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"Back to the Basics The ABC's of Grease Additive Performance"

Joseph P. Kaperick Afton Chemical Corporation Richmond, VA

Abstract

Research in the arena of grease chemistry can reach from the mundane to the esoteric but sometimes it's good to step back and examine the basic assumptions and "common wisdom" upon which those studies are often based. This paper will examine in more depth some of the foundational aspects of grease performance using test data to support or refute the commonly held "facts" of grease additives. The main focus will be on the role of additives in providing the essential performance characteristics typically required by bearing greases and other fully formulated lubricating greases. These focal areas will include:

- Comparison of primary and secondary ZDDPs
- Sulfur and EP performance
- AO combinations and high temperature performance
- Additive package response

Background work

Much work has been done in the evaluation of different additive components using a variety of grease bench & rig tests. Some of this work which focuses on tests included in this study is reflected in published literature on the subject.

Many authors in the literature use the 4 Ball Weld test as a measure of the effectiveness of novel EP agents or in studies of synergies or tribochemical interactions that improve boundary lubrication protection [1-9].

Pressurized Scanning Differential Calorimetry (PDSC) was used by Reyes-Gavilan [10] to evaluate different antioxidants in polyurea and lithium-thickened greases by a standard test method (ASTM D5483). Senthivel et al [11] looked at PDSC as well as a variety of other techniques including spectroscopic analysis and thermal aging to investigate the high temperature behaviour of greases. Samman [12] took a wider approach in a discussion of relative characteristics of different components in greases and their relation to high temperature performance utilizing case studies of greases in high temperature applications.

Rheological techniques similar to those used in this study have become more common in evaluating performance of high temperature greases in recent years. Nolan and Sivik [13,14] used this technique to compare the high temperature performance of a variety of different thickeners by rheology while comparing it to results from the dropping point apparatus. Coe [15] also looked at high temperature applications of grease formulations examining the claimed performance and how it related to dropping point as well as a variety of other high temperature bench tests. Kaperick
[16] also looked at the effect of boron additives in lithium greases on performance in the dropping point test.

Rhee [17] used PDSC and a Thermal Gravimetric Analysis (TGA) procedure to build a "decomposition kinetic model" which he then correlated to the high temperature wheel bearing rig test (ASTM D3527), while Ward and Fish [18] also used PDSC and the D3527 wheel bearing test as a guide and evaluated several finished greases in the FAG FE8 and FE9 rig tests. Additionally, Kaperick [19] investigated tribolayer formation and the effectiveness of different additive systems in various high temperature tests including the FAG FE9 rig test.

Recent papers that looked at the use of the Fafnir fretting rig to evaluate additive response with ASTM D4170 include Fish [20], Shiller [21] and Kaperick [22,23].

Methods and Materials

For this study, a core slate of additives was used to examine basic responses in commonly used grease test and interactions that might occur in grease formulations. Additionally, several different additive packages were included in the study to show performance differences that could be experienced by formulators. These components and packages are shown in Table 1 where some of the physical characteristics (elemental concentrations) are given along with the "ID" that will be used in various tables and graphs to illustrate the results of the study. Different colors are also used for various components for better differentiation in graphs used in this paper.

ID	Description	%Zn	%P	%S	%N	%B
1° ZDDP	Primary ZDDP	9	8	16.7	-	-
2° ZDDP	Secondary ZDDP	9	8.2	17.1	-	-
1°/2° ZDDP	Mixed ZDDP	9.2	8.35	17.8	-	-
SIB	Sulfurized Isobutylene	-	-	46	-	-
SO	Sulfurized Olefin	-	-	12	-	-
AO	Phenolic/Aminic AO Mix	-	-	-	1.17	-
BPD	Boron-Phos Dispersant	-	0.7	-	1.7	1.0
ZDDP Pack 1	Core ZDDP/Sulfur	4	3.5	22.9	0.1	-
ZDDP Pack 2	ZDDP/Sulfur + AO/RI	2	1.8	12.1	0.6	-
S/P Pack 1	Core S/P	-	1.2	36.1	0.8	-
S/P Pack 2	Core S/P + AO	-	0.8	25.6	0.9	-
S/P Pack 3	Core S/P	-	1.3	29.6	0.8	-
S/P Pack 4	Core S/P	-	1.2	32.5	1.1	-

Table 1 - Descriptions of components and packages used in study

The specific types of zinc dithiodiphosphates (ZDDP) used in the study are shown in Table 2 along with the carbon chain lengths of the alcohols used to make them and whether they are secondary or primary alcohols.

ID	Alcohol chain	Alcohol type	%Zn	%P	%S
1° ZDDP	**C4/C5/C8**	**Primary**	**9**	**8**	**16.7**
2° ZDDP	**C3/C6**	**Secondary**	**9**	**8.2**	**17.1**
1°/2° ZDDP	**C3/C4/C8**	**Primary/Secondary**	**9.2**	**8.4**	**17.8**

Table 2 - ZDDP descriptions

Two types of sulfur compounds were used in the study – a sulfurized isobutylene with high active sulfur content and a sulfurized olefin with a low active sulfur content. Details of these two components are shown in Table 3.

ID	Chemistry type	% Sulfur	% Active Sulfur
SIB	**Sulfurized Isobutylene**	**46**	**32**
SO	**Sulfurized Olefin**	**12**	**2**

Table 3 - Sulfur component description

To examine the effect of high temperature componentry on grease formulations, an antioxidant mixture and a borated dispersant were included as detailed in Table 1. These types of components are often used to provide oxidative stability to the oil component (AO) and stability to the thickener at higher temperatures (BPD).

Finally, the packages used were of two basic types – those based on ZDDP chemistry and those based on ashless S/P componentry. Some of the packages include a primary antioxidant, while some benefit from the secondary antioxidant impact of ZDDP. Details of each of the packages is included in Table 1.

Grease Samples

The base greases used for the work done in this study were made in the author's facility using a lab-scale, covered and jacketed 5-gallon kettle operated at atmospheric pressure with a single-motion, anchor-style agitator with scraper blades and fixed vertical baffle attached to the bottom of the lid cover. Heating and cooling were achieved by the circulation of heat transfer oil through the kettle's jacket using a loop consisting of an oil reservoir, pump, heater and heat exchanger. The kettle was connected to a second pump used to circulate the contents of the kettle through a colloid mill, to provide additional agitation, and to discharge the final product. The operation of the entire unit was computer controlled.

All greases were lithium 12-hydroxy stearate greases prepared with a blend of ISO 150 paraffinic Group I oils. The alkalinities are reported in %LiOH (not $LiOH•H_2O$) as calculated by ASTM D128, Section 21 – Free Alkali [].

Test Methods

The following test methods were employed with variations from standard ASTM methodology noted:

ASTM D1403 "Standard Test Methods for Cone Penetration of Lubricating Grease Using One-Quarter and One-Half Scale Cone Equipment" [24]

The half-scale cone method was employed with each of the samples being worked 60 times prior to analysis.

ASTM D2265 "Standard Test Method for Dropping Point of Lubricating Grease Over Wide Temperature Range"

[25] ASTM D2266 "Standard Test Method for Wear Preventive Characteristics of Lubricating Grease (Four-Ball Method)" [26].

ASTM D2596 "Standard Test Method for Measurement of Extreme-Pressure Properties of Lubricating Grease (Four-Ball Method)" [27]

This testing was carried out with the modification of using test loads at 10 kg intervals to more accurately monitor the incremental performance of the greases under extreme pressure.

ASTM D1743 "Standard Test Method for Determining Corrosion Preventive Properties of Lubricating Greases"

[28] This test was also run using a 67-hour duration to increase the severity of the test.

According to ASTM D1743, a bearing with no spots larger than 1.0 mm in diameter is considered a pass, and two out of three bearings must pass for the grease to be considered acceptable. In the present study, a modified system of rating bearings from D1743 tests was employed in order to better estimate the impact of each variable on the level of corrosion present. The raceway on the inside of each bearing cup was rated on the basis of a visual estimate (without the use of magnification) of the percent surface area covered by rust. This rating method is described in more detail in previous work [29]. To minimize variability in this modification, a single technician did all the evaluations used in this study.

