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Fullerene-like inorganic nanoparticles (*IF*-WS2) - novel grease EP additive.

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Introduction

The super performance of nanosized solid based lubricants has been a focus of various research groups in academia and industries for the past 10 years.

The following paper is focused on closed-caged nanoparticles of WS_2, also known as inorganic fullerene like nanoparticles (*IF*-WS2), and various products based on this material. The material was first synthesized in the research group of prof. Reshef Tenne from Weizmann Institute of Science in 1992. Later, a company called NanoMaterials was established based on available know-how. Today, NanoMaterials together with its parent company NIS are able to supply nanosized tungsten disulfide and various commercial products on its base at industrial scale. More than 80 patents covering a wide spectrum of methods, materials, and applications of the novel material were granted. The variety of morphologies (closed-caged onions and nanotubes) is internationally recognized. The variety of possible layered materials: disulfides as well as other chalcogenides of transition metals (tungsten, molybdenum, vanadium and titanium to name a few) are covered by existing IP. In addition, technological innovations and know-how being under current development are being patented on an ongoing basis.

Today, is a good time to reflect and provide an assessment as to the level of performance of nanosized solid based lubricants. In this paper the recent data mostly from third party research institutes and commercial customers will be presented, showing the actual benefits from using nanosized solid based lubricants.

I. Background.

Back in 1992 the first closed-caged nanostructures of tungsten disulfide were first observed under the e-beam irradiation of thin films of amorphous tungsten oxide in transmission electron microscope (TEM)[1] by the researches in the group of Professor Reshef Tenne in Weizmann Institute of Science (WIS) [Fig. 1].

The unusual nanosized particles attracted much attention being closely related structurally to recently reported carbon fullerenes[1,2]. The nanoparticles were 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 nanotubes[6]. 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.

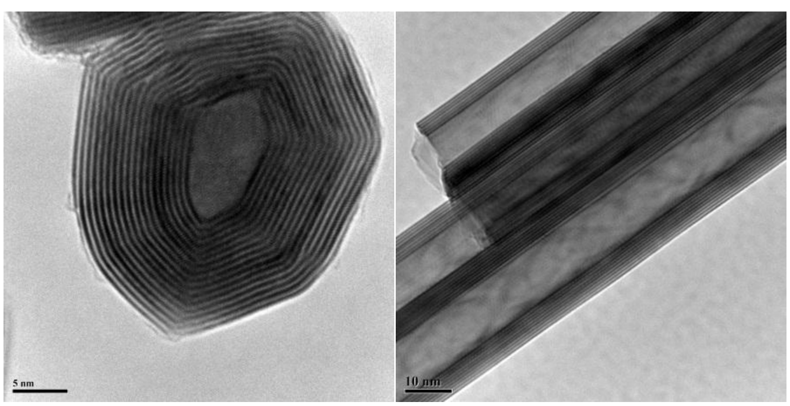


Fig. 1. TEM image of closed-caged nanoparticle of IF-WS_2 (left) and group of aligned WS_2-nanotubes (right)

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]. Later other possible applications resulting from unique properties of discussed nanoparticles were tested and reported by various scientific groups world-wide.

The reported behavior of the novel nanoparticles suggested possibility for promising and innovative commercial applications of the material in the field of tribological applications.

The availability of possible commercial applications and technology for production of material triggered establishing of commercial company, named NanoMaterials in 2002 with its mission to commercialize the technology developed by WIS.

II. *IF*-WS2 nanoparticles and their applications

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 can be distinguished [Fig. 2].

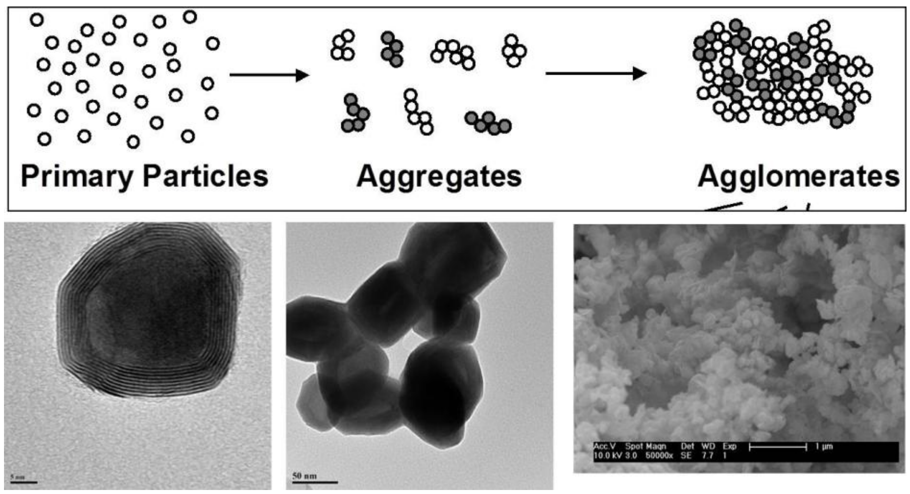


Fig. 2. Individual particles and formation of particles observed in real product.

The agglomeration of particles is explained mainly by high surface area enhanced by small size of primary nanoparticles. Various de-agglomeration techniques were tested: ultrasonification, high shear mixing, treatment with surfactants, etc. Some of the techniques were adopted either for laboratory or industrial use. It should be noted that individual closed caged nanoparticles of WS_2 have a tendency to re-agglomerate forming aggregates and agglomerates, due to their small size and high surface area.

The availability of de-agglomerated powders of nanosized closed-caged *IF*-WS_2 gave boost to research and development of solid lubricant based products: anti friction coatings, dry lubrication of e.g. bearings, etc. In addition the de-agglomerated powders enabled development of 1st generation of ready to use dispersions of nanoparticles of IF WS_2. The lengthy study resulted in series of formulations with nanoparticles homogeneously dispersed in oils (e.g. as lubricant additives) or other medias (e.g. as reinforcement for composite materials). For instance, the top-up additive for engine oil enhanced with *IF*-WS_2 showed the tribology efficacy of nanoparticles in world recognized standard performance tests (ASTM D2596) [Fig. 3]

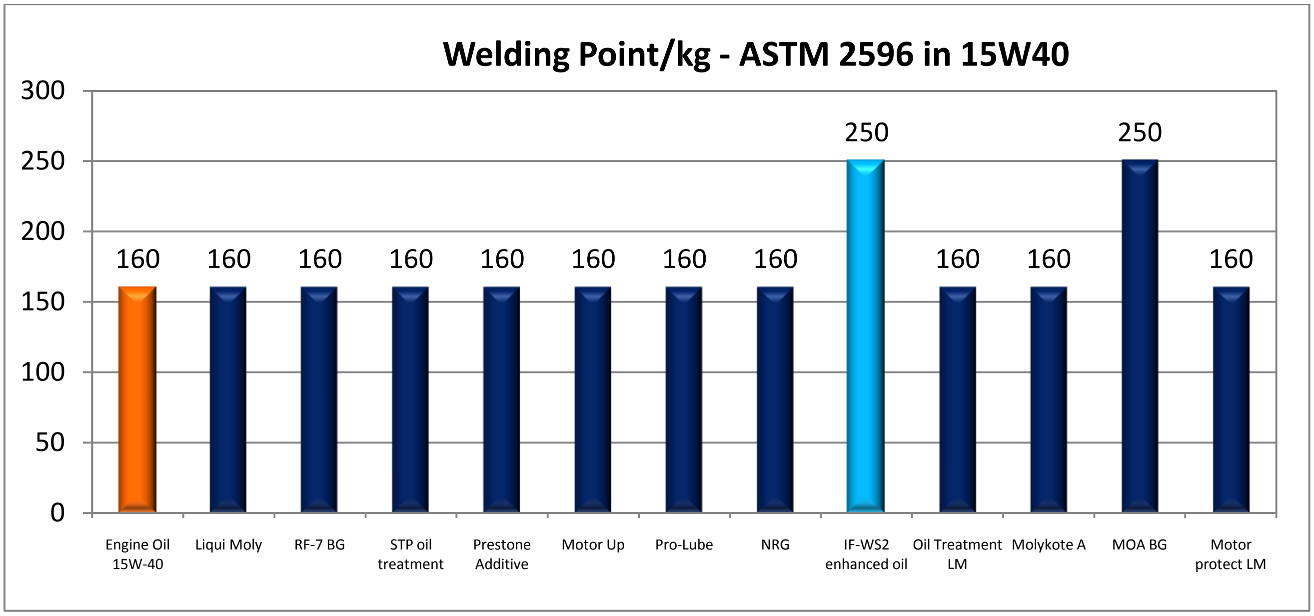


Fig. 3. Extreme pressure properties of engine oil top-up additives

The closed caged nanoparticles of *IF*-WS2 have been tested for tribological applications since their first development in 1992. However the interest for closed caged nanoparticles has boosted and more detailed research have been conducted since their industrial scale production become available. 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 lubricity of nanoparticles may be explained by variety of mechanisms, depending on external conditions, mainly contact pressure. 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].

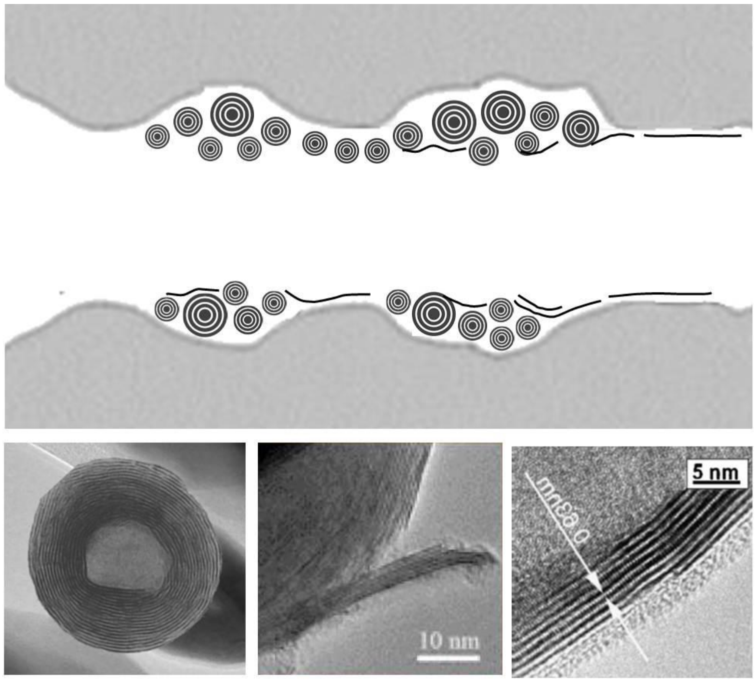


Fig. 4. Tribofilm formation.

Various researches proved tribofilm formation by study of oils and greases enhanced by closed-caged nanoparticles of *IF*-WS_2.

