricants.

I. Background.

The history of the Company can be traced back to early 90's, when the closed-caged nanostructures of tungsten disulfide were first observed under the e-beam irradiation in transmission electron microscope (TEM)¹ by the researches in the group of Professor Reshef Tenne in WIS [Fig. 1].

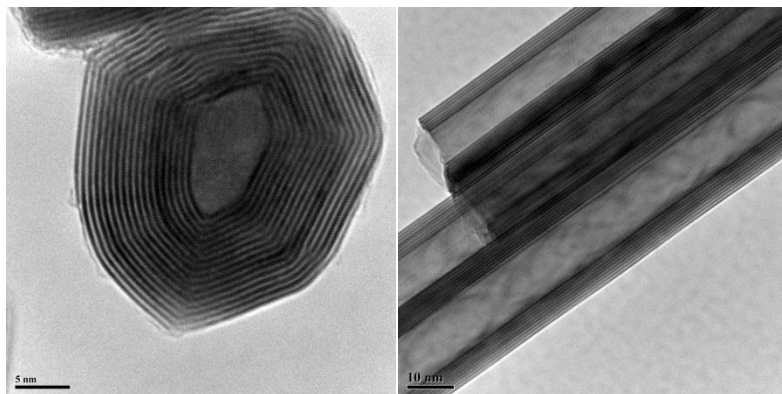


Fig. 1. TEM image of closed-caged nanoparticle of WS₂ (left) and group of aligned WS₂-nanotubes (right)

The unusual nanosized particles attracted much attention being closely related structurally to recently reported carbon fullerenes^{1,2}. The nanoparticles are described as inorganic closed-caged onion-like nanostructures of metal dichalcogenides.

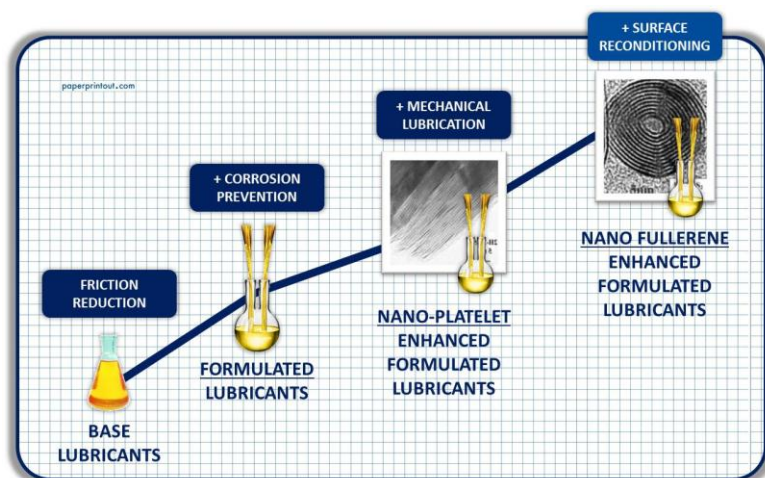
Later, the selenides and tellurides of tungsten were reported, followed by molybdenum, vanadium, titanium, etc. compounds^{3,4,5}. It was found that virtually any layered (2-D) material can fold into closed-caged nanostructures: either quasi-spherical onion-like or nanotubes⁶. The unique structure of those particles was believed to result in changed properties of nanoparticles as compared to layered predecessors, while nanometric size of particles suggests enhanced properties as compared to relative 2-D materials. Later on the methods for reproducible synthesis of gram quantities of those particles were developed^{7,8}. The developing of synthetic pathways was a critical step, because availability of pure phase material made it possible to study its properties systematically. Since the traditional application of layered structures is lubrication, the new material was studied as solid lubricant and component for lubricating formulations. Numerous scientific papers reported the super-lubricity as result of using and testing novel material^{7,9,10}.

The reported behavior of the novel nanoparticles suggested possibility for promising and innovative commercial applications of the material [Fig. 2].



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The availability of scalable technology for production and the possible commercial applications was the trigger for establishing NML in 2002 with its mission to commercialize the technology developed by WIS.

II. 2002-2008. Scale-Up of powder production. First generation of products.

The initial technological process licensed from WIS made it possible to obtain tens grams of nano-sized powder in a batch process⁷. It was sufficient for academic researches all over the world, but could not serve the needs of neither the company nor the industry. The continuous series of scale-ups lasted for more than 5 years [Fig. 3].