ASTM D6138 "Standard Test Method for Determination of Corrosion-Preventive Properties of Lubricating Greases Under Dynamic Wet Conditions (Emcor Test)" [30]

Distilled water and 100% Synthetic Sea Water (SSW) were used in this study.

ASTM D 4048 "Standard Test Method for Detection of Copper Corrosion from Lubricating Grease" [31]

Copper strips were immersed in grease samples at test temperature and pulled at the standard 24 hours then rated against the ASTM standard template. The test was also run at 80˚C and 120˚C in addition to the standard temperature of 100˚C.

ASTM D 4170 "Standard Test Method for Fretting Wear Protection by Lubricating Greases" [32]

A <u>High Frequency Reciprocating Rig (HFRR)</u> was used to generate the HFRR Coefficient of Friction (COF) data. The HFRR test measures the ability of a lubricant to affect friction between the contacting parts and the wear of surfaces in sliding motion under load. A 6 mm diameter ANSI 52100 steel ball oscillates in contact with an ANSI 52100 steel flat under standard test conditions. The coefficient of friction is measured by the HFRR tool. The test was run with a 400 g load, while oscillating through a 1 mm path at 20 Hz. Test temperatures of 30ºC, 50ºC, 70ºC, 90ºC, 110ºC and 130ºC were employed sequentially with data taken every 5 seconds for 3 minutes at each test temperature once the temperature had stabilized.

An Anton-Paar oscillatory rheometer (MCR301) was used to measure the rheological properties of the grease. The grease was compressed between a bottom plate and a parallel top plate. Both plates were 25 mm in diameter and sand-blasted. A hood which contains a temperature-controlled Peltier device was placed over the test grease and bottom plate. A temperature sweep (2°C/min) was performed on the test greases in the rheometer ranging from 40°C up to 250°C with a constant oscillating shear strain of 0.05%. Both storage modulus (G') and loss modulus (G")
measurements were taken and the ratio of the two was plotted as "Tan Delta" (G"/G'). A typical interpretation of this ratio is that as the value moves from less than one to more than one, the internal structure of the grease is moving from a more solid-like material (G') to a more liquid-like material (G").

Thermal Gravimetric Analysis (TGA) was completed using a Perking Elmer Pyris 1 instrument. The principle behind TGA involves the measurement of sample weight loss as a function of temperature. Grease samples were heated from 50°C to 900°C under a nitrogen atmosphere (60 ml/min) using a constant ramp of 20°C/min. The first derivative is plotted and shows the rate of weight loss and can be correlated to % weight loss as a function of temperature.

ASTM D5483 "Standard Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry" [33] Samples were run by the standard test method at 155°C under 500 psi oxygen atmosphere. The extrapolated onset time was measured and reported as the oxidation induction time (OIT) for each sample.

ASTM D942 "Standard Test Method for Oxidation Stability of Lubricating Greases by the Oxygen Pressure Vessel Method"
[34]

Samples of grease were oxidized in a pressure vessel heated to 99 °C (210 °F) and filled with oxygen at 110 psi (758 kPa) for 100 hours. At the end of the test period, the loss of pressure (in psi) was recorded.

Results and Discussion

ZDDP Testing

To study differences between types of ZDDP components, a series of six greases were formulated as shown in Table 4. Due to slight differences in elemental makeup of the different types, a constant level of phosphorus (640 ppm) was targeted. A "typical" treat rate of 0.6 wt% of SIB was used to assess the impact of this component on performance of the ZDDPs under various test conditions.

Component	Base Grease	1° ZDDP	2° ZDDP	1°/2° ZDDP	1° ZDDP + SIB	2° ZDDP + SIB	1°/2° ZDDP + SIB
Lithium base	100	99.20	99.22	99.23	98.60	98.62	98.63
1° ZDDP		0.80			0.80		
2° ZDDP			0.78			0.78	
1°/2° ZDDP				0.77			0.77
SIB					0.60	0.60	0.60

Table 4 - ZDDP formulations

No significant differences were seen in standard tests (penetration and dropping point) that might show impacts on grease structure (Table 5).

Test	ASTM	Base Grease	1° ZDDP	2° ZDDP	1°/2° ZDDP	1° ZDDP + SIB	2° ZDDP + SIB	1°/2° ZDDP + SIB

Penetration (60x, 1/2 work), mm/10	**D1403**	**233**	**239**	**239**	**240**	**241**	**241**	**240**
Dropping Point, °C	**D 2265**	**205**	**205**	**201**	**201**	**200**	**209**	**209**

Table 5 - ZDDP structural test results

Corrosion testing shows some differentiation between different formulations as seen in Table 6.

Test	**ASTM**	**Base Grease**	**1° ZDDP**	**2° ZDDP**	**1°/2° ZDDP**	**1° ZDDP + SIB**	**2° ZDDP + SIB**	**1°/2° ZDDP + SIB**
Standard bearing corrosion, DI, % Rust	**D1743**	**5/15/15**	**0/0/0**		**0/0/0**	**0.5/1/15**		**0/5/15**
Ave % rust		**11.7**	**0**		**0**	**5.5**		**6.7**
Standard bearing corrosion, DI, 67 hrs, % Rust	**D1743 mod**		**0.5/0.5/0.5**			**25/5/15**		
Ave % rust			**0.5**			**15.0**		
Emcor (DI Water), Rating	**D6138**	**5/5**	**2/2**	**2/2**	**2/2**	**2/2**	**2/2**	**2/2**

Table 6 - ZDDP steel corrosion results

In all steel corrosion testing, the presence of ZDDP improved the result compared to base grease by itself. Of interest is the fact that the addition of SIB negatively affected the ability of ZDDP to prevent rust in the standard bearing test under both standard and extended length conditions. However, this same phenomenon was not seen in the more dynamic Emcor corrosion test. The higher temperature of the D1743 test may be activating ZDDP to form a protective layer and the presence of SIB interferes with this activation, either by going to the surface itself or by interacting with the ZDDP.

Copper corrosion testing also showed some differences between formulations as seen in Table 7.

Test	**ASTM**	**Base Grease**	**1° ZDDP**	**2° ZDDP**	**1°/2° ZDDP**	**1° ZDDP + SIB**	**2° ZDDP + SIB**	**1°/2° ZDDP + SIB**
Cu corrosion, 80°C, 24 hrs	**D4048**	**3a**	**2a**	**1b**	**1b**	**1b**	**1b**	**2a**
Cu corrosion, 100°C, 24 hrs	**D4048**	**3a**	**2a**	**1b**	**1b**	**1b**	**2a**	**2a**
Cu corrosion, 120°C, 24 hrs	**D4048**	**3a**	**2a**	**1b**	**1b**	**1b**	**2b**	**2a**

Table 7 - ZDDP copper corrosion results

Again, the addition of ZDDP improved the results in all cases although the primary ZDDP was less effective by itself than the secondary or mixed ZDDP components. The addition of SIB had the opposite effect with the secondary ZDDP and mixed ZDDP being less effective in the presence of SIB. This points to either interactions with the ZDDP or competition for the surface with the SIB causing copper corrosion as the active sulfur it contains is well known to do. This might explain the temperature-related severity seen with the secondary ZDDP/SIB mixture while the activity of the sulfur may be suppressed by interaction with the ZDDP in the other two cases.

The properties of ZDDP as a secondary antioxidant through its role as a peroxide decomposer are well known. As can be seen in Table 8, all the formulations containing ZDDP had a positive impact on D942 results with the secondary and mixed ZDDP showing the biggest impact, while SIB appears to have a slightly negative effect. However, none of the results for ZDDP-containing greases are statistically different from each other, so additional testing would be needed to confirm any differences.