III. Dispersion IF WS2 nanoparticles.

It was soon realized that remarkable tribology results shown earlier were not always repeated while testing the materials by various sources. It was found that available 1st generation of dispersions lacked stability with clear tendency for sedimentation of the particles over time. It was not only a question of the poor appearance of the dispersions, but the observed settling of the particles reduced performance of material.

A new challenging task faced the researchers: developing a way of converting the powder into liquid-type material with enhanced stability and performance. The additional requirements to be mentioned are cost efficiency and technological compatibility as compared with available alternatives.

The efforts of researchers and engineers resulted in 2d generation of dispersions of *IF*-WS_2 nanoparticles combining the best knowledge of nature of nanoparticles with advanced manufacturing techniques, resulting in new level of stability [Fig. 5] and performance of lubricating materials.

In addition the available data and experience in developing lubricating formulations made it possible to build dispersions of nanopowders in liquids targeting specific operation conditions. For instance the additives for engine oils, gear oils, heavy industrial equipment have been developed. The difference in formulation and way of manufacturing of this ready to use additives is a result of careful study of operation conditions and environment specific to particular application.

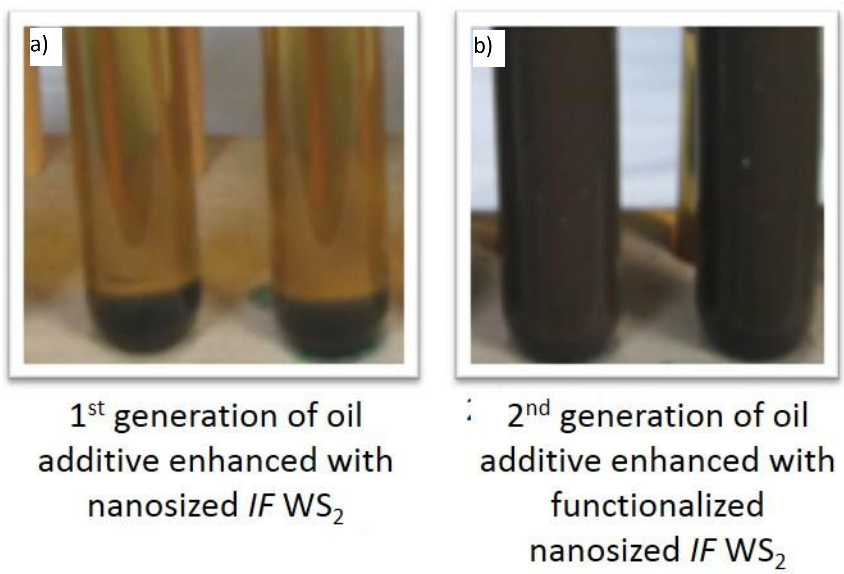


Fig. 5. first generation predecessor (a) vs revised second generation oil additive (b).

IV. *IF*-WS_2 nanoparticles as an EP additive for greases

The research in the field of grease enhancement by nanosized *IF* WS_2 resulted in developing grease additives that are currently commercially available. The newly developed grease additive enhances extreme pressure properties of Lithium greases and outperforms greases that typically use MoS_2, as their EP properties enhancer, as evidenced by ASTM D2596 test [Fig. 6].

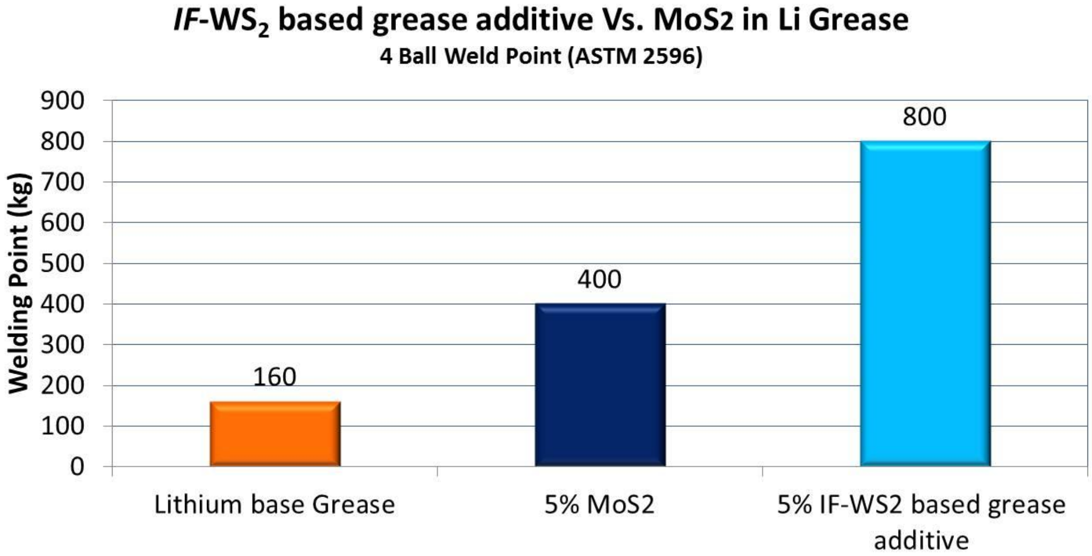
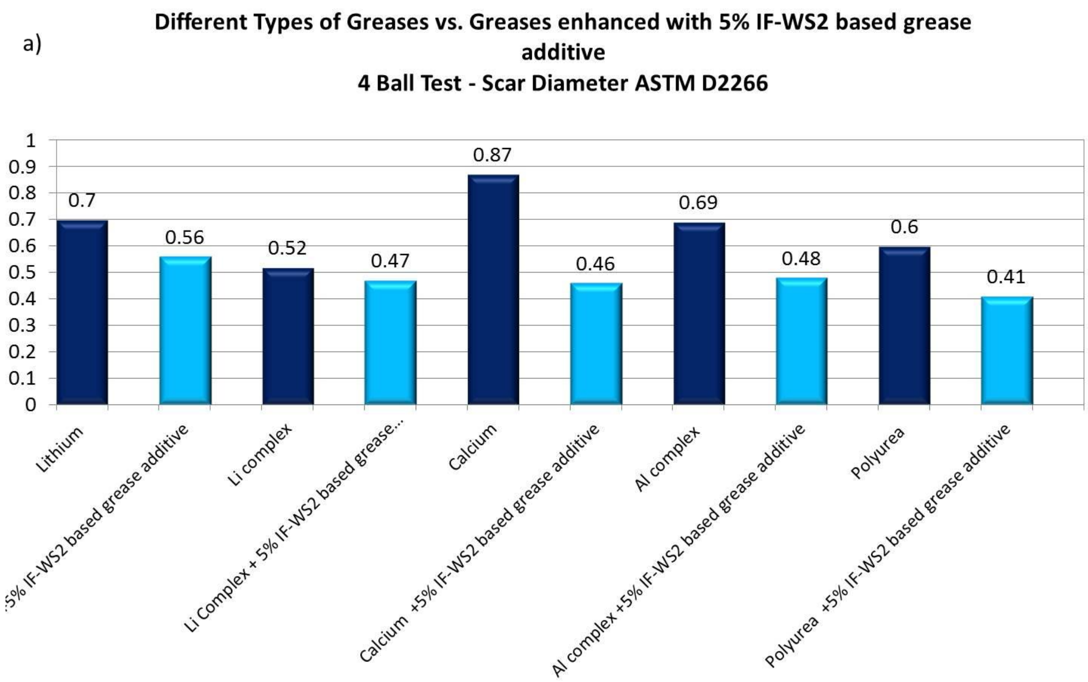


Fig. 6. ASTM D2596 testing of lithium grease and derivatives.

The suggested grease additive is developed having in mind compatibility with other types of greases: lithium complex, calcium, aluminum complex and polyurea. The 4-Ball tests according to ASTM D2266 and ASTM D2596 proved that discussed grease additive improves both extreme pressure and anti-wear properties of wide range of available greases. [Fig. 7]

a)



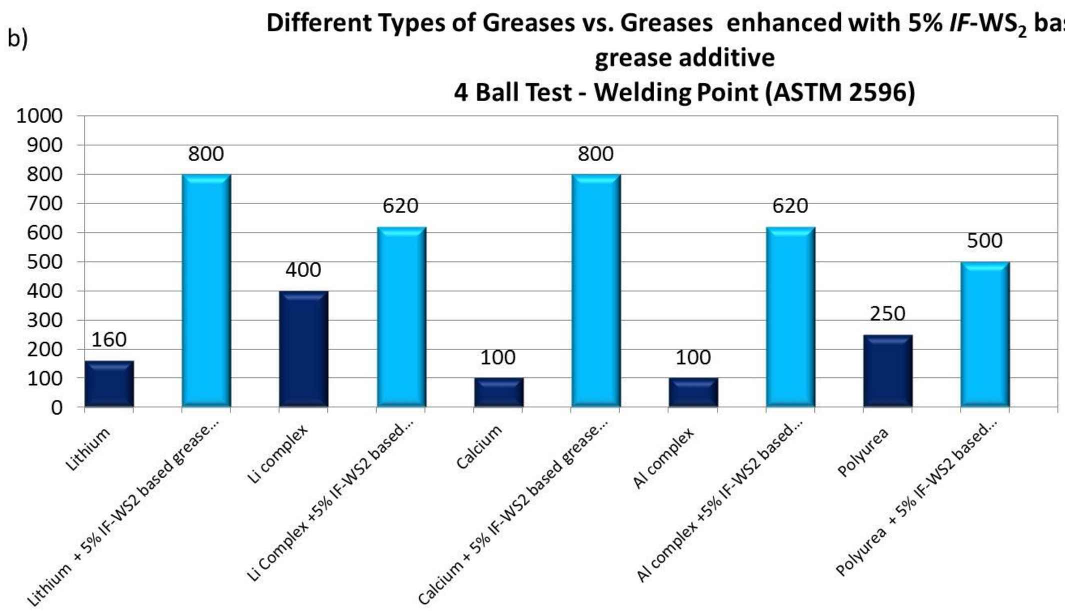
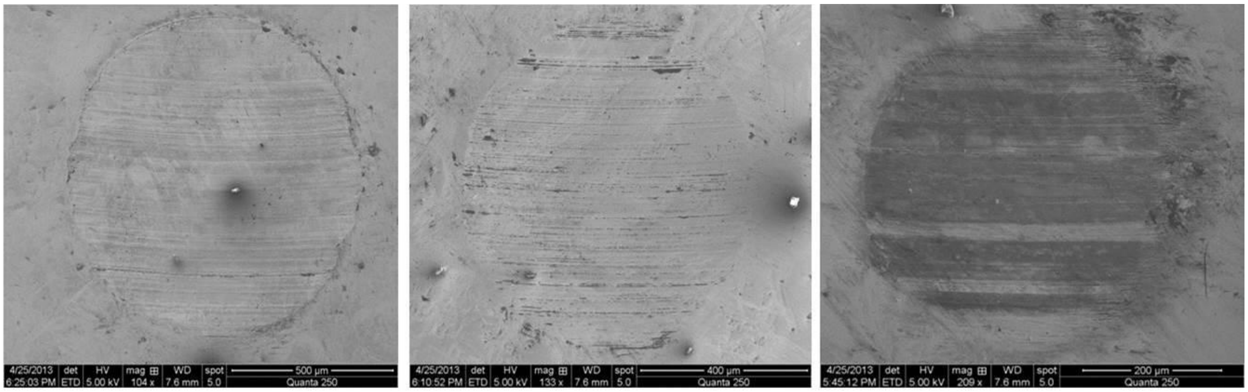


Fig. 7. Comparative testing of various types of greases enhanced with *IF*-WS2 based additive for greases: a) scar diameter (ASTM D2266) and b) welding point (ASTM D2596)

In another study the anti-wear properties of lithium base grease were compared to the same grease formulated with conventional micron sized 2H-WS_2 and the grease enhanced with additive based on nanosized *IF*-WS_2. The testing was done according to ASTM standard. The reduction of wear scar diameter from 820 µm (pure grease) to 682 µm (with 2H-WS_2) and to 500 µm (formulation with *IF*-WS_2) was observed [Fig. 8]. The advanced protecting properties of grease with nano-additive were attributed to the formation of tribofilm visible on SEM image.