R&D TIMELINE

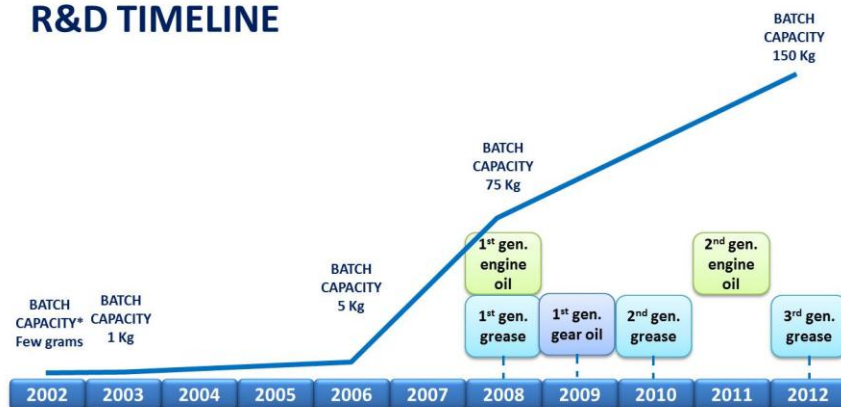


Fig. 3. Scale-up process.

The progress in scale-up resulted in ability to produce the powders of nanoparticles in industrial scale. Currently the company operates 3 production set-ups: laboratory, pilot and industrial. The last is capable to obtain of up to 150 kg of industrial grade material per batch. It should be noted here that the scale-up process included not only enlarging the amount of available

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material produced, but an intense optimization of chemical process and entire technological chain. One of the significant by products of the optimization process was the reduction of the cost of the powder in more than 90% than its original base cost per gram.

Throughout the scale up process the available nanopowders were tested for tribological applications, but more detailed studies was dictated and required by commercial needs and partners. It was found that earlier data with respect to the particle's *modus operandi* should be reconsidered. For instance the early studies suggested that the rolling of nanoparticles between the contact surfaces is predominated mechanism of lubrication by onion-like nanostructures. The recent studies suggest that the lubricating effect by nanoparticles may be explained by variety of mechanisms, depending on external conditions. It was proved, that the predominant mechanism is formation of tribofilm. The tribofilm consists from thin layer of tungsten disulfide on the contact surface, obtained via exfoliation of external layers of disulfide from nanoparticles present in contact point [Fig. 4].

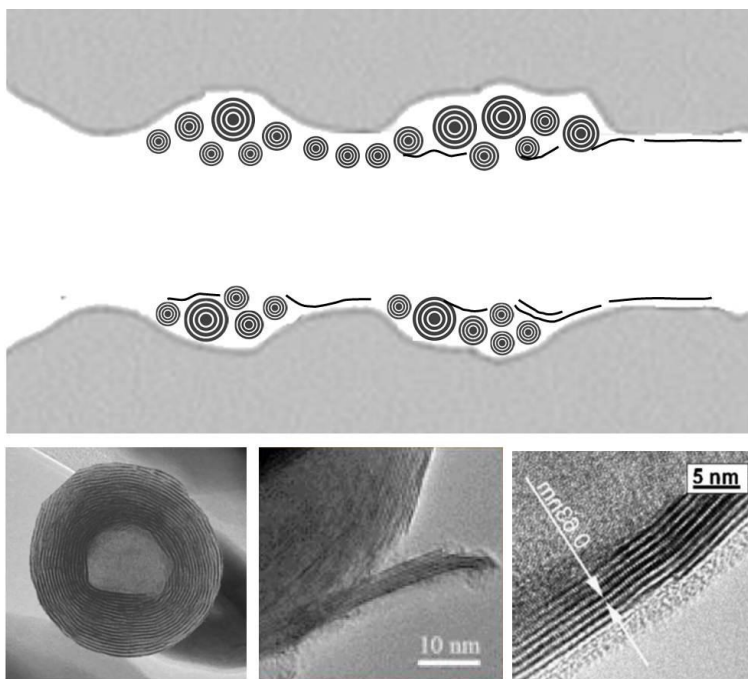


Fig. 4. Tribofilm formation.

Various researches proved tribofilm formation by study of oils and greases enhanced by nanoparticles produced by the Company.