Test	ASTM	Base Grease	1° ZDDP	2° ZDDP	1°/2° ZDDP	1° ZDDP + SIB	2° ZDDP + SIB	1°/2° ZDDP + SIB
Bomb oxidation (100 hr), psi loss	**D942**	**6.1 5.6**	**3.6**	**2.7**	**2.5**	**3.1**	**3.8**	**3.9**

Table 8 - ZDDP oxidation results

To further examine the impact of ZDDP on the thermal stability of grease formulations, TGA testing was used. Since the technique is commonly used one for analysis of greases, the base grease was run followed by repeat testing of the same grease to evaluate repeatability. As seen in Figure 1, the base grease has two main components which are separated by their thermal stability under the conditions of the test. The majority of the grease sample (the base oil component) is burned off between 200ºC and 430ºC, while the thickener itself, which is more thermally stable, is eliminated between 440ºC and 600ºC. The repeatability of the technique can be seen with duplicate runs of a representative sample "B".

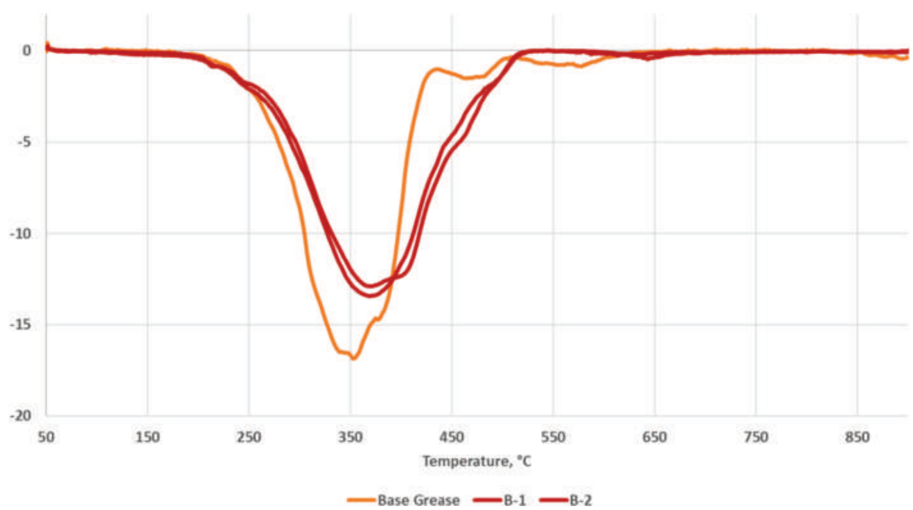

Figure 1 - Base grease response and repeatability of TGA

The addition of ZDDP adds to the base grease stability as seen in Figure 2. While the primary ZDDP shows a distinct difference at around 350ºC, all three ZDDPs seem to increase the thermal stability of the thickener structure as seen with the increase peak size between 400ºC and 500ºC. The addition of SIB to the secondary ZDDP seems to particularly affect the thermal stability of the grease structure and causing the loss of base oil at a significantly lower temperature as seen in Figure 3. However, the impact on the primary and mixed ZDDPs is not as pronounced and may even show some positive benefits in the grease thickener stability as seen around 450ºC. Additional study is needed to better understand how this data relates to grease structure and the impact of additives on it.

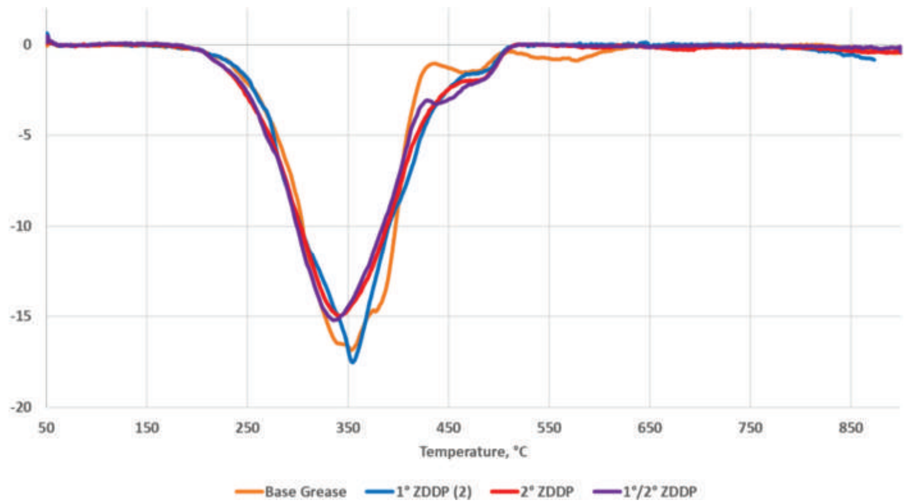

Figure 2 - ZDDP thermal stability (TGA)

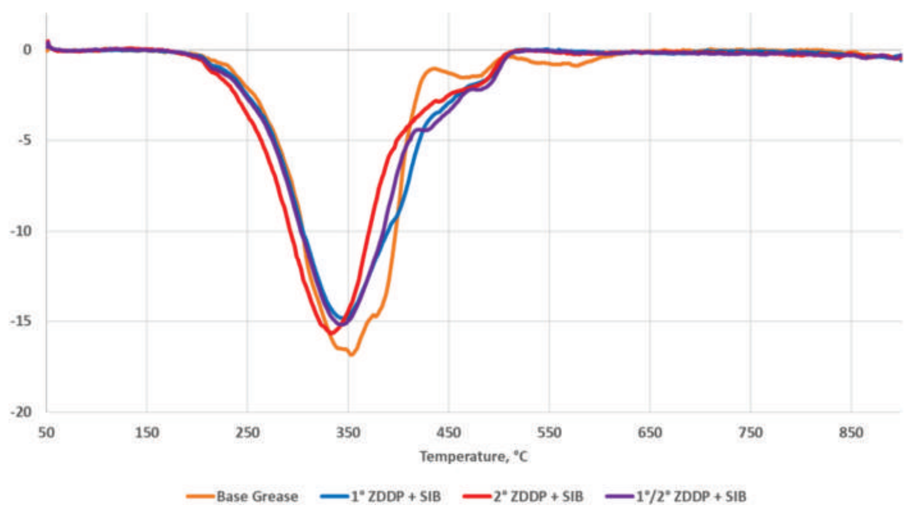

Figure 3 - Impact of SIB on ZDDP thermal stability (TGA)

High temperature rheology is another way to look at thermal stability of the grease structure and has been used more in recent research. By monitoring the ratio of G" and G' while raising the temperature gradually, the impact of temperature on grease behavior can be more closely observed. This ratio is typically referred to as "Tan Delta". The shift of the grease sample from more "solid" behavior at low Tan Delta values to more "liquid" behavior at higher values is commonly seen with the increase in temperature. The sudden rise in Tan Delta can be roughly correlated to dropping point but can also provide significantly more information about high temperature performance of greases. As seen in Figure 4, the rise in temperature leads to an initial slight "solidification" of the grease structure starting at around 60ºC followed by a gradual move to a more "liquid" phase from 100ºC to about 190ºC.

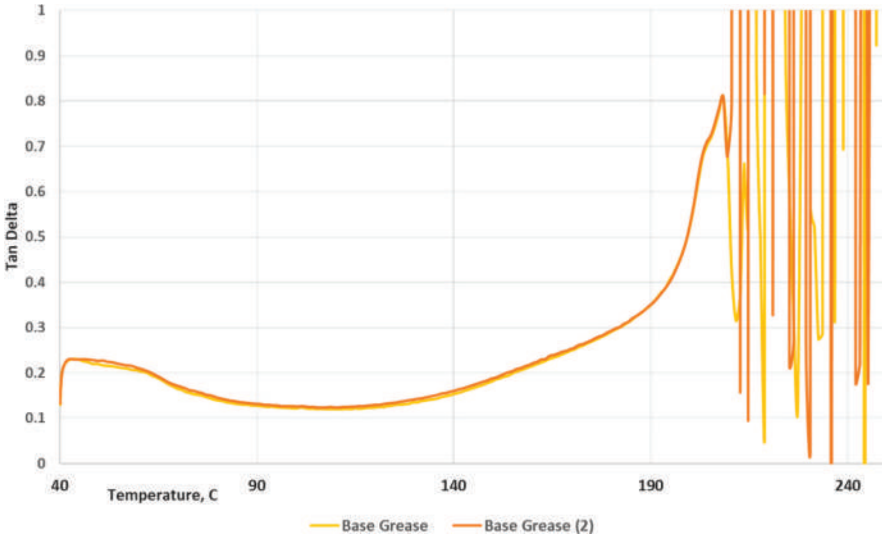

Figure 4 - Base grease response in high temperature rheology

This is followed by a sharp increase in Tan Delta that correlates roughly to the 205ºC dropping point seen with this base grease. As the temperature continues to increase, the signal deteriorates rapidly as the oil runs out of the grease and consistent contact between the plates is lost. As can be seen from the two runs, the repeatability of the method is also quite good.