Li grease with 5 % MoS_2
D= 820 µm

Li grease with 5% 2H-WS_2
(micron sized)
D= 682 µm

Li grease with 5 % *IF*-WS_2
based grease additive
D= 500 µm

Fig. 8. Anti-wear properties of Li base grease and grease enhanced with different morphologies of WS2 nanoparticles. The building of tribofilm is clearly visible in case of grease enhanced with nanoadditive.

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 enhanced with nanosized *IF*-WS_2. The series of testing were performed using 4-Ball machine (ASTM D2296 and ASTM D2596) [Fig. 9]. It was shown, that grease additives containing nanoparticles of *IF*-WS_2 improve extreme pressure and anti-wear properties of greases. It was also shown, that the additives based on tungsten disulfide nanoparticles (*IF* WS_2) outperform molybdenum disulfide-based formulations.

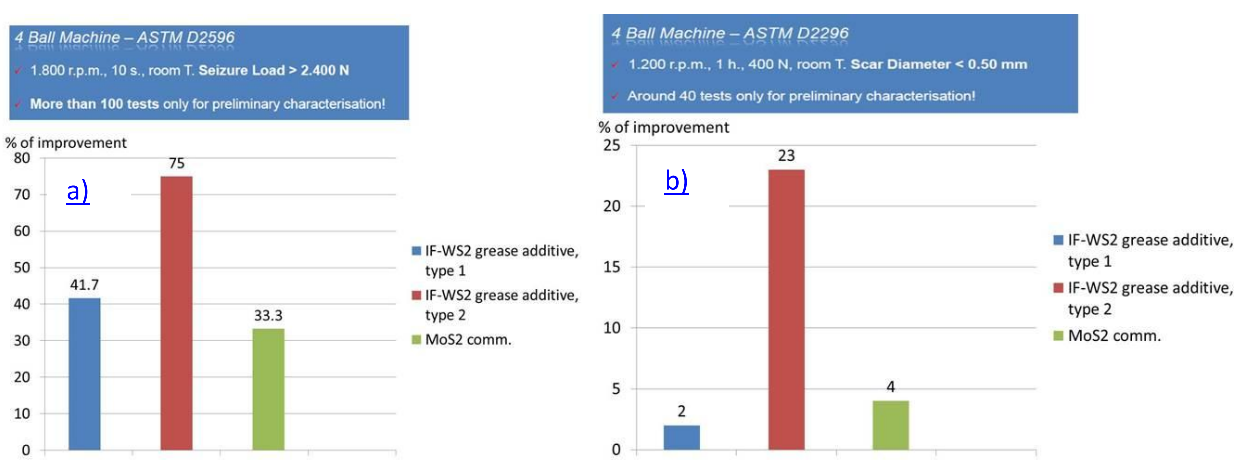


Fig. 9. Comparative testing of greases with 4-Ball machine. a) according to ASTM D2296; b) according to ASTM D2596

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.

Conclusions

Today, after 10 years of intense R&D work the high quality lubricating materials based on inorganic fullerene-like nanoparticles of tungsten disulfide (*IF*-WS_2) are commercially available. The variety of developed materials target specific needs of industry in a cost effective manner.

Novel inorganic fullerene-like nanoparticles of tungsten disulfide (*IF*-WS_2) outperform platelet type particles (2H WS_2 and MoS_2) in any application, due to controlled geometry, size and unique morphology. For example, *IF*-WS_2 enhanced grease exhibited wear scar diameter reduction up to 2.5 times with significant improvement of EP properties.

The next and immediate challenge for the researchers is to take advantage of the recently obtained data and use available nanoparticles to come up with new products saving the environment, reducing downtime costs and increasing life of equipment.

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Extreme-Pressure, Antiwear and Friction-Reducing Performances of Molybdenum Dithiophosphate and DMTD Derivatives in Greases

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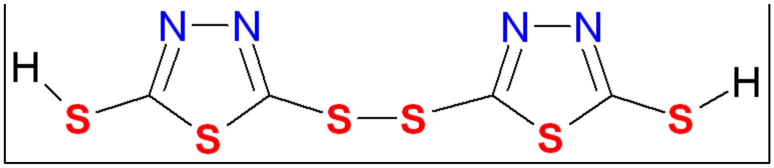
Abstract: The four-ball test was employed to evaluate the extreme-pressure (EP), antiwear (AW) and friction-reducing (FR) performances of molybdenum dialkyl dithiophosphate, and 2,5-dimercapto-1,3,4-thiadiazole (DMTD) derivatives, i.e., DMTD dimer, and its complex with polyalkylene glycol (PAG), in greases. DMTD dimer and its complex with PAG exhibit excellent EP properties, which can achieve high weld load in lithium complex greases, polyurea greases and calcium sulfonate complex greases. In lithium complex grease, molybdenum dialkyl dithiophosphate possesses outstanding AW and FR performances, which results in low wear scar and low friction coefficient. In calcium sulfonate complex grease, molybdenum dialkyl dithiophosphate provides good EP properties with high last non-seizure and weld loads, and excellent FR performances. But in polyurea grease, molybdenum dialkyl dithiophosphate does not exhibit obvious EP, AW and FR capacities. In lithium complex grease, with the combinations of molybdenum dialkyl dithiophosphate and boron ester or DMTD dimer complex with PAG, excellent EP, AW and FR performances can be achieved simultaneously. In polyurea grease, just the combination of molybdenum dialkyl dithiophosphate and DMTD dimer complex with PAG can get good EP, AW and FR results. In calcium sulfonate grease, the combination of molybdenum dialkyl dithiophosphate and DMTD dimer could achieve high weld load, low wear scar and low friction coefficient.

Keywords: grease, 2,5-dimercapto-1,3,4-thiadiazole, DMTD dimer, molybdenum dithiophosphate, antiwear agents, friction reducing agent, EP additive

1. Introduction

Use of anti-friction, antiwear and extreme pressure additives in lubricant oils and greases is a common practice. These antiwear and extreme pressure additives play an important role in forming surface protective films either by adsorption or reaction. Such surface films can prevent direct metal to metal contact, thus provide metal surface protection against wear and weld between metal surfaces in relative motion under high load conditions. 2,5-dimercapto-1,3,4–thiadiazole (DMTD) derivatives are generally used in lubricants as metal passivating agents. Such additives also have antioxidant and antiwear properties, and are used in a wide range of lubricant applications. For example, as an additive for engine oil, gasoline engine oil oxidation stability can be significantly improved. In antiwear hydraulic oils, it can provide good anti-corrosive effect on copper and assist in improving hydrolytic stability [1]. Due to the high sulfur content of DMTD, their derivatives have potential as an extreme pressure additive. Previous studies showed DMTD dimer and DMTD dimer polyether complex, a new type high performance extreme pressure additive for greases, have excellent extreme pressure properties. The structure of DMTD provides its multifunctional properties which allows it to perform as an extreme pressure agent, metal deactivator, metal passivator/antioxidant. As such, this type of additive can overcome the limitations in reduced oxidation resistance and corrosion of copper that are inherent problems with other traditional EP additives [2-8]. DMTD dimer has following chemical structure:



This additive in its physical form is a solid/powder and has been shown to exhibit excellent extreme pressure performance in four-ball EP test [2, 9]. In four-ball EP test, most base greases will have four-ball weld point between 126 kgf and 160 kgf. When 2.0% DMTD dimer is added to these base greases, four-ball weld point can be increased to 250 to 400 kgf. When DMTD dimer treat rate is increased to 3.0%, four-ball weld point can reach 620 kgf., or up to 800 kgf or above [9]. Extreme pressure performance of DMTD dimer comes from its bidentate adsorption on the metal surface [9]. Figure 1 is a diagram of this bidentate adsorption, i.e. the two ring structure of DMTD oriented parallel to the metal surface to form a bidentate complex structure, and if only one ring is desorbed from the surface, the molecule is still attached to the surface by the other ring.

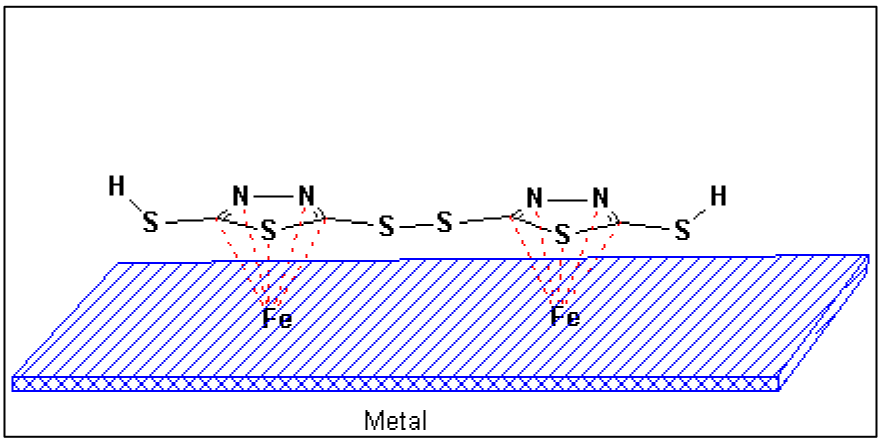


Figure 1. DMTD dimer adsorption on metal surface

Four-ball weld point results of DMTD dimer in different base greases are listed in Table 1 [2]. As can be seen from Table 1, DMTD dimer exhibits good extreme pressure properties.

Grease Type	Four-Ball Weld Point, kgf	
	Base grease	+3% DMTD Dimer
Ca Complex	400	800
Bentonite Clay	126	315
Al Complex	160	500
Li Complex	200	800
Polyurea	100	315

Table 1. Extreme pressure performance of different greases with 3.0% DMTD dimer

DMTD dimer can be dissolved in a polyalkylene glycol (PAG) solution to obtaining a biodegradable liquid product of DMTD/PAG complex. The product has excellent Timken extreme pressure properties and good Four-ball extreme pressure performance [8, 9]. Instead of bidentate adsorption of DMTD dimer, DMTD/PAG complex forms multidentate adsorption on the surface, the strongest adsorption possible [9]. DMTD/PAG complex adsorption on metal surface is shown in Figure 2.