In the early years of the Company's activity the only product considered to be supplied to the customers was the powder of nanoparticles. The powder obtained in chemical process consists from so called "primary" nanoparticles of tungsten disulfide (30-150 nm) stacked together



forming agglomerates (around 50-150 μm). In most cases intermediate aggregates of several (5-10) primary nanoparticles are observed as well [Fig. 5].

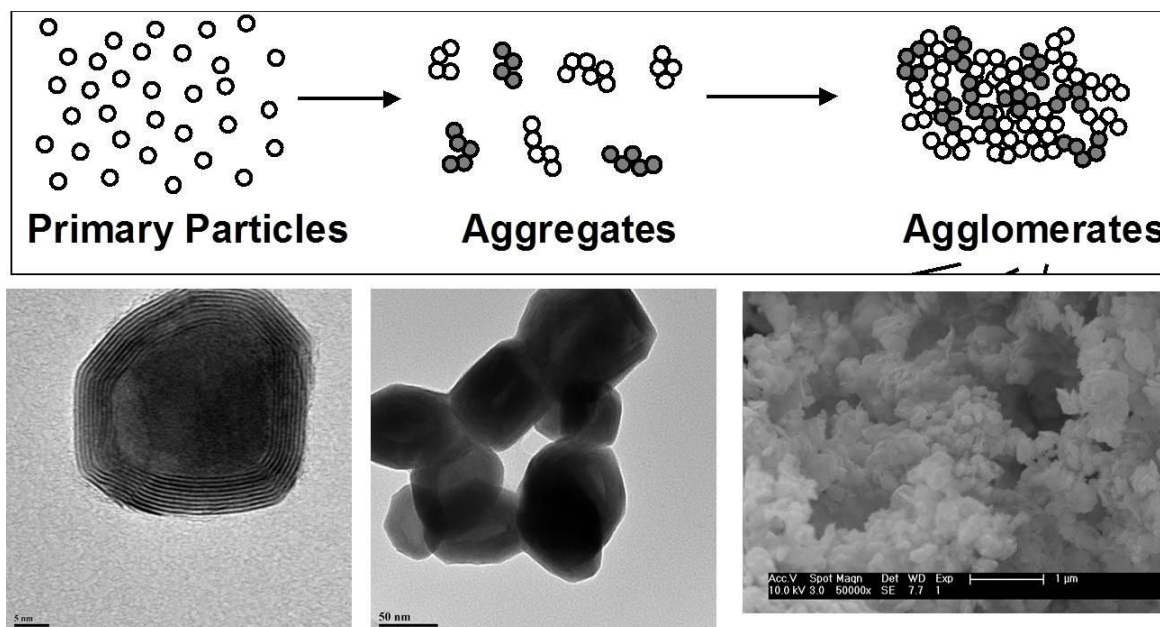


Fig. 5. Individual particles and formation of particles observed in real product.

After being added to lubricant formulations the powder can be hardly dispersed equally in the volume and therefore have tendency to settle. The de-agglomeration of powders became of vital importance. It should be noted that in ambient individual nanoparticles have a tendency to re-agglomerate forming aggregates and agglomerates.

In addition it was realized that our partners in traditional industry of lubricating materials are neither willing to impregnate the powders into their formulations nor capable to perform it. The difficulties were found both in psychologies of manufacturers and in technical incompatibilities of suggested additive with technological process used in industry. The first generation of oil additives was developed in the company in order to meet the demands of the customers. The top-up additive for engine oil is a dispersion of nanoparticles in the host oil. The performance tests (ASTM D2596 and ASTM D4172) showed the tribology efficacy of additive developed by the Company [Fig. 6, 7]