The effect of ZDDP addition on grease structure at high temperature can be seen in Figure 5.

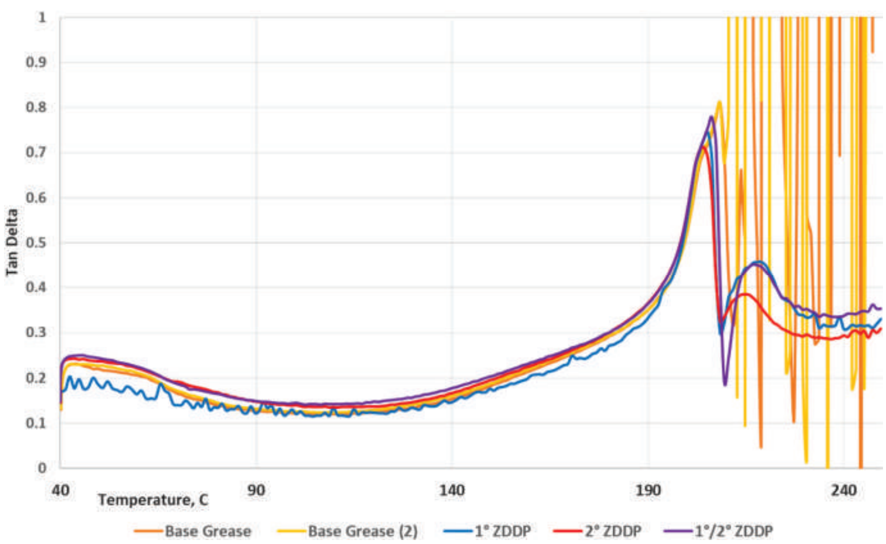

Figure 5 - ZDDP response in high temperature rheology

The obvious impact of the ZDDP is to maintain some structural stability of the grease past 240ºC. The same characteristic rise in "liquid" nature is seen around 200ºC (at the dropping point) but the grease maintains it stability past that point. It is interesting to note that the dropping point measured for these greases is very similar to the base grease but the high temperature behavior of the ZDDP-containing greases is obviously changed significantly.

The addition of SIB, as seen in Figure 6, also seems to impact the high temperature stability of the grease by lessening the sharp increase in "liquid" nature that occurs around the dropping point of the greases. Again, the dropping point itself showed no significant increase with addition of either ZDDP or SIB, but the high temperature characteristic as measured by rheology is obviously changed. Additionally, there appeared to be no significant differences between ZDDP type and response in high temperature rheology testing.

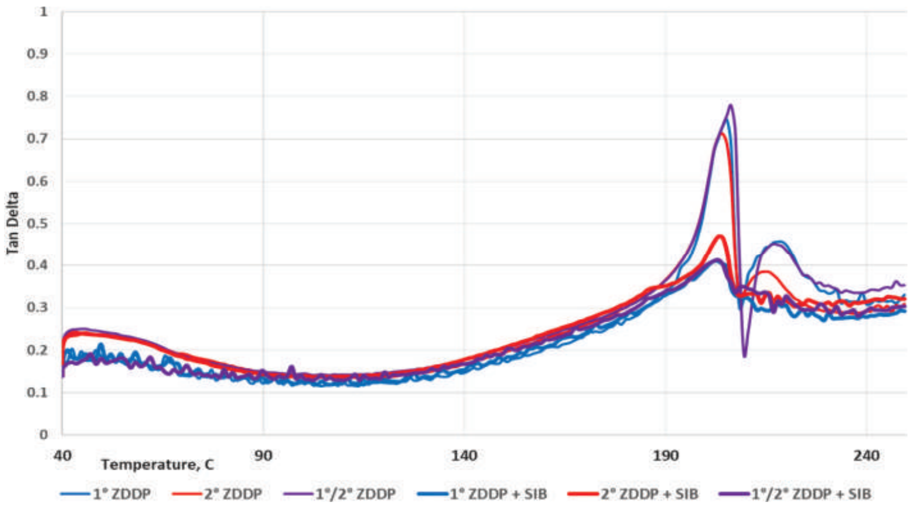

Figure 6 - Impact of SIB on ZDDP response in high temperature rheology

ZDDP is often used as a primary antiwear component in grease formulations so the impact on the commonly used 4-ball weld and wear tests was evaluated. As seen in Figure 7, ZDDP not only lowers wear significantly as compared to the base grease alone, but it adds EP protection as seen in the boost in 4 ball weld results seen with each formulation. Interestingly, while the primary and secondary ZDDPs boost the EP by 20 kg, the mixed ZDDP gives a response that is 30 kg higher than that. This same directional response is seen in the presence of SIB which provides a 60 kg boost in combination with the primary and secondary ZDDPs but an additional 30 kg (for a total of 90 kg) weld load when added to the mixed ZDDP. This may be due to the ability of the mixed ZDDP to decompose (and thus form a protective tribolayer) over a wider temperature range than either of the other two ZDDPs. While the ZDDP provided significant wear protection both with and without SIB present, no significant differences were seen between ZDDP type.

Test	ASTM	Base Grease	1° ZDDP	2° ZDDP	1°/2° ZDDP	1° ZDDP + SIB	2° ZDDP + SIB	1°/2° ZDDP + SIB
4 Ball EP, Weld Point	D 2596	180	200	200	230	240	240	270
4 Ball Wear (40kg, 75C, 1200 rpm, 1 hr), mm	D 2266	0.67	0.53	0.47	0.51	0.49	0.50	0.48

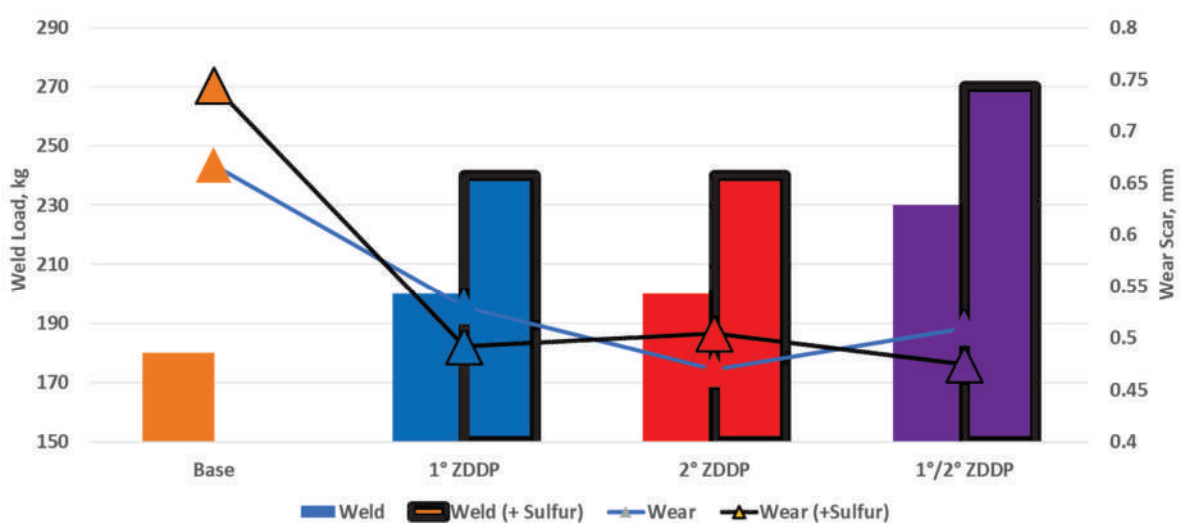

Figure 7 - ZDDP extreme pressure and wear testing

The Fafnir Fretting Wear test is a commonly used test for oscillating wear and therefore of interest in evaluating wear protection provided by ZDDP. As seen in Table 9, the fretting wear response of different ZDDPs shows that the mixed ZDDP provides some measure of fretting protection over the base grease while neither of the other ZDDP components significantly improved fretting. The addition of SIB negatively impacts the ability of the mixed ZDDP to protect against fretting while there is no apparent effect on the primary and secondary ZDDPs possibly due to a lack of any initial protection seen by those components.