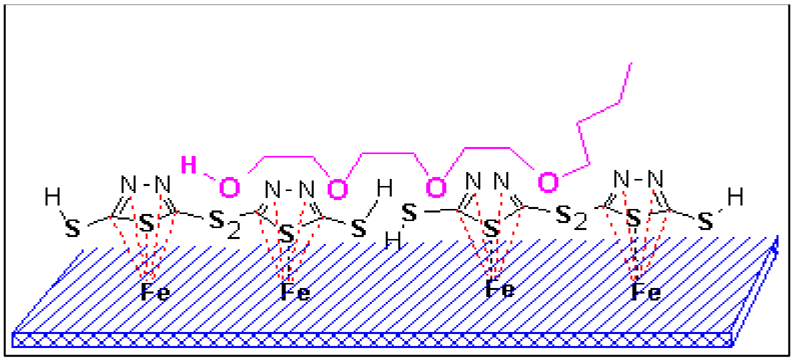


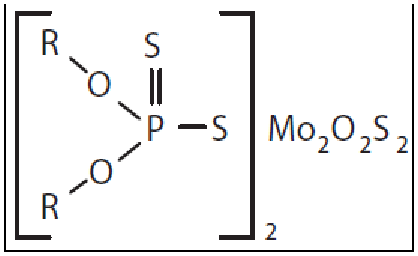
Figure 2. adsorption of DMTD dimer / butoxy triethylene glycol complex on metal surface

Excellent EP performance supports the theory of such strong surface adsorption. Table 2 lists DMTD/PAG complex EP performance in various base greases [8, 9]. As can be seen from Table 2, this additive at low treat rate of 2% can provide a Timken OK load of up to 80 pounds and four-ball weld point up to 400 kgf in some base greases. To achieve this level of extreme pressure performance, normally heavy metals-containing EP additive is needed at 5% treat rate.

Base Grease	Treat Rate, m%	ASTM D2509: Timken OK load, lb	ASTM D2596: Four-ball weld, kgf	ASTM D2266: Four-ball wear, mm
Simple Li	2.0	80	400	0.67
	1.5	70	315	0.59
	1.0	50	250	0.63
Li Complex	2.0	80	400	0.60
	1.5	60	315	0.64
Al Complex	2.0	80	315	0.95
	1.5	50	250	---
Polyurea	3.0	40	250	0.84
	2.0	40	200	1.02

Table 2. Extreme pressure properties of DMTD/PAG complex in different base greases

Molybdenum dialkyl dithiophosphate (MoDDP) is generally considered as a friction-reducing and antiwear additive, but it also can act as extreme pressure additive. Its chemical structure is as follows:



Extreme pressure performance of molybdenum dithiophosphate is mainly reflected in its ability to significantly improve last nonseizure load by reducing the four-ball wear scar diameter and steady state friction coefficient of the oil treated with this additive. A four-ball friction and wear tester was used in the evaluation of friction, wear and extreme pressure properties of a 650 SN base oil treated with this additive. Standard ASTM D4172 four-ball wear test method conditions were used, except test load was reduced from 40 kgf to 30 kgf for the base oil, only. All the other tests were run at 40 kgf load, 1200rpm, 60 minutes and 75℃ The base oil without additives could sieze at 40 kgf. For extreme pressure properties test, standard ASTM D2783 four-ball EP test method was used (1760 rpm, 10 seconds, room temperature). Molybdenum dialkyl dithiophosphate additive evaluated is a typical product of MoDDP (molybdenum content of 8.1%, 6.1% phosphorus content, sulfur content of 12.3%) [10]. Test results are shown in Table 3.

	Four-Ball Wear, mm	C of F	LNSL, Kgf	Weld Point, Kgf
650SN Base oil	0.802 (30Kgf)	0.100 (30Kgf)	36	100
+ 1.0% MoDDP	0.478	0.083	95	160
+ 2.0% MoDDP	0.376	0.077	100	160

Table 3. Four-ball friction and wear tests on 650 SN base oil with MoDDP

As can be seen from Table 3, LNSL value of oil treated with MoDDP will increase from 36 kgf to 95-100 kgf, showing good extreme pressure performance but the weld point is only improved marginally. For four-ball wear test, the wear scar diameter under load of 30 kgf for base oil is 0.802 mm, by adding 1.0% and 2.0% MoDDP , the wear scar diameter under 40 kgf load is reduced to only 0.478 mm and 0.376 mm, respectively. It can also be seen from Table 3, the coefficient of friction (C of F) for oil with MoDDP will be reduced by 20%, from 0.083 to 0.077.

In general, though extreme pressure additives in grease can greatly improve the weld point, this often leads to lower antiwear performance of the grease, resulting in an increase in four-ball wear scar. As we know, MoDDP additive not only can provide excellent anti-friction and antiwear properties, but also can significantly improve the last nonseizure load. While on the other hand, DMTD derivatives can improve the EP performance in either 4-ball weld point or Timken OK load or both. Although for any lubricant oil or grease, four-ball weld point, the last nonseizure load (LNSL), four-ball wear scar diameter and friction coefficient are often mutually restrained since all these additives are competing for the same metal surface area for adsorption. In this paper, a combination of DMTD derivatives as EP additive and MoDDP as antiwear additive and friction reducer in various base greases were studied with several common grease performance evaluation test methods. It is expected that the combination of DMTD extreme pressure additive and molybdenum dialkyl dithiophosphate antiwear agent can provide the best balance of extreme pressure, antiwear and anti-friction properties in treated greases.

2. Experimental / Materials and Methods

2.1 Base Greases and Additives

Base greases used in this study include a lithium complex grease, a polyurea grease and a calcium sulfonate complex grease. All three base greases were obtained from real production batches courtesy of several grease manufacturers. DMTD dimer [10] used in this study has a sulfur content of 62.0-67.0%, a nitrogen content of 17.4-19.4%. DMTD dimer/polyalkylene glycol complex [10] has a sulfur content of 20-28%, and a nitrogen content of 6.0 to 10.0%. Molybdenum dialkyl dithiophosphate (MoDDP) has molybdenum, phosphorus and sulfur contents of approximately 8.1%, 6.1% and 12.3% respectively. All three additives are available commercially [10].

2.2 4-Ball Friction and Wear Test

Standard ASTM D2266 four-ball friction and wear test method was used to evaluate additive performance in lubricating grease. Experimental conditions were: 40 kgf load, 1200 rpm speed, 60 minutes, 75℃ Real-time recording of coefficient of friction during the test is also available with the specific four-ball test machine used, in addition to measurement of wear scar diameters.

2.3 Four-Ball EP test

Standard ASTM D2596 four-ball EP test method was used to evaluate additive EP performance in greases. Experimental conditions were: 1770 rpm speed, time duration 10 seconds. Both last nonseizure load (LNSL) and weld point were measured.

3. Results and Discussion

3.1 DMTD derivatives and molybdenum dialkyl dithiophosphate synergistic combination in lithium complex grease

MoDDP, DMTD dimer and DMTD/PAG complex were added to the lithium complex base grease at the indicated treat levels. Four-ball wear and extreme pressure tests were performed on the treated grease, see results in Table 4.

Grease	Wear Scar, mm	C of F	LNSL, Kgf	Weld point, kgf
Li Complex base grease	0.552	0.119	48	126
+ 1.0% MoDDP	0.378	0.077	94	160
+ 2.0% MoDDP	0.365	0.076	114	160
+ 3.0% MoDDP	0.359	0.077	121	200
+ 2.0% DMTD dimer	0.650	0.113	66	400
+ 1.0% DMTD/PAG complex	0.685	0.105	82	250
+ 2.0% DMTD/PAG complex	0.766	0.086	94	315
+ 2.0% MoDDP + 1.0% DMTD dimer	0.385	0.066	121	250

+ 1.0% MoDDP + 2.0% DMTD dimer	0.461	0.077	88	400
+ 2.0% MoDDP + 2.0% DMTD dimer	0.441	0.064	88	315
+ 1.0% MoDDP + 1.0% DMTD/PAG complex	0.412	0.067	82	250
+ 1.0% MoDDP + 2.0% DMTD/PAG complex	0.418	0.060	94	315

Table 4. Additive performance on friction, wear and extreme pressure properties in treated lithium complex base grease

As can be seen from Table 4, MoDDP has excellent friction and wear performance in lithium complex grease. After adding MoDDP, both the friction coefficient and four-ball wear scar diameter, have been substantially decreased, while the last nonseizure load has been increased greatly. After adding extreme pressure agents DMTD dimer and DMTD/PAG complex, extreme pressure performance of the lithium complex grease was greatly improved. Both LNSD and weld point have been increased significantly, especially the weld point. But the four-ball wear scar diameter has been increased, indicating that these DMTD derivatives are good at improving EP performance but are poor in antiwear or wear resistance.

On the other hand, it is obvious from Table 4, that combinations of MoDDP and DMTD dimer or DMTD/PAG complex, can significantly improve both extreme pressure, antiwear/friction performance simultaneously in lithium complex grease. Figure 3 and Figure 5 showed the different effects on friction reducing performance between individual additive and additive combinations. And Figure 4 and Figure 6 showed the different effects on antiwear performance between individual additive and additive combinations.