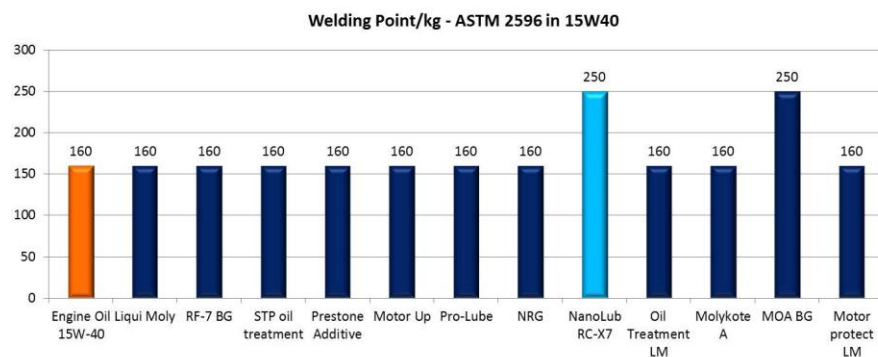


Fig. 6. Extreme pressure properties of engine oil top-up additives

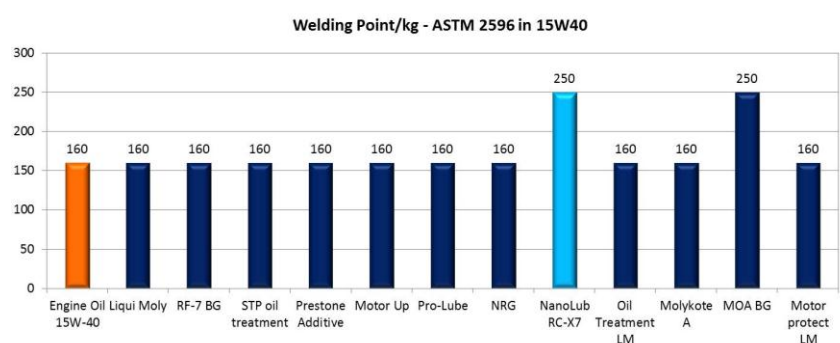


Fig. 7. Anti wear properties of engine oil top-up additives

III. 2008-2012. Second generation of products.

The remarkable tribology results shown in by the Academia were not always proven and repeated while testing the products by customers. Furthermore – the poor appearance of the dispersions attributed to the observed sedimentation/settling of the particles – made it very difficult to market the end products.

Once again it was seen that early promise is not always enough and the company faced a risk of falling a victim to its early promise that could not be repeated after commercial scale up was achieved.

The Company faced a new challenging task - the task of converting the powder into a salable product that will:

1. Better perform competitors' products
2. Be more cost effective
3. Be easily adopted into the technological process and practices used by the industry



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Therefore the main task and priority of the company was to develop technology and knowhow to disperse and integrate its particles into lubricants. The second generation of its oil additives utilizes advanced manufacturing techniques and revised formulation [Fig. 8].

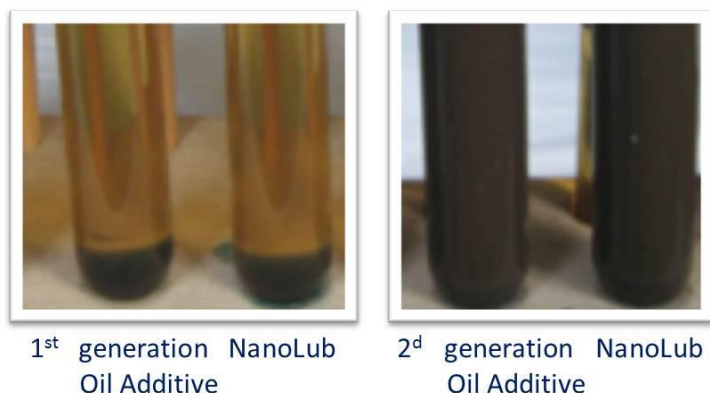


Fig. 8. The revised second generation NanoLub oil additive vs. first generation predecessor.

Executing on its strategy of developing additives and not powders, and further focusing on solutions for specific applications via tailor made additives, the Company focused its R&D efforts on developing this line. During the past two years the company launched a variety of products impregnating nanopowders with enhanced lubrication properties, which are now being adopted by manufactures as additives and components in their final products.

The available product line consists from oil additives being targeted for various applications, like: engine oil, gear, chain, heavy industrial equipment, etc. [Fig. 9].