Test	ASTM	Base Grease	1° ZDDP	2° ZDDP	1°/2° ZDDP	1° ZDDP + SIB	2° ZDDP + SIB	1°/2° ZDDP + SIB
Fretting wear, mg	**D4710**	**27.8** **33.6**	**28.3**	**29.2**	**23.3** **24.3**	**25.3** **31.2**	**30.7**	**27.2** **27.7**

Table 9 - ZDDP fretting wear results

The coefficient of friction (COF) of the greases containing different ZDDP types was evaluated by HFRR at different temperatures from 30ºC to 130ºC. The data in Figure 8 represents 3 minutes of COF measurements after the temperature has stabilized at each increment. At the initial temperature of 30ºC, the addition of ZDDP makes very little difference compared to the base grease by itself. As the samples approach 70ºC, the degradation of ZDDP is beginning and the change in COF is seen as a tribofilm is formed. The region from 70ºC to 110ºC shows widely variable COF data as the tribolayer is formed and grows with increasing temperature. By the time the samples have reached 130ºC the tribolayer has somewhat stabilitzed although there is still some variability in the measurements. Higher temperatures might give more consistent results but the instrument used could not safely be used higher than 130ºC. The tribolayer formed by ZDDP is typically a thicker film but still provides some reduction in friction as compared to the base grease alone. Some evidence is seen of the formation of a thinner, smoother tribolayer (with a lower COF) by the primary ZDDP with the mixed and secondary ZDDPs giving slightly thicker tribolayers with correspondingly higher COF measurements at 130ºC.

When SIB is added to the ZDDP-containing greases [Figure 9], more variability is seen in the mid-temperature range as the tribolayers are forming possibly due to the surface active SIB interfering with formation of the ZDDP film. At 130ºC, the variability is less with both the primary and secondary ZDDPs at around the same level as the samples without SIB although the mixed ZDDP still shows some wide variation. Longer intervals or higher temperatures might show better consistency in the signal as the tribolayer becomes better established.

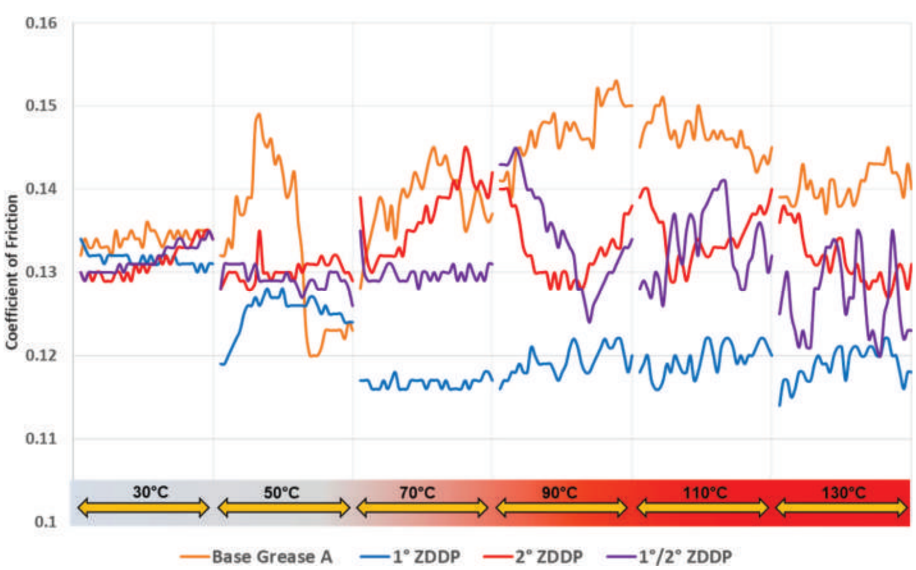

Figure 8 - ZDDP Friction data

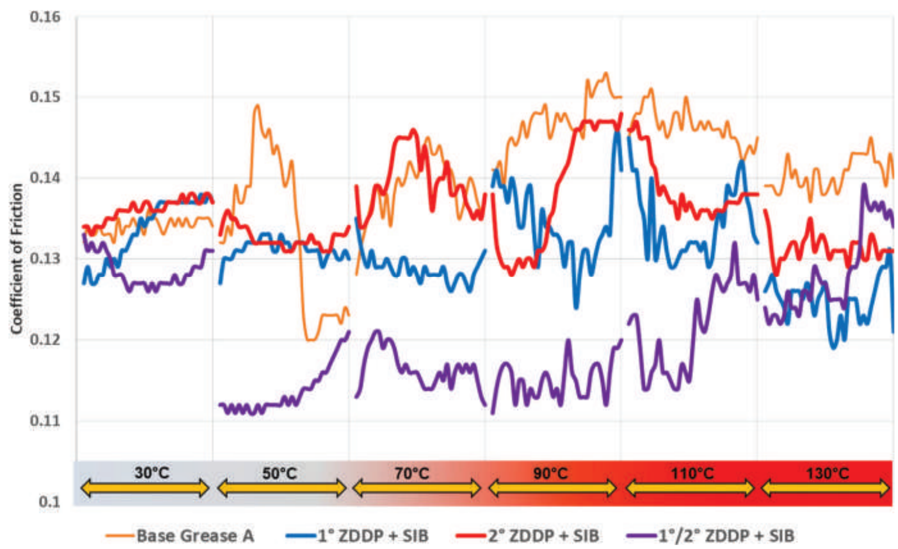

Figure 9 - ZDDP friction data with SIB added

<u>Sulfur Testing</u>

The two sulfur sources were blended into four formulations to investigate the impact of the different sulfur by themselves and in the presence of the primary ZDDP as shown in Table 10. Due to the wide disparity in sulfur content, the level of each sulfur component was calculated to target an equivalent level of sulfur (2780 ppm) in each formulation. The level of ZDDP used was kept the same as in the study of ZDDP components above.

	Base Grease	SIB	SO	SIB + 1° ZDDP	SO + 1° ZDDP
Lithium base	**100**	**99.20**	**99.22**	**99.23**	**98.60**
SIB		**0.60**		**0.6**	
SO			**2.19**		**2.19**
1° ZDDP				**0.80**	**0.80**

Table 10 - Formulations for sulfur study

Again, no significant differences were seen in standard tests (penetration and dropping point) that might show impacts on grease structure (Table 11).

Test	ASTM	Base Grease	SIB	SO	SIB + 1° ZDDP	SO + 1° ZDDP
Penetration (60x, 1/2 worker), mm/10	**D1403**	**233**	**239**	**242**	**241**	**241**
Dropping Point, °C	**D 2265**	**205**	**200**	**209**	**200**	**200**

Table 11 - Sulfur structural test results

In all steel corrosion testing, the presence of sulfur improved the result compared to base grease by itself. The results obtained above with the primary ZDDP by itself have been included in Table 12 for comparison purposes. As seen in the ZDDP testing, the combination of ZDDP with either sulfur source shows a negative impact on the ability of either ZDDP or sulfur alone to prevent corrosion. While still within the repeatability of the method, the EMCOR results give indications of the same phenomena. This again seems to indicate the formation of some kind of protective layer by either sulfur or ZDDP individually and that this protection is interfered with by combining the two components.