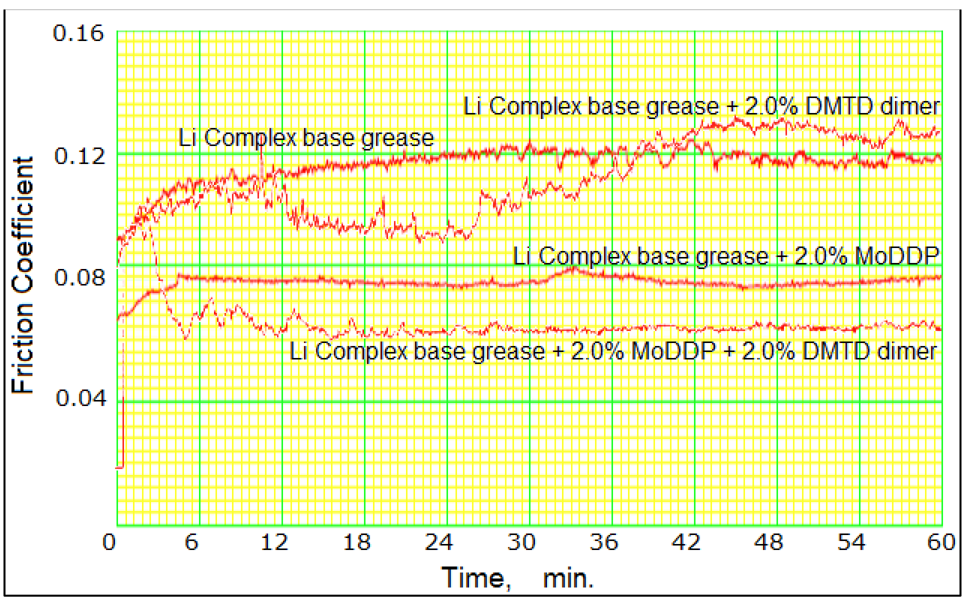


Figure 3. Friction reducing performance of MoDDP and DMTD dimer in lithium complex grease

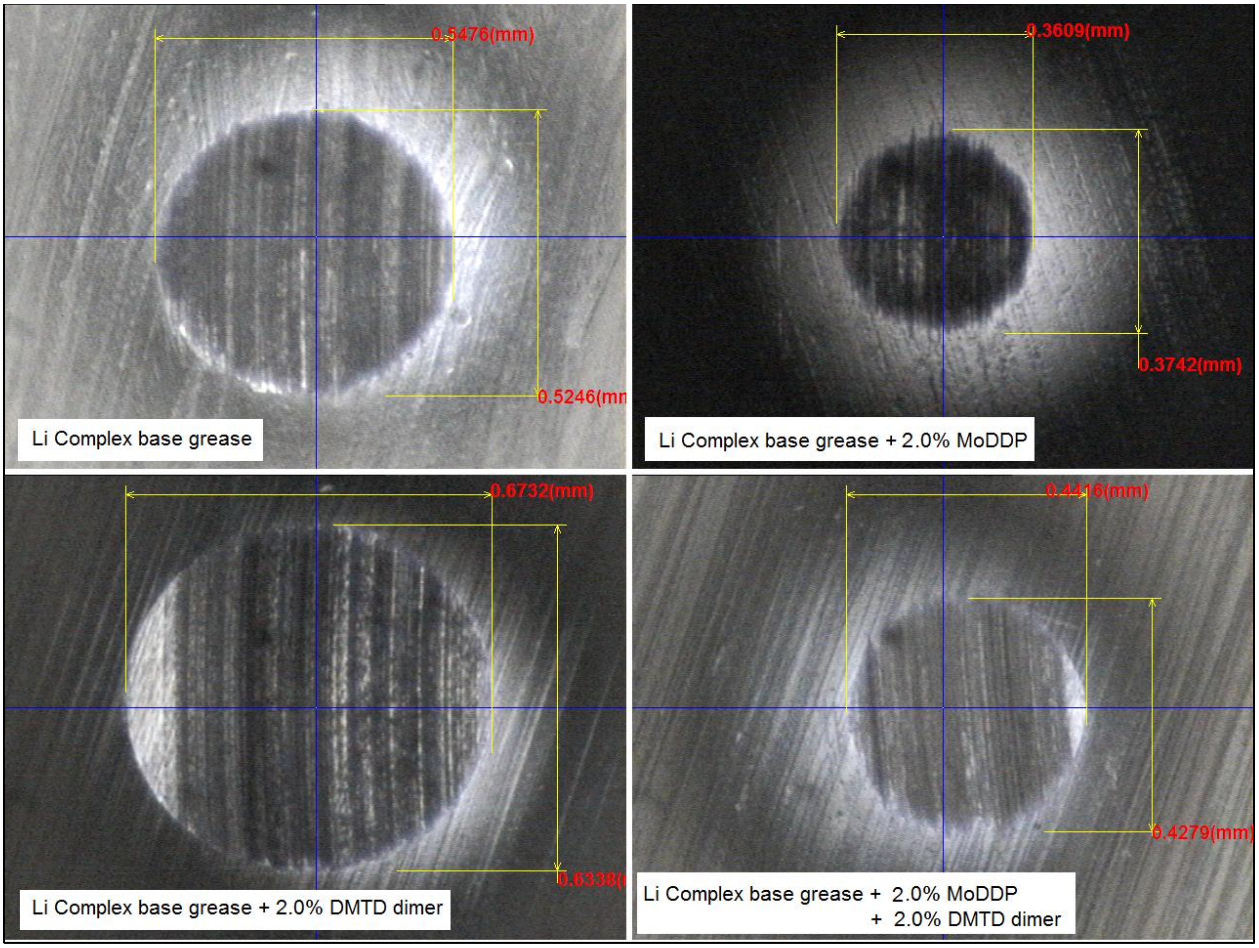


Figure 4. Antiwear performance of MoDDP and DMTD dimer in lithium complex grease

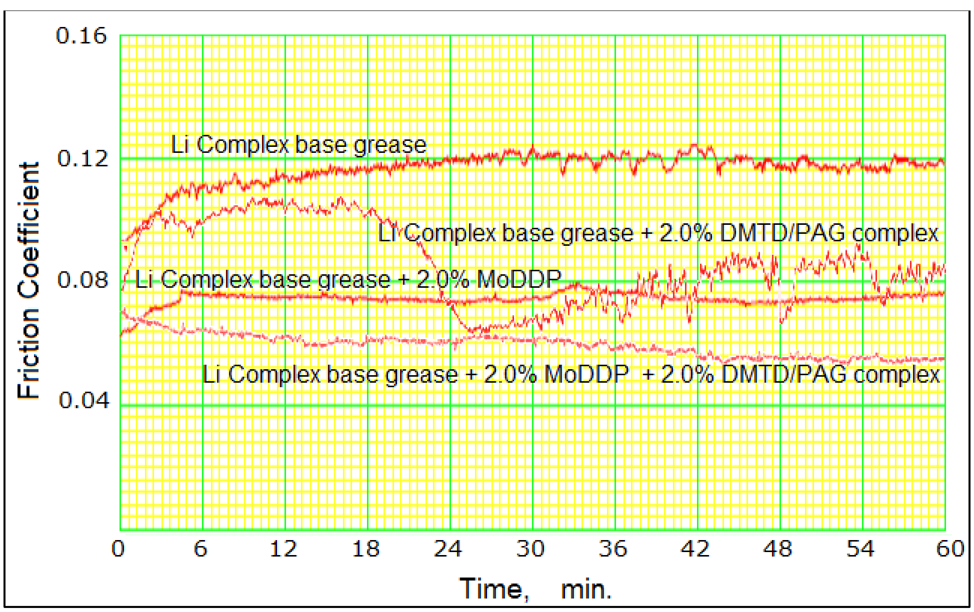


Figure 5. Friction reducing performance of MoDDP and DMTD/PAG complex in lithium complex grease

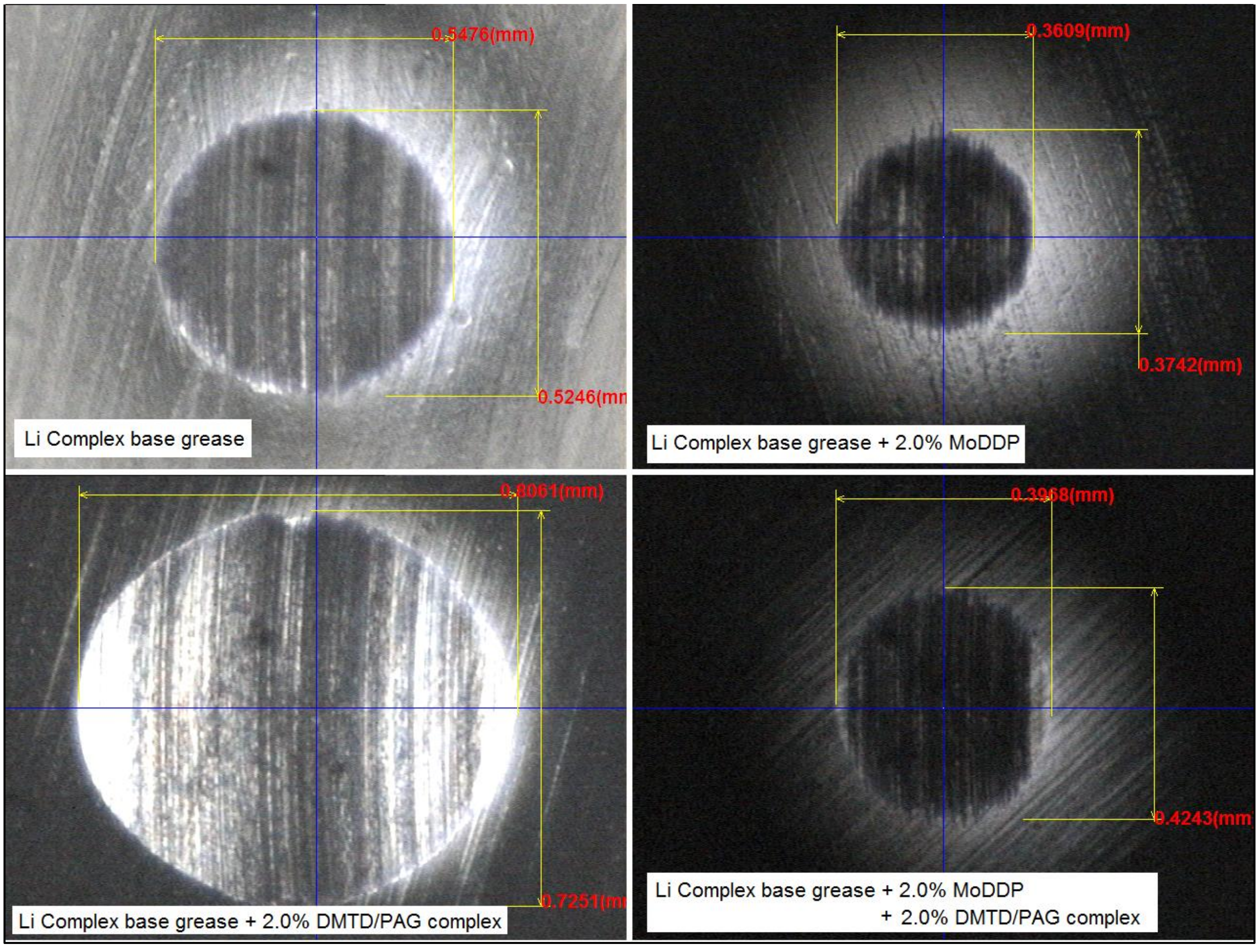


Figure 6. Antiwear performance of MoDDP and DMTD/PAG complex in lithium complex grease

3.2 DMTD derivatives and molybdenum alkyl dithiophosphate synergistic combination in polyurea grease

MoDDP, DMTD dimer and DMTD/PAG complex were added to the polyurea base grease at the indicated treat levels. Four-ball wear and extreme pressure tests were performed on the treated grease, results shown in Table 5.