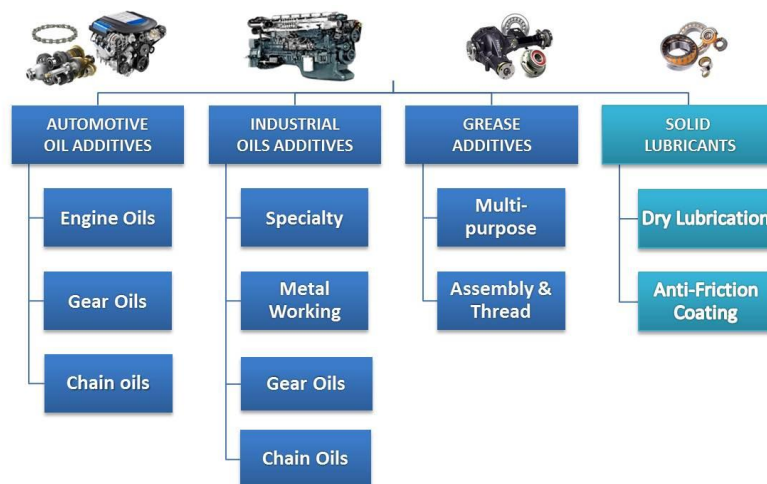


Fig. 9. Product line by NanoMaterials.

The products are supplied as additives for lubricant manufacturers and as products for end



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users as in the case of top up additive.

One of our European partners has observed that adding oil additive by the Company to Shell Helix 5W40 oil lowers coefficient of friction [Fig. 10]. The analysis of obtained data suggests creation of protecting tribofilm on contact surfaces.

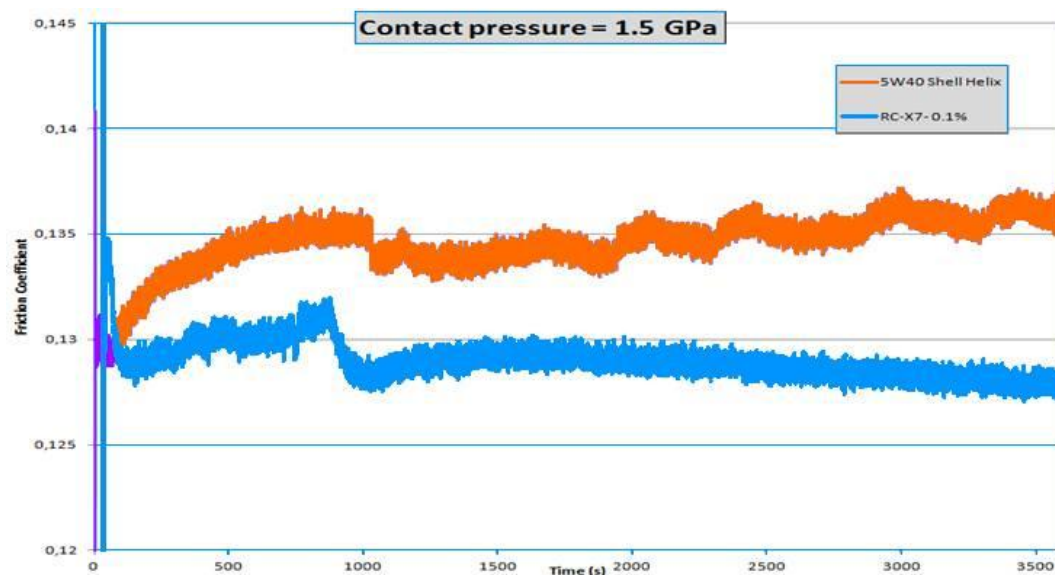


Fig. 10. NanoLub oil additive in Shell Helix 5W40 oil.

However, few customers, that have made the effort to make their own formulations based on our commercial products (inc. powders) showed fuel economy improvement in lab as well as field tests. The experiments were performed by our customers both in Europe as well as in the US. Various passenger cars [fig. 11] and heavy trucks [fig. 12] were tested.






  					 			
CAR	Maker	Toyota Avensis	Subaru NA	VW Tiguan	CAR	Car Type	Honda NA	Lexus LS 430
	Type	1.8 Liter	2.5	2.0 turbo DSG tranny		Motor	2.7 (4 cyl.)	4.3 (6 cyl.)
	Year	2007	2004	New car		Year	NA	NA
	KMs	90,000	NA	NA		KMs	32,000	145,800
	Base Oil	0W30	5W-30 HDD synthetic (PAO)	NA		Base Oil	Shell Rotella	Shell Rotella
OIL	Brand	Amsoil	Amsoil	NA	OIL	Brand	Shell	Shell
	Quantity of SR-X	300 ml	7%	4gr of WS2 powder (0.1% in final oil)		Quantity	Own mix with 4-5% material	Own mix with 4-5% material
TEST	Usual fuel economy with SR-X	7.8 litres per 100km	6,4 L/100km	13L/100km	TEST	Usual fuel economy with SR-X	NA	NA
	Driving mode	NA	Highway	50/50 hwy/city		Driving mode	Lab	Lab
	Weather temp.	Winter – ca. -20°C	NA	NA		Weather temp.	NA	NA
	RESULTS	% fuel saving/km	-6%	-13%		-19%	RESULTS	% fuel saving/km

Fig. 11. Fuel economy in passenger cars.