Test	ASTM	Base Grease	SIB	SO	SIB + 1° ZDDP	SO + 1° ZDDP	1° ZDDP
Standard bearing corrosion, DI, % Rust	D1743	5/15/15	0/0/0	0/0/0	0.5/1/15	0.5/1/5	0/0/0
Ave % rust		11.7	0	0	5.5	2.2	0
Standard bearing corrosion, DI, 67 hrs, % Rust	D1743 mod		15/15/15	0/5/5	5/15/25	15/15/25	0.5/0.5/0.5
Ave % rust			15.0	3.3	15.0	21.7	0.5
Emcor (DI Water), Rating	D6138	5/5	1/2	1/2	2/2	2/3	2/2

Table 12 - Sulfur steel corrosion results

Interestingly, the addition of SIB to the base grease did cause a decrease in copper corrosion compared to the base grease by itself as seen in Table 13. The addition of sulfurized olefin by itself, or ZDDP in combination with either sulfur source, resulted in high levels of protection against copper corrosion. While it's not surprising that the higher level of active sulfur in SIB would cause more copper corrosion than sulfurized olefin, it is surprising that it seems to lower the amount of copper corrosion seen in the base grease alone. This might be due to the interaction of the active SIB sulfur interacting with "bad actors" in the base grease but further study would be recommended to investigate these results.

Test	ASTM	Base Grease	SIB	SO	SIB + 1° ZDDP	SO + 1° ZDDP
Copper corrosion, 80C, 24 hrs	D4048	3a	2c	1b	1b	1b
Copper corrosion, 100C, 24 hrs	D4048	3a	2c	1b	1b	1b
Copper corrosion, 120C, 24 hrs	D4048	3a	2c	1b	1b	1b

Table 13 - Sulfur copper corrosion results

Sulfurized olefin is used as an antioxidant in engine oil and other formulations so it is not surprising to see that it provides oxidative stability compared to the unadditized base grease as shown in Table 14. The addition of ZDDP does not appear to provide any synergy but the low levels of oxidation in this particular base grease don't provide much opportunity to differentiate. SIB does not appear to provide any improvement in oxidative stability but the combination of SIB and ZDDP does reduce oxidation, likely due to ZDDP's role as a secondary antioxidant.

	Base Grease	SIB	SO	SIB + 1° ZDDP	SO + 1° ZDDP
Bomb oxidation (100 hr), psi loss	6.1 5.6	5.3	2.4	3.1	3.3

Table 14 - Sulfur oxidation results

TGA results shown in Figure 10 seem to indicate that SIB provides much more thermal stability than sulfurized olefin when used as individual components. This may be due to the higher activity of the SIB providing more crosslinking, and therefore more structural stability to the grease thickener at higher temperatures. The addition of ZDDP seems to improve the thermal stability of both sulfur components to about the same level. On the whole, the combination of sulfur and ZDDP seems to provide additional thermal stability than either of the components by themselves.

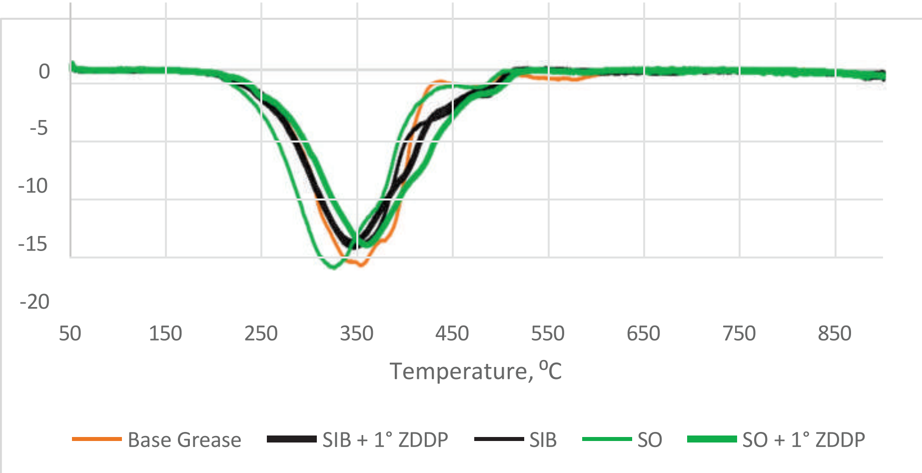

Figure 10 - Sulfur TGA results

The high temperature rheology testing showed no signs of improvement of the grease structure by either of the sulfur sources used individually [Figure 11]. As seen in the TGA study, however, the addition of ZDDP did significantly improve the structure at high temperatures as the grease maintained a signal and showed relatively low Tan Delta values. However, no differentiation was seen between the sulfur types.

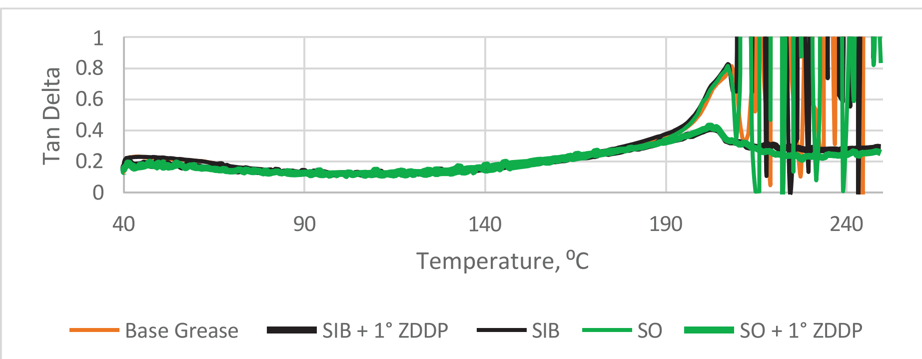

Figure 81 - Sulfur high temperature rheology results

Since sulfur is often used primarily for extreme pressure protection, testing was done for both 4 ball weld and 4 ball wear as shown in Figure 12. Perhaps not surprisingly, the more active sulfur in SIB leads to a higher 4 ball weld result even though both were treated at equal levels of sulfur. Both still provide a significant boost over the base grease by itself, although both also contribute to roughly equal levels of increased wear. The addition of ZDDP not only reduces the wear (as expected) but also provides a small boost in EP protection which seems to level out the differences seen by the individual sulfur components.

Test	ASTM	Base Grease	SIB	SO	SIB + 1° ZDDP	SO + 1° ZDDP
4 Ball EP, Weld Point	D 2596	180	230	210	240	230
4 Ball Wear (40kg, 75C, 1200 rpm, 1 hr), mm	D 2266	0.67	0.91	0.97	0.49	0.50

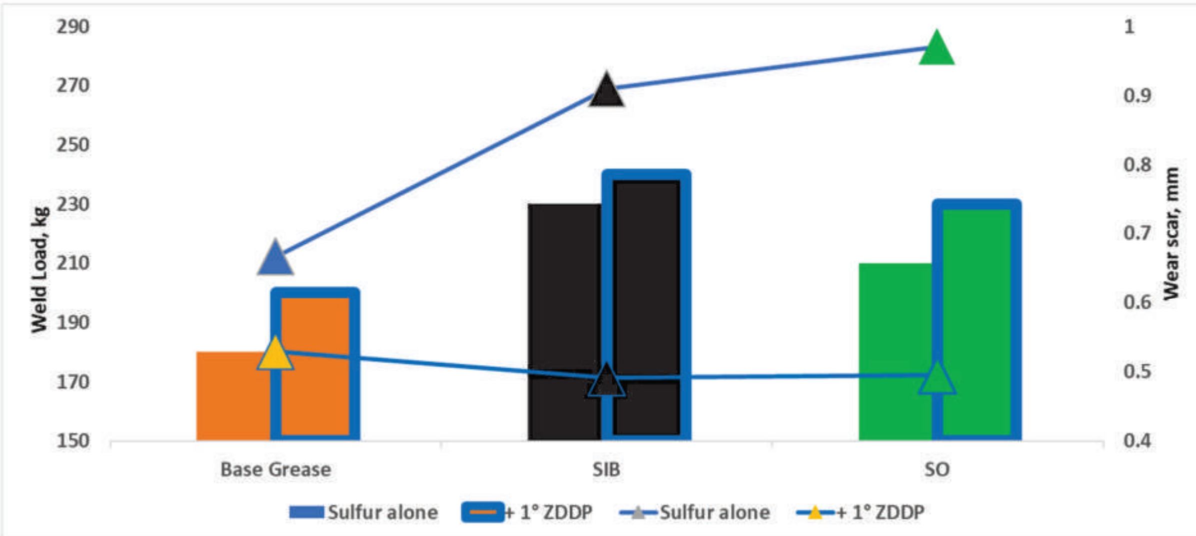

Figure 92 - Sulfur extreme pressure and antiwear results

As expected, neither sulfur source had a positive impact on fretting wear testing as seen in Table 15. Even the addition of ZDDP did not improve the performance of either component.