Grease	Wear Scar, mm	C of F	LNSL, kgf	Weld point, kgf
Polyurea base grease	0.423	0.089	107	250
+ 1.0% MoDDP	0.419	0.085	88	250
+ 2.0% MoDDP	0.413	0.080	94	250
+ 2.0% DMTD dimer	0.694	0.083	76	315
+ 1.0% DMTD/PAG complex	0.553	0.103	82	315

+ 2.0% DMTD/PAG complex	0.625	0.077	76	400
+ 1.0% MoDDP + 2.0% DMTD dimer	0.570	0.085	88	400
+ 2.0% MoDDP + 2.0% DMTD dimer	0.551	0.084	82	315
+ 1.0% MoDDP + 2.0% DMTD/PAG complex	0.535	0.095	66	400
+ 2.0% MoDDP + 2.0% DMTD/PAG complex	0.491	0.063	66	400

Table 5 Additive performance on friction, wear and extreme pressure properties in treated polyurea base grease

As can be seen from Table 5, polyurea grease treated with MoDDP does not show any improvement in extreme pressure performance. Its friction reducing and antiwear properties are also not obvious. But this does not mean that all organic molybdenum additives are not effective in polyurea greases. As a matter of fact, molybdenum dibutyl dithiocarbamate, i.e. a MoDTC [10] with molybdenum content of approximately 28%, sulfur content of about 24.5% is very effective in friction reducing and antiwear performance in the same polyurea used in this study. Adding 1.0% and 2.0% of MoDTC in the polyurea grease can effectively reduce friction coefficient from 0.089 to 0.071 and 0.058, respectively. It can also reduce 4-ball wear scar diameter from 0.423 mm to 0.359 mm and 0.349 mm, respectively. At the same time, the weld point can be improved from 250 kgf to 315 kgf. Therefore, MoDTC might be more effective than MoDDP in polyurea greases (data for MoDTC treated grease is not shown in Table 5).

It can also be seen from Table 5, polyurea grease treated with DMTD extreme pressure agents DMTD dimer and DMTD/PAG complex, the weld point of the grease can be effectively increased, but there is no improvement in four-ball wear scar diameter, indicating that these additives are poor in antiwear performance. But unexpectedly, 2.0% DMTD/PAG complex can reduce friction coefficient from 0.089 to 0.077 in the treated grease, showing a strong friction reducing performance. When combination of MoDDP and DMTD dimer or DMTD/PAG complex was used in this grease, the weld point of the treated grease can remain at high values (though LNSL is lower), and four-ball wear scar diameter is smaller than when only DMTD extreme pressure agent was used, although still higher than the value for the base grease. This indicates that MoDDP can be used to improve the antiwear performance when DMTD containing extreme pressure agents are used. When combination of 2.0% MoDDP and 2.0% DMTD/PAG complex was used, the overall performance of the polyurea grease is well balanced with a high weld point, a low wear scar diameter and a small coefficient of friction.

3.3 DMTD derivatives and molybdenum alkyl dithiophosphate synergistic combination in calcium sulfonate complex grease

MoDDP, DMTD dimer and DMTD/PAG complex were added to the calcium sulfonate complex base grease at the indicated treat levels. Four-ball wear and extreme pressure tests were performed on the treated grease, results shown in Table 6.

Grease	Wear Scar, mm	C of F	LNSL, Kgf	Weld Point , Kgf
Ca Sulfonate Complex base grease	0.375	0.098	100	315
+ 1.0% MoDDP	0.396	0.087	88	400
+ 2.0% MoDDP	0.373	0.072	152	400

+ 2.0% DMTD dimer	0.531	0.086	94	620
+ 2.0% DMTD/PAG complex	0.472	0.102	71	400
+ 1.0% MoDDP + 2.0% DMTD dimer	0.521	0.096	48	620
+ 2.0% MoDDP + 2.0% DMTD dimer	0.426	0.078	40	620
+ 1.0% MoDDP + 2.0% DMTD/PAG complex	0.472	0.104	76	500
+ 2.0% MoDDP + 2.0% DMTD/PAG complex	0.475	0.096	44	500

Table 6. Additive performance on friction, wear and extreme pressure properties in treated calcium sulfonate complex base grease

As it can be seen from Table 6, molybdenum dithiophosphate MoDDP can provide some extreme pressure performance in calcium sulfonate complex grease, and friction reducing effect is also relatively obvious, but there is almost no antiwear improvement. This is mainly due to the calcium sulfonate complex base grease having very good antiwear performance, making MoDDP less effective. Overall, calcium sulfonate complex grease treated with 2.0% MoDDP performed pretty well. The weld point was increased from 315 kgf to 400 kgf, and last nonseizure load was increased from 100 kgf to 152 kgf , friction coefficient was lowered from 0.098 to 0.072, and wear scar diameter at 0.373 mm is still considered very good.

It can also can be seen from Table 6, adding an extreme pressure agent such as DMTD dimer or DMTD/PAG complex to calcium sulfonate complex grease, can effectively improve the weld point of the grease, especially when DMTD dimer was added. When 2.0% DMTD dimer was added to the grease, the weld point can reach 620 kgf. In fact, when 3.0% DMTD dimer was added to the grease, the weld point will reach 800 kgf (data not shown in Table 6). But, in both cases when DMTD dimer or DMTD/PAG complex was added to the grease, the grease will have an increased four-ball wear scar diameter, indicating that antiwear performance of the grease actually deteriorated. When combination of MoDDP and DMTD/PAG complex was used, the overall performance of the grease did not show any major improvement, except a slight increase of the weld point to 500 kgf. On the other hand, when a combination of 2.0% MoDDP and 2.0% DMTD dimer was used, the treated grease gave a very high weld point (620 kgf) , small wear scar diameter (0.426 mm) and low coefficient of friction (0.078).

4. Conclusions

(1) DMTD extreme pressure agents, DMTD dimer and DMTD/PAG complex, exhibit excellent extreme pressure performance. Adding these EP agents to lithium complex grease, polyurea grease and calcium sulfonate complex grease can effectively improve the four-ball weld point of these greases.

(2) Molybdenum dialkyl dithiophosphate (MoDDP) has excellent friction reducing and antiwear performance in lithium complex grease. This additive can greatly reduce wear scar diameter and friction coefficient in lithium complex grease. In calcium sulfonate complex grease, it has good extreme pressure properties (increasing the last nonseizure load and weld point in four-ball EP test), and excellent friction reducing properties. But in polyurea grease, it does not show obvious extreme pressure, antiwear and anti-friction properties.

(3) When combination of molybdenum dialkyl dithiophosphate (MoDDP) and DMTD dimer or DMTD/PAG complex was used in the lithium complex grease, the treated grease exhibited excellent friction reducing, antiwear and extreme pressure properties.

(4) When combination of molybdenum dialkyl dithiophosphate (MoDDP) and DMTD/PAG complex was used in the polyurea grease, the treated grease exhibited excellent friction reducing, antiwear and extreme pressure properties.

(5) When molybdenum dialkyl dithiophosphate (MoDDP) was used in the calcium sulfonate complex grease, the treated grease achieved very high weld point, reduced wear scar diameter and lowered the coefficient of friction.

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The Development of Extended Life Greases

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Abstract

The demand for greases capable of lasting longer is growing. As equipment power density has increased, the stress on automotive component and industrial machinery greases has also increased. According to the NLGI grease production surveys, a greater proportion of semi-synthetic and fully synthetic greases are now being used. Additionally, over the last few years there has been a marked shift to premium thickeners for many applications. In 2004, the North America volumes of simple lithium and lithium complex were approximately equal at 34% of the market. In 2012, the amount of lithium complex greases had increased to 39% with simple lithium declining to 28% of the market. Over the same period the global volume of high performance urea thickened greases grew by 60%.

In India, the market is dominated by simple lithium greases which accounted for 78% in 2004 and increased to 83.5% in 2012, with the increase mostly replacing sodium and hydrated calcium greases. The portion of higher performance thickener greases rose from ~5% in 2004 to ~9% in 2012. Base fluids, however, are still dominated by mineral oils with >99% in 2012. As the India market grows, the need for premium greases is increasing and with that the need for higher performance thickeners and longer life additives.

At the 2011 NLGI India Annual Meeting, the development process for a new longer life, higher temperature grease additive package was outlined. The additives referenced typically gave wheel bearing grease lives of 80 to 160 hours in the ASTM D3527 high temperature test, depending on the base grease and thickener. The NLGI GC requirement for wheel bearing greases in this test is a minimum of 80 hours. Subsequent work has shown that it is possible to achieve in excess of 300 hours grease life with an appropriate additive package and a high performance base grease. Additional testing has been carried out comparing the performance of these new greases with those of premium industry products based on running FAG FE9 testing at 160 °C and ASTM D3336 at 177 °C. This paper outlines the activities to screen and develop additives and packages to boost the performance of greases for extended life bearing applications.

Introduction

As reported in the 2012 NLGI Grease Production survey (1), the grease market in India is dominated by simple lithium soap greases which account for 83.5% of the market, up from 78% in 2004, with the increase mostly replacing sodium and hydrated calcium greases. The overall reported production of greases in India rose from 64,420 metric tonnes in 2003 to a recent maximum in 2009 of 93,154 metric tonnes falling back slightly to 86,520 metric tonnes in 2012. The reporting of base oil types started in 2010, but only 75% of Indian respondents submitted base fluid data. For every one of the last three years the reported value was >99% mineral oil, suggesting that this has not changed significantly over the period under review. As the India market grows, the need for premium greases is increasing and with that the need for higher performance thickeners and longer life additives. It is known that many non-domestic companies manufacturing automotive components in India use imported premium greases due to a perceived lack of availability of high performance greases with semi-synthetic and synthetic base fluids. The portion of higher performance thickener greases rose from ~5% in 2004 to ~9% in 2012. Of this 9% only a very small amount of grease is aluminium, titanium, and calcium complexes. The two main premium thickeners are lithium complex with around 7.4% and calcium sulfonate (including calcium sulfonate complexes) at 1.4% of the total reported grease market, up from 3.8 and 0.4% respectively in 2003. Prior to 2010, no urea thickened greases were manufactured in India but in the last two years <3 tonnes were produced. It is not known where these urea greases were manufactured nor what their end use was. From these numbers it is clear that the production of premium greases is currently small but there is clearly a growing demand.

The components of industrial machinery requiring grease lubrication include bearings, couplings, open gears and a variety of other moving components. The widest use of grease is in lubricating bearings, which are critical elements in equipment used in steel mills, mining, construction and transportation. In industrial equipment, both plain and rolling-element bearings are used. In either case, a film of lubricant separating moving surfaces is essential for a long service life. According to figures published by Lugt (2), 90% of rolling element bearings used in industrial applications are lubricated with grease, the majority of which have to be re-lubricated at regular intervals. In the Indian market today, a significant amount of grease is sold which has minimal or no treatment of additives. Much of this grease is used in industrial applications where extremely frequent re-lubrication is necessary to avoid failures and downtime. By raising the quality level of industrial greases, less frequent re-lubrication would be possible and this would save a significant amount of resources.

In the 1960s, it was recommended that all vehicle chassis components should be re-greased every 500 or 1,000 miles. Wheel bearings also needed to be replaced at periodic intervals of 10,000 to 20,000 miles or so. Vehicle warranties were typically one year and 10,000 miles. In today's automobile passenger car bearings and components, the majority of applications are sealed for life, but in busses, trucks both light and heavy duty, and off-highway applications, most bearings and components still have to be re-lubricated at regular intervals. In 1990, automotive greases accounted for 50% of the world's grease use, but today, it is only 35 to 40% (3) due to the filled-for-life applications seen in passenger cars and increased service intervals for commercial vehicles.