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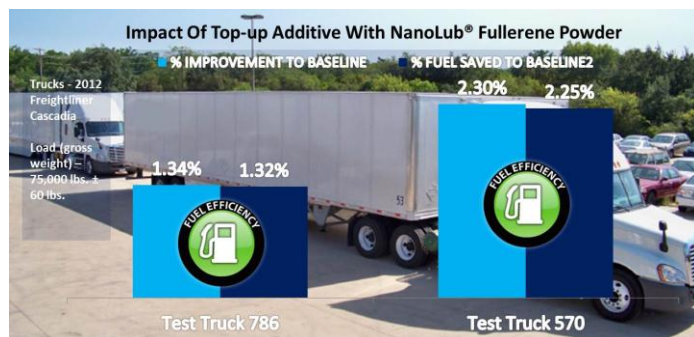


Fig. 12. Fuel economy observed for trucks.

Additional third party verification data was obtained from a leading independent European test lab with respect to EP properties of transmission oil enhanced with our transmission oil additive. The FZG machine test performed according to ASTM D5182 [Fig. 13] showed that adding transmission oil additive to BV Total transmission oil delays (and thus improves) scoring and scuffing in gear transmission [Fig. 14].

Load stage N°	75W80 Transmission BV Total			75W80 Transmission BV Total + NanoLub MP-X		
	T _i (°C)	T _r (°C)	Observation	T _i (°C)	T _r (°C)	Observation
1						
2			Run in			Run in
3						
4	90	90	Scoring	90	90	No damage
5	90	90	Scoring +	90	90	No damage
6	90	94	Scoring ++	90	94	No damage
7	90	100	Scoring +++	90	102	No damage
8	90	101	Scoring +++	90	110	No damage
9	90	116	Scoring+ Scuffing	90	124	No damage
10	90	127	Scoring+ Scuffing	90	133	Scoring
11	90	140	Scoring+ Scuffing	90	139	Scoring +
12	90	143	Scoring+ Scuffing	90	143	Scoring ++

Fig. 13. Results of FZG test for gear oils.



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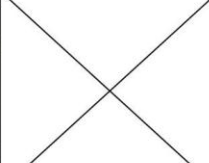
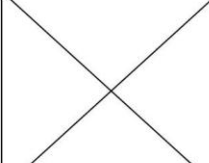


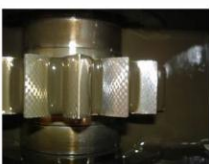
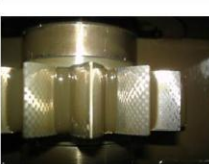

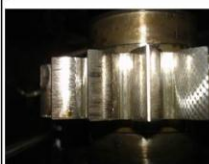
	STAGE #1	STAGE #6	STAGE #7	STAGE #8
PAO6				
Traces size (mm)	3mm	>20mm		
PAO6+ 0.5%wt IF				
Traces size (mm)	No traces	No traces	No traces →	>20mm

Fig. 14. Protecting gear box by NanoLub transmission oil additive (FZG test)

Furthermore - series of tests performed by the company using 4 Ball machine suggests that NanoLub oil transmission additive improves extreme pressure and anti-wear properties of Gear-220 and Brightstock oils [Fig. 15].

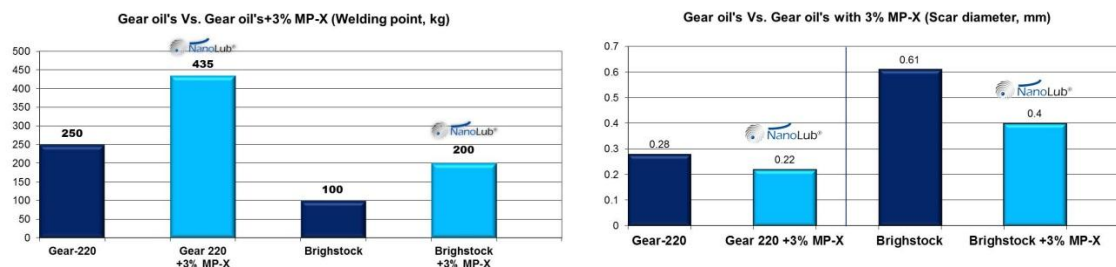


Fig 15. 4-Ball testing of gear oils: ASTM D2596 (left) and ASTM D4172 (right)