Test	ASTM	Base Grease	SIB	SO	SIB + 1° ZDDP	SO + 1° ZDDP
Fretting wear, mg	D4710	27.8 33.6	25.2 29.2	41.2 24.0	25.3 31.2	26.5

Table 15 - Sulfur fretting wear results

In friction testing by HFRR, as seen in Figure 13, the sulfur components brought a little improvement in overall COF by the time the sample reached 130ºC. Prior to that it appears that sulfurized olefin increases the friction sometimes even above the base grease. It appears that ZDDP helps improve the overall friction by end of test, but more study would be needed to confirm the behavior and possible interactions seen here.

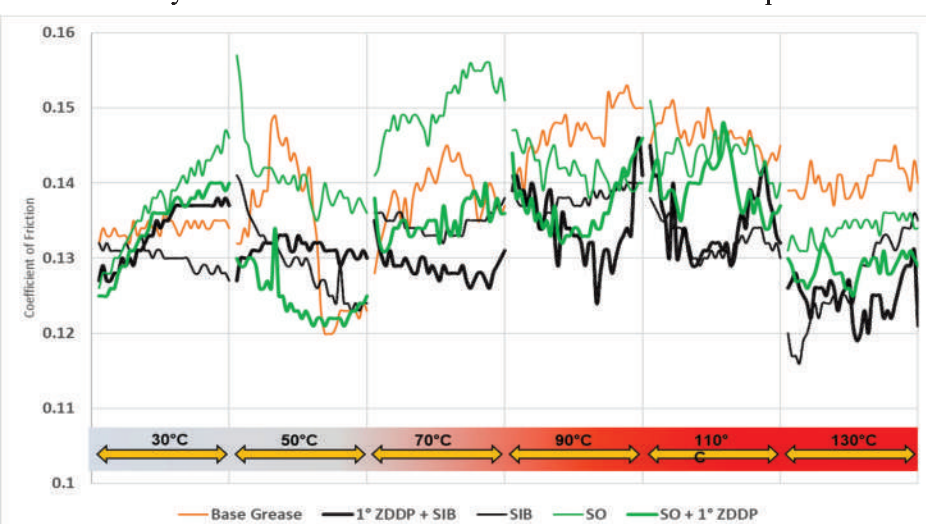

Figure 103 - Sulfur friction testing results

Antioxidant/Borate Testing

A third category of additives was tested because of the importance of high temperature performance for many greases. Antioxidants are considered useful for enhancing the oxidative stability of the base oil (the major component of grease formulations) under high temperature or other conditions of oxidative stress. Borated components are also considered useful for high temperature performance due to their ability to strengthen the grease thickener structure at high temperatures.

For comparison purposes, ZDDP was included with the antioxidant mixture and borate added sequentially. Two levels of the borate were examined in combination with the ZDDP and the AO mixture as shown in Table 16.

	Base Grease	1° ZDDP	1° ZDDP + AO	1° ZDDP + AO + BPD (1.5%)	1° ZDDP + AO + BPD (3%)
Lithium base	100	99.20	99.22	99.23	98.60
1° ZDDP		0.8	0.8	0.8	0.8
AO			1.0	1.0	1.0
BPD				1.5	3.0

Table 16 - AO/Borate formulations

Although no significant differences were seen in the penetrations of the grease formulations, the effect of the borate in raising dropping point is obvious from the data in Table 17. This is commonly seen with borates especially in combination with ZDDP and is likely due to some kind of cross-linking structural stabilization of the grease thickener structure allowing it to hold on to the oil at higher temperatures.

Testing:	ASTM	Base Grease	1° ZDDP	1° ZDDP + AO	1° ZDDP + AO + BPD (1.5%)	1° ZDDP + AO + BPD (3%)
Worked 60 Penetration - 1/2 worker (mm/10)	D1403	233	239	239	238	237
Dropping Point	D 2265	205	205	209	239	288

Table 17 - AO/Borate physical structure results

Minimal testing was done with copper or steel corrosion due to the expectation that these components were unlikely to affect performance significantly. However, the results of EMCOR corrosion testing in Table 18 showed a surprising
impact of having the boronated dispersant present. It's possible that this is due to the borated species reacting with the water and keeping it away from the surface or it may be providing some kind of tribofilm that protects against corrosion. Further study would be needed to confirm the mechanism.

Testing:	ASTM	Base Grease	1° ZDDP	1° ZDDP + AO	1° ZDDP + AO + BPD (1.5%)	1° ZDDP + AO + BPD (3%)
Emcor (DI Water), Rating	D6138	5/5	2/2		1/0	0/0

Table 18 - AO/Borate steel corrosion results

As expected in the pressurized vessel oxidation testing, the addition of the AO mixture appears to have an incremental benefit when used in combination with the ZDDP which provides some oxidation stability itself as see in Table 19. The addition of the borate has no significant impact under the conditions of this test.

	ASTM	Base Grease	1° ZDDP	1° ZDDP + AO	1° ZDDP + AO + BPD (1.5%)	1° ZDDP + AO + BPD (3%)
Bomb oxidation (100 hr), psi loss	**D942**	**6.1 5.6**	**3.6**	**2.5**	**2.2**	x

Table 19 - AO/Borate oxidation results

Testing by TGA shows definite evidence of increased thermal stability of the grease in Figure 14. As expected from the dropping point results, it can be seen that borate containing greases hold on to the oil in its matrix at a significantly higher temperature than those without it. Interestingly, the grease that contained only ZDDP and AO, showed a lowering of the thermal stability of the grease with the oil coming off at a significantly lower temperature. This grease does not appear to affect the stability of the grease thickener as seen by the peak at around 500ºC. This may indicate that oil itself is thermally less stable with the AO present but further testing would be needed to confirm this.

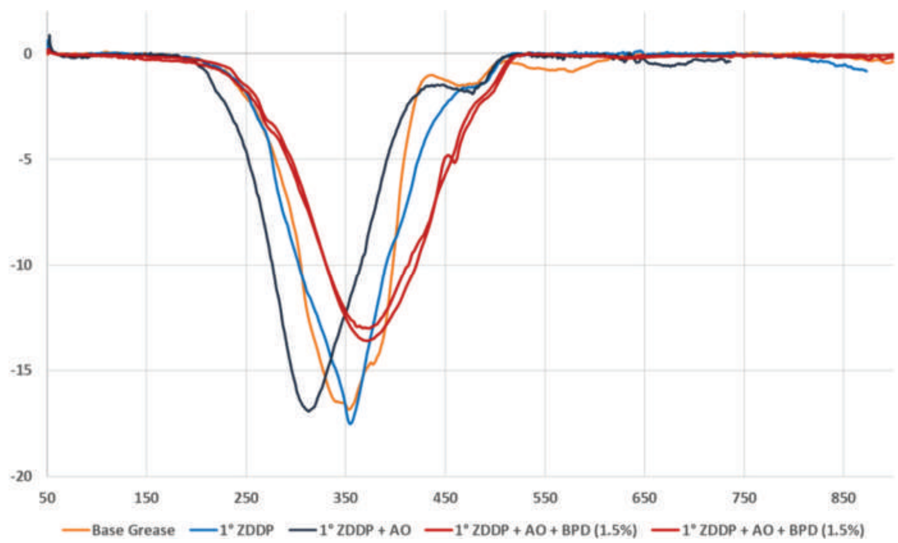

Figure 114 - AO/Borate TGA results

High temperature rheology of these greases also highlights the ability of the borate to help maintain a consistent grease structure at higher temperatures as seen in Figure 15. The impact of the ZDDP by itself and in combination with the AO mixture is seen to provide some continuous structure through the temperature at which the dropping point was measured showing that some benefit is provided here. However, the borate almost eliminates the sharp increase in liquid nature seen around 200ºC and appears to keep a more solid nature through that entire temperature zone. This sample was measured up to 300ºC and the slow increase in liquid nature is seen through this higher temperature range. Further work at these higher temperatures with some of the other greases studied would be of interest as well.