In the domestic car market in India, the warranties offered to owners (normally three years and 30,000 miles) are much shorter than typically offered in North America, where vehicle manufacturers have extended the warranty period to the current level of 10 years and 100,000 miles. In order to satisfy this increased demand, grease performance was upgraded. As India's passenger car makers move to export vehicles, vehicle warranties will need to rise to match the performance of export markets. If trucks are exported, factory fill greases used in chassis and bearing components will have to be upgraded to allow for the longer service intervals used in export markets, where the re-lubrication intervals of commercial vehicles have increased from 10,000 miles to 25,000 miles. In North America, the desired point is that grease re-lubrication should be the same interval as the crankcase oil at 40,000 miles. Significantly improved greases are needed to satisfy this requirement. Both of these automotive drivers necessitate an increase in the quality and performance of the greases used.

As was explained in 2009 (4), the role of the lubricant in a rolling element bearing is to help maintain the bearing's anti-friction characteristics. It does this by minimizing rolling resistance due to deformation of the rolling elements and raceway under load by separating the mating surfaces. It is also there to minimize sliding friction occurring between rolling elements, raceways and cage, especially in roller bearings, where much more sliding occurs. In industrial applications, the performance of the sealing is typically much less than that seen in sealed-for-life automotive bearings. A very important role for grease is the prevention of contaminant ingress. In many cases, the grease cannot totally prevent water from entering into the bearing, and so the grease also needs to protect the mating surfaces from water-induced corrosion.

At the 2011 NLGI India Annual Meeting, the development process for a new longer life, higher temperature grease additive package was outlined (5). The additives referenced typically gave wheel bearing grease life of 80 to 160 hours in the ASTM D3527 high temperature test, depending on the base grease and thickener. The NLGI GC requirement for wheel bearing greases (6) in this test is a minimum of 80 hours. Recent discussions within the grease industry (7) have suggested that the current required life is a minimum value and much longer life is really needed. Many vehicle and off-highway equipment manufacturers suggest that their own brand of premium greases perform better than the levels required by GC-LB, requiring them to be used within the warranty period, but offer GC-LB greases as a minimum quality back up if the branded grease is not available.

As reported previously (4) a number of failed grease lubricated bearings were analysed and the reasons for the failure identified. In all cases, the failure of the bearings was linked to grease breakdown. According to a major bearing manufacturer (8), rolling element bearings are so well engineered and manufactured today that they will last an order of magnitude longer than the grease that is used to lubricate them. The key to longer life greases is to understand how the current products fail and what components are necessary to achieve longer life.

The factors that influence grease life in bearings, can be grouped into effects of the three basic components, the base oil, thickener and additives, and into overall properties. These effects are identified in table 1.

Comparing these factors against the known failure modes of grease lubricated bearings, the following items are keys to the development of longer life bearing greases: oxidation, corrosion and degradation stability; load carrying capacity (LCC); wear resistance and improving surface protection.

Component effect			Overall effect
Base oil	Thickener	Additives	
Type	Type	Oxidation stability	Grease flow behaviour
Viscometrics	Structure and content	Wear resistance	Bleed characteristics
Low temperature properties	Consistency	Load carrying capacity	Unsaturated hydrocarbons
	Shear stability	Corrosion resistance	Homogeneity
		Friction	Water resistance

Table 1: The effects of grease properties on performance

Wear resistance and oxidation are very closely linked. Anti-oxidants prevent the degradation of the base fluid either by trapping radicals or decomposing radicals or in rare cases doing both. Base oil oxidation and degradation are promoted by transition metal catalysts. If the surface of the bearing wears, two things will happen. The first is that the wear processes will generate particles of finely divided iron and other transition metal alloying elements which can promote degradation. The second effect is that the wear will produce fresh metal surfaces which can undergo oxidation and reaction with species in the lubricant and further catalyse the degradation. If wear can be mitigated then a double benefit of increased life can be achieved.

The grease needs to have the correct level of load carrying additives. If insufficient surface protection is achieved, adhesive wear will occur, which will cause a deterioration of the bearing performance. Any wear particles formed will also promote three body abrasive wear and base oil degradation. Excess amounts of extreme pressure (EP) additives will promote high load carrying capacity, but in turn may promote surface corrosion and increased wear. Based on this it is challenging to try to make greases with both very high load carrying and long bearing life, and in most cases two different greases with optimized additive packages and base oil viscometrics would give both applications longer life than if a universal grease was used.

One of the further challenges with the development of grease additive packages is to balance the rate of reactivity of the components. If a higher concentration of a phosphorus anti-wear additive is used in a package alongside a sulfurized olefin EP additive, a rust inhibitor and a corrosion inhibitor, competition for the surface will occur. If the phosphorus compound gets on the surface first, the grease will have very good anti-wear properties but may not have sufficient LCC and adhesive wear would ensue. If the rust inhibitor gets to the surface first, the grease may do better in higher moisture applications but would suffer from poorer wear and higher friction.

Testing methods

In the original 2009 paper (4) there is an explanation of the test methods used to determine the lubricating properties of grease. As bearing testing to determine grease life is time consuming and expensive with tests running for several hundred hours and costing thousands of dollars, screening tests are heavily used to help in the selection of additives and components. In addition to the standard greases tests typically seen in grease specifications, a few specialized tests are employed to help in the selection of additives. Thermogravimetric analysis (TGA) is used to screen the high temperature thermal and oxidative stability of additives. A sample of the grease is heated at a controlled rate and the weight loss is measured. When run in a stream of nitrogen, thermal stability is evaluated and when run in air, oxidative stability is also checked. Pressure differential scanning calorimetry (PDSC) is used to determine the oxidative stability of greases under a high pressure oxygen environment. It has been suggested that PDSC oxidation induction time (OIT) correlates with high temperature grease life tests such as the D3527 wheel bearing life test (9) but recent testing has shown that the tests do not correlate very well (10). The reasons for the lack of correlation between the two methods are clearly related to the fact that in D3527 and in the FAG FE9 test listed below, the degradation mechanism of the grease is not just pure oxidation, which the PDSC tests. The DIN 58397t1 test is a thin film baking test that was originally designed to characterize base oil volatilization for lubricants for clock mechanisms. By running it at elevated temperature and for an extended time period, additional information can be obtained about the thermal and oxidation stability of greases (4). Once the standard grease tests have been passed, and the additional accelerated aging tests have been completed, good candidates are tested in the key bearing grease tests, which are listed and explained in table 2. Depending on the customer preferences, one of the oxidation life tests listed in table 2 is carried out along with typically a wear test. Historically, the FE8 test was only used in Europe but today it has a wide appeal and is starting to appear in global grease specifications. The FE9 is now the arbiter for the determination of a grease's upper operating temperature with an F_{50} passing requirement of 100 hours minimum at the claimed temperature (11).

Test	Standard	Type of bearing	Test temperature	Characteristics tested
Pope - grease life at elevated temperature	ASTM D3336	6204D3 deep group ball bearing	149 and 177°C	Oxidation life hours (Weibull life)
High temperature wheel bearing life test	ASTM D3527	LM67048-LM67010 and LM11949-LM11910 tapered roller bearings (TRB)	160°C	Oxidation life hours (minimum hours)
FAG FE8	DIN 51819-2	AC 7312B (polyamide or brass cage) TRB 31312	Ambient, 120, 140, 160, 180, 200 °C	Rolling element and cage wear weight loss (Weibull F50)
FAG FE9	DIN 51821-2	AC 7206 ball bearing	120, 140, 160, 180, 200 °C	Oxidation life hours (Weibull F50)

Table 2: Key grease performance tests using bearings

3. Zinc containing additive package for grease

Building on what was reported in 2009 (4) and 2011 (5), a premium zinc containing package was developed that gave outstanding performance in a lithium complex grease, passing the D3527 with a life of 80 hours and an FE9 at 160°C with a F50 life of 134 hours. The grease that was tested is labelled Grease 1 in subsequent tables. It was manufactured in a pilot kettle and had a base oil that was a blend of ISO VG 68 API group I paraffinic oil and low molecular weight PIB. The base oil viscosity was 168 mm^2/s at 40 °C and the viscosity index was 113. In order to map the performance of this new additive package, a series of other lithium complex base greases was prepared which included the new package at a 4%wt treat rate and additional testing was carried out. In all cases, the greases were targeted at meeting the NLGI GC-LB specification with additional standard tests such as copper corrosion which do not feature in the ASTM D4950 requirements. The salient test data for the 4 greases labelled 1 through 4 is included in table 3.

Grease 2 was a commercially manufactured lithium complex grease with 12-hydroxystearic and sebacic acids as the thickener. The base fluid was a single cut European manufactured paraffinic oil with a viscosity of 115 mm^2/s at 40°C.

Grease 3 was a commercially manufactured lithium complex grease with 12-hydroxystearic and sebacic acids as the thickener. The base fluid was a blend of API Group II and paraffinic bright stock and the viscosity was within ISO VG 150.

Grease 4 was a commercially manufactured lithium complex grease with 12-hydroxystearic and sebacic acids as the thickener. The base fluid was a blend of PAO 6 and PAO 100 and the viscosity was within ISO VG 150.

Property	Test method	GC-LB requirement	Grease 1	Grease 2	Grease 3	Grease 4
Worked penetration	D217	NLGI 1, 2, or 3	306	251	275	277
Dropping point (°C)	D2265	≥ 220	278	253	279	265
Bearing rust	D1743	pass	pass	pass	pass	pass
4-ball wear scar (mm)	D2266	≤ 0.60	0.54	0.50	0.48	0.52
4-ball EP Weld point LWI	D2596	 ≥ 200 ≥ 30	 315 45.7	 315 45.2	 315 47.4	 315 47.4
Fretting wear weight loss (mg)	D4170	≤ 10	< 1.0	8.7	8.0	9.6
Wheel bearing life (hours)	D3527	≥ 80	80	80	80	82
Copper corrosion	D4048		1B	1B	1B	1B
PDSC OIT at 180°C (minutes)	D5483		120.0	24.4	60.5	93.0
Timken OK load (pounds)	D2509		40	30	35	50
F50 FE9 life at 140°C (hours)	DIN 51821-2		343	200		

Table 3: Zinc containing additive package for grease – salient GC-LB and other tests

One of the areas of interest from customers was the use of this package in simple lithium and in urea thickened greases. How would the properties compare to the lithium complex greases reported above?

The first simple lithium grease was manufactured in a pilot grease system using a high quality source of 12-hydroxystearic acid, and had a base oil blend of an ISO VG 68 API group I paraffinic oil with a paraffinic bright stock giving a base oil viscosity of 170 mm^2/s at 40°C. The thickener content of this grease was around 6.5%wt. The same base had previously been used to develop an EP package.