The grease additive developed by the company enhances extreme pressure properties of Lithium greases and over performs greases that typically use MoS₂, as their EP properties enhancer, as evidenced by ASTM D2596 test [Fig. 16].

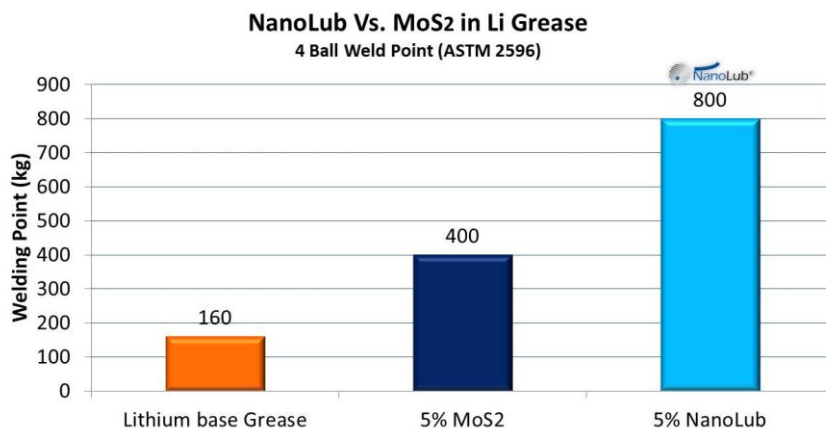


Fig. 16. ASTM D2596 testing of lithium grease and derivatives.

The developed grease additive is compatible with other types of greases: lithium complex, calcium, aluminum complex and polyurea. The 4-Ball tests according to ASTM D2596 and ASTM D4172 proved that grease additive developed by the company improves both extreme pressure and anti-wear properties of compatible greases. [Fig. 17]

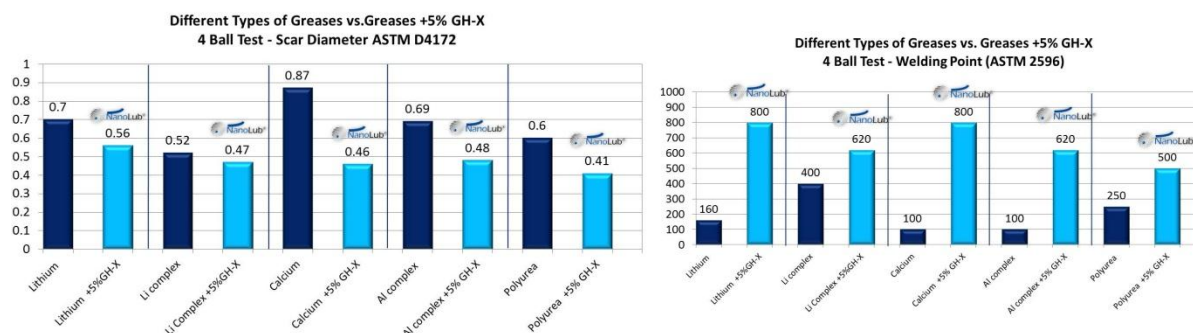


Fig. 17. Comparative testing of various types of greases enhanced with NanoMaterials' paste additive for greases: a) scar diameter (ASTM D4172) and b) welding point (ASTM D2596)

A recent study done by a European grease manufacturer compared the tribological behavior of grease enhanced with traditional molybdenum disulfide and two types of grease additives developed by the company. The series of testing were performed using SRV machine (ASTM D5707) [Fig. 18] and 4-Ball machine (ASTM D2296 and ASTM D2596) [Fig. 19]. It was again evidenced, that grease additives by the Company improve extreme pressure and anti-wear properties of greases. It was also shown, that the additives based on nanopowder of tungsten disulfide over-perform molybdenum disulfide-based formulations.

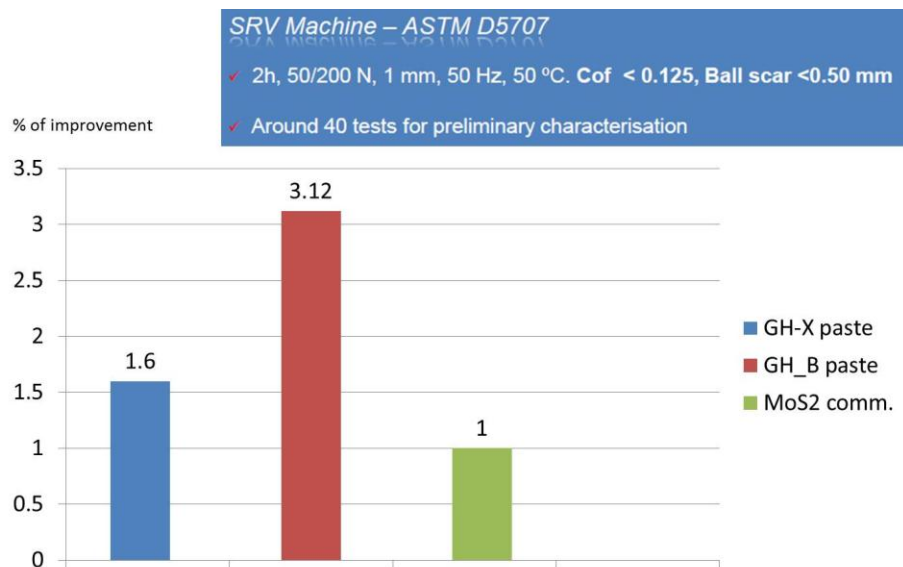


Fig. 18. Comparative testing of greases, SRV machine.



Fig. 19. Comparative testing of greases with 4-Ball machine. Left – according to ASTM D2296; Right – according to ASTM D2596

The intense study of greases enhanced by additives containing solid lubricants by the European grease manufacturer resulted in the following conclusions:

1. The nanoparticles do not affect the dropping point of the greases.
2. Some nano-based additives are hydrophilic, affecting water wash-out properties, but this can be effectively controlled with specific additives.
3. Extreme pressure properties are obtained with only 1% treat rate.
4. Wear reduction is evident in both 4-Ball machine and SRV machine.
5. Promising results in friction coefficient.



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Conclusions / The Future

As can be evidenced from the paper, the path taken was not easy and certainly far longer than the company had ever envisaged.

However – today after 10 years of R&D work the Company seems to have found its voice and its place and is able to produce high quality products, solving clear needs in a cost effective manner.

To be fair as well as realistic, although 10 years in existence – the company is still in early commercial phase, and the best is yet to come. The next and immediate challenge for the company is to take advantage of the fuel efficiency data obtained by third parties in 2012 and try and use them to come up with a new series of fully formulated engine oils, approved by the OEM's.



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References:

1. R. Tenne, L. Margulis, M. Genut and G. Hodes, *Nature*, **1992**, 360, 444
2. L. Margulis, G. Salitra, R. Tenne and M. Talianker, *Nature*, **1993**, 365, 113
3. M. Hershfinkel, L. Gheber, V. Voltera, J. Hutahinson, L. Margulis and R. Tenne, *J. Am. Chem. Soc.*, **1994**, 116, 1914
4. T. Tsirlina, V. Lyakhovitskaya, S. Fiechter and R. Tenne, *J. Mater. Res.*, **2001**, 15, 2636
5. A. Margolin, R. Popovitz-Biro, A. Albu-Yaron, L. Rapoport, R. Tenne, *Chem. Phys. Lett.* **2005**, 411, 162-166
6. R. Tenne, L. Margulis and G. Hodes, *Adv. Mat.*, **1993**, 5, 386
7. L. Rapoport, Yu. Bilik, Y. Feldman, M. Homyonfer, S. Cohen and R. Tenne, *Nature*, **1997**, 387, 761
8. A. Margolin, Thesis for the degree Doctor of Philosophy, WIS, 2005
9. M. Chhowalla and G. Amaratunga, *Nature* **2000**, 407, 164
10. L. Rapoport, M. Lvovsky, I. Lapsker, Yu. Volovik, Y. Feldman, A. Margolin, R. Rosentsveig, and R. Tenne, *Nano Letters*, **2001**, 1, 137