The second simple lithium grease was manufactured in a pilot grease system using a high quality source of 12-hydroxystearic acid and had a base oil blend of an API group II paraffinic base oil and the same polyisobutylene as was used in grease A to give an ISO VG 220 fluid. The thickener content of this grease was around 7%wt.

The urea grease was manufactured in a closed laboratory flask using the same base oil as lithium complex grease 1. The thickener content was 12%wt, and it was manufactured via a Japanese style diurea grease process using MDI as the isocyanate and stearylamine. After manufacturing, the grease was milled and the zinc containing package was treated at 4 %wt then de-aerated. The grease was slightly softer than the intended NLGI 1grade.

As limited amounts of some of the grease were available, not all the required tests could be completed but the data did show outstanding results as shown in table 4. The two lithium greases both did very well in the wheel bearing life test at 160°C. The biggest difference between the lithium and lithium complexes were that, at the end of test, the lithium greases were totally destroyed but, as expect the lithium complexes were still reasonably grease-like. As expected, the urea thickened greases gave longer D3527 life and was showing no signs of degradation when the test was suspended due to motor failure after 140 hours. The grease looked in very good condition and would likely have lasted much longer.

Property	Test method	GC-LB requirement	Grease 5	Grease 6	Grease 7
Worked penetration	D217	NLGI 1, 2, or 3	265	308	348
Dropping point (°C)	D2265		198	205	298
Bearing rust	D1743	pass	pass	pass	pass
4-ball wear scar (mm)	D2266	≤ 0.60	0.53	0.52	0.42
4-ball EP Weld point LWI	D2596	≥ 200 ≥ 30	250 43	250 47.7	200 39.3
Fretting wear weight loss (mg)	D4170	≤ 10	6.5	9.8	5.1
Wheel bearing life (hours)	D3527	≥ 80	100	140	140 suspended
Copper corrosion	D4048		1A		
PDSC OIT at 180°C (minutes)	D5483		45.8	86.4	
Timken OK load (pounds)	D2509		35		
F50 FE9 life at 120°C (hours)	DIN 51821-2		544	372	

Table 4: Zinc containing additive package in other thickeners

Ashless additive packages for grease

The long life performance of the zinc containing package in the laboratory made urea grease raised the question of what life could be achieved by an ashless grease additive package in a urea grease. There are ashless EP packages for greases available but a review of some of them suggested that they in many cases they appeared to be industrial gear oil additive packages with the anti-foam and demulsifier additives removed. Some of the ashless packages examined were high in polysulfides, ashless dithiocarbamates and zinc-free dithiophosphates, all of which could give rise to malodorous finished greases. In discussion with customers, there appeared to be a need for an ashless high performance grease that could be used in urea-thickened and lithium complex greases.

The starting point for the development was a commercially manufactured urea thickened NLGI #3 grease with an API Group I ISO VG 150 base oil. The greases were all additized as discussed below and cut to an NLGI Grade #2 using the base oil mixture while keeping a constant thickener level among all the greases. The typical grease blending procedure entailed diluting the base greases at 80 ºC with the base oil mixture, mixing in the pre-blended additive concentrates for ≈20 minutes, homogenizing on a triple roller mill and de-aerating under vacuum. Half-scale penetrations and dropping points were checked on all greases to understand any impact of different formulation components on the penetration range and dropping point.

A matrix of tests was used to evaluate the influence of the various components of the intended ashless package on performance: sulfur extreme pressure additives (S-EP); a phosphorus anti-wear/multi-purpose additive (P-AW); an antioxidant (AO); and corrosion/rust inhibitors (INH). The additives were formulated as a typical 4%wt treatment, looking first at individual components, then binary followed by tertiary mixtures of additive concentrates with base oil replacing the components removed to keep the percent thickener constant. This required a total of 16 different combinations to be made up. Table 5 illustrates the grease additives matrix breakdown used in this study.

	Additive Matrix 0 = additive not present and 1 = additive is present.			
Grease Identification	AO	P-AW	S-EP	INH
A	0	0	0	0
B	1	0	0	0
C	0	1	0	0
D	0	0	1	0
E	0	0	0	1
F	1	1	0	0
G	1	0	1	0
H	1	0	0	1
I	0	1	1	0
J	0	1	0	1
K	0	0	1	1
L	1	1	1	0
M	1	0	1	1
N	1	1	0	1
O	0	1	1	1
P	1	1	1	1

Table 5: The grease additives matrix breakdown

Penetration and dropping point tests were carried out on all samples, followed by ASTM D1743 rust testing, 4-ball wear and then 4-ball EP. All samples were then tested for oxidation stability by PDSC and tested for their wheel bearing life. The data from all the tests is in Table 6 attached at the end.

In order to investigate if the new ashless package was suitable for use in electric motor bearings, two commercially available high performance ashless urea greases, Q and R, recommended for use in electric motor bearings were submitted for comparative testing. In North America, the most important tests for electric motor greases are the D2595, which looks at high temperature evaporation loss, 4-ball wear and the D3336 Pope test for high temperature oxidation life. In addition to this, PDSC testing was carried out at 210°C to see if there was a correlation between the Pope test and PDSC. The data from the testing is in table 7.

Test	Method	Grease P	Grease Q	Grease R
Evaporation Loss 177°C, 22hr, %	D2595	5.53	3.79	4.11
4-Ball Wear scar diameter, mm	D2266	0.44	0.48	0.53
PDSC at 210°C, OIT (min.)	D5483	41.5	14.9	36.3
Pope High Temperature Bearing Test 10,000rpm, 177°C, F_{50}, hours	D3336	425	290	304

Table 7 Comparative data for electric motor greases

As can be seen from the data in table 7, Grease P performed similarly in the evaporation loss and the 4-ball wear scars were similar. Directionally the Grease P had longer lives than the two commercial products but the data needs to be treated with caution as the numbers obtained are not statistically significantly different.

A further Grease, S, was made up. The additive formulation from matrix Grease P was blended the same ISO 150 VG lithium complex base as Grease 3 and cut to NLGI #2. The grease was then tested for conformance to D4950 GC-LB requirements for comparison to Grease P. The complete GC-LB data for both greases is in table 8. Both greases fully met the requirements of the NLGI GC-LB specification and additionally gave much longer D3527 lives than is required.

Property	Method	GC-LB requirement	Grease P	Grease S
Worked penetration	D217		281	276
NLGI Grade		NLGI 1, 2, or 3	2	2
Dropping point (°C)	D2265	≥ 220	265	255
Bearing rust rating	D1743	pass	pass	pass
4-ball wear scar (mm)	D2266	≤ 0.60	0.44	0.55
4-ball EP Weld point LWI	D2596	 ≥ 200 ≥ 30.0	 200 37.8	 315 46.8
Fretting wear weight loss (mg)	D4170	≤ 10	<1.0	7.2
Wheel bearing life (hours)	D3527	≥ 80	200	120
Water washout (%)	D1264	≤ 15.0	1.3	5.3
Oil separation (%)	D1742	≤ 6.0	0.8	1.8
CR Compatibility Δ Volume (%) / Δ Hardness (Shore A)	D4289	0 to 40 / -15 to 0	15.8 / -6	13.6 / -7
NBR-L Compatibility Δ Volume (%) / Δ Hardness (Shore A)	D4289	-5 to +30 / -15 to +2	11.9/-2	9.7/-4
Wheel Bearing Leakage (g)	D4290	≤ 10	5.7	3.2
Low Temp Torque, -40°C (Nm)	D4693	≤ 15.5	7.4	3.8

Table 8 – GC-LB testing on greases P (urea) and S (lithium complex)

Additional testing was carried out on Grease P. The Timken OK load was determined to be 75 pounds which exceeds 40 pounds, indicating that it has EP properties. The D4048 copper corrosion rating of 1B indicates yellow metal compatibility. FAG FE9 testing was initially carried out at 177°C and the F_{50} result was 62 hours. In the grease industry there is an estimate that due to more severe contact conditions in the FE9 test, the results in this test are between 10% and 20% of the life as determined by the Pope test at the same temperature. Comparing the two data points, the FE9 hours are within this range 42 to 85 hours. The FE9 test was re-run at 160°C and an F_{50} life of 110 hours was obtained. This confirms the high performance of the ashless package in the urea thickened grease.

Summary & Conclusions

The work presented here has shown that it is possible, using two different approaches, zinc-containing and ashless additive packages, to develop greases with significantly extended life.

Using the zinc-containing approach, greases have been developed with lithium complex thickeners in a variety of base oils which will pass the NLGI GC specification for high performance wheel bearing applications. It has also been demonstrated that lithium complex greases formulated with the new package give long bearing lives as shown by passing data in the FAG FE9 test at 140°C. Additional testing has also shown that the package will significantly increase the life of simple lithium and urea thickened oils.

With the ashless approach, a grease package was developed, which passed the NLGI GC-LB requirements in both lithium complex and in urea thickened mineral oil greases.

The ashless package in the urea thickened mineral oil grease was also compared to two commercially available electric motor greases and gave similar values in key tests and directionally gave longer bearing life.

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Grease Identification	Additive Matrix (0= not present; 1= present)				D1403 W0 / W60	Dropping point (°C)	D1743 rust rating	D2266 Avg. Scar Diam. (mm)	D2596 Weld Point / LWI (kgf)	D3527 (hours)	D5483 OIT at 210°C (min.)
	AO	P-AW	S-EP	INH							
A	0	0	0	0	249 / 265	285	Fail Light	0.79	126 / 24.6	60	<1.0
B	1	0	0	0	279 / 275	290	Fail Light	0.52	126 / 21.2	140	3.4
C	0	1	0	0	275 /291	312	Pass	0.59	126 / 28.1	>320	2.0
D	0	0	1	0	273 / 273	297	Fail Light	0.63	250 / 32.9	120	23.9
E	0	0	0	1	275 / 281	305	Fail Light	0.65	160 / 25.4	100	<1.0
F	1	1	0	0	275 / 291	314	Pass	0.61	160 / 28.1	140	10.2
G	1	0	1	0	279 / 279	297	Fail Light	0.61	250 / 32.9	140	42.6
H	1	0	0	1	265 / 283	316	Fail Light	0.70	126 / 23.8	120	2.0
I	0	1	1	0	265 / 285	301	Pass	0.43	250 / 46.0	140	16.9
J	0	1	0	1	255 / 277	312	Pass	0.58	160 / 28.0	180	2.0
K	0	0	1	1	259 / 275	303	Fail Light	0.68	200 / 31.8	160	19.9
L	1	1	1	0	259 / 283	302	Pass	0.46	200 / 32.5	240	46.4
M	1	0	1	1	259 / 275	293	Fail Light	0.54	250 / 40.7	200	41.6
N	1	1	0	1	265 / 285	315	Pass	0.44	200 / 28.3	142	8.8
O	0	1	1	1	265 / 285	303	Pass	0.42	200 / 44.3	200	19.3
P	1	1	1	1	265 / 281	265	Pass	0.44	200 / 37.8	200	41.5

Table 6: The grease additives matrix test results