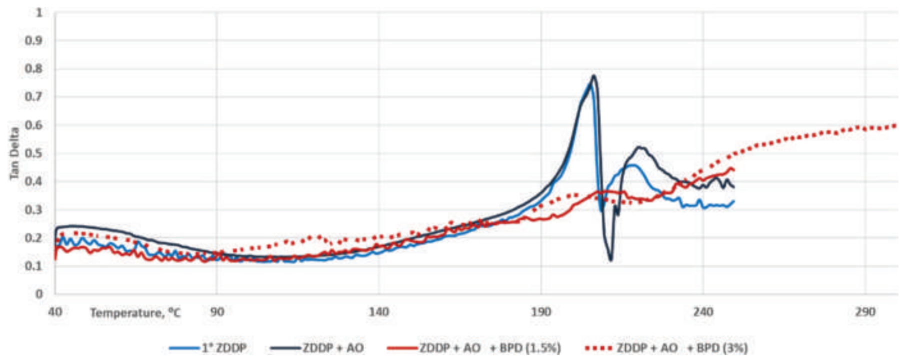

Figure 125 - AO/Borate high temperature rheology results

While the AO would not be expected to have an impact on EP performance, a slight boost in seen in all three greases that contain the AO mixture as seen in Table 20. Surprisingly, the AO mixture in combination with the ZDDP seems to lower wear as well. This may indicate some interaction with ZDDP that allows the ZDDP to provide more EP and AW protection but the repeatability of the tests would require additional testing to confirm this. On the other hand, the presence of the borate degrades the antiwear protection of the ZDDP giving wear scars that are comparable to the base grease alone. This may be due to the formation of a thinner borate film that is not as good at protecting against wear. As discussed further in this study, HFRR testing shows significant lowering in friction with the borated dispersant and this is usually indicative of thinner films which can provide less protection from wear.

Test	**ASTM**	**Base Grease**	**1° ZDDP**	**1° ZDDP + AO**	**1° ZDDP + AO + BPD (1.5%)**	**1° ZDDP + AO + BPD (3%)**
4 Ball EP, Weld Point	**D 2596**	**180**	**200**	**220**	**210**	**220**
4 Ball Wear (40kg, 75C, 1200 rpm, 1 hr), mm	**D 2266**	**0.67**	**0.53**	**0.42**	**0.70**	**0.72**

Table 20 - AO/Borates EP and AW results

In the case of fretting wear, as seen in Table 21, there is no statistically significant indication of improvement from the ZDDP, the AO or the boronated dispersant.

Test	**ASTM**	**Base Grease**	**1° ZDDP**	**1° ZDDP + AO**	**1° ZDDP + AO + BPD (1.5%)**	**1° ZDDP + AO + BPD (3%)**
Fretting wear, mg	**D4710**	**27.8** **33.6**	**28.3**	**31.9**	**32.3**	**25.9**

Table 21 - AO/Borate fretting wear results

Finally, as mentioned above, the HFRR test results show a clear reduction in friction at the 1.5% treat level of the borate as seen from the duplicate runs in Figure 16. The increasing the borate level seems to raise the friction possibly due to formation of a thicker film with the higher level of boron and phosphorus present. Of additional interest is the higher friction seen with the addition of AO to the ZDDP. This may also be due to an increase in film formation and could be linked to the reduction in wear seen with that formulation.

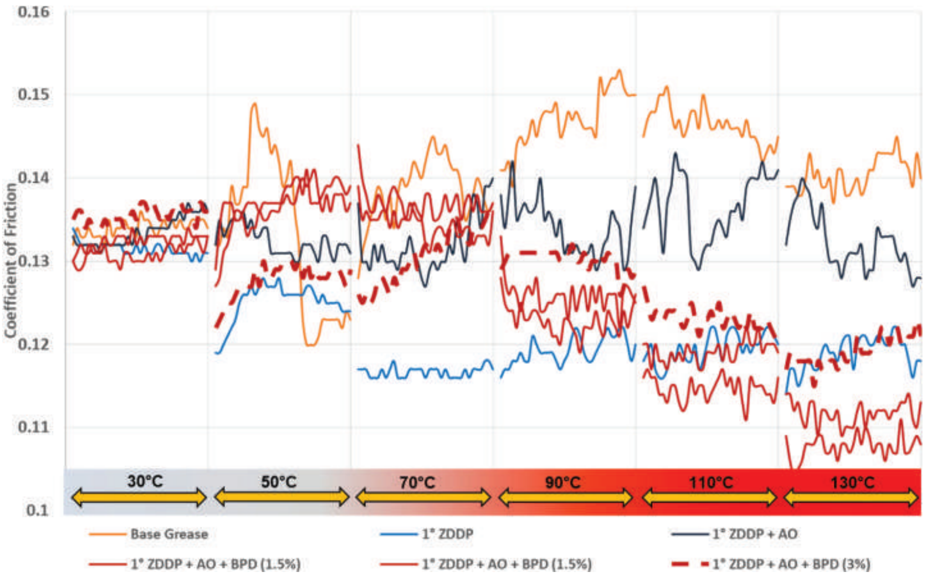

Figure 136 - AO/Borate HFRR friction results

Package Testing

While understanding the behavior of different components individually or in binary combinations with other commonly used additives is important, a finished grease formulation often include some combination of all these components. While additive packages have some shortcomings in terms of flexibility of use, they are often used when they can help meet clear performance goals in higher volume greases. In this study, six packages were blended in the same lithium base grease with treat rates calculated to deliver an equivalent amount of sulfur (~5400 ppm) in each finished formulation [Table 22].

	Base Grease	ZDDP Pack 1	ZDDP Pack 2	S/P Pack 1	S/P Pack 2	S/P Pack 3	S/P Pack 4
Lithium base, % wt	100	97.64	95.54	98.50	97.89	98.18	98.34
Package Treat, % wt		2.36	4.46	1.50	2.11	1.82	1.66
Calculated S, ppm		5404	5397	5415	5402	5387	5395
Calculated P, ppm		826	803	180	169	237	199
Calculated Zn, ppm		944	892	0	0	0	0
Calculated N, ppm		24	268	120	190	146	183

Table 22 - Package grease formulations

No significant differences were seen in standard tests (penetration and dropping point) that might show some weakening of grease structure due to interaction with additive components (Table 23).

Test	ASTM	Base Grease	ZDDP Pack 1	ZDDP Pack 2	S/P Pack 1	S/P Pack 2	S/P Pack 3	S/P Pack 4
Penetration (60x, 1/2 worker), mm/10	D1403	264	267	275	269	279	277	273
Dropping Point, °C	D 2265	197	197	204	204	211	204	207

Table 23 - Packages physical testing results

Each of the packages showed varying degrees of rust protection with S/P Pack 1 and 4 being the least effective in the D1743 bearing corrosion test as shown in Table 24. In the dynamic corrosion (Emcor) test, ZDDP Pack 1 was the least effective with ZDDP Pack 1 and S/P Pack 2 showing slight corrosion in one bearing. This not only shows the variation in rust protection systems of various packages but the differences in the severity of different corrosion tests and the response of additives to them.

Test	ASTM	Base Grease	ZDDP Pack 1	ZDDP Pack 2	S/P Pack 1	S/P Pack 2	S/P Pack 3	S/P Pack 4
Std bearing corrosion, DI, % Rust	D1743		0/0/0	0/0/0	0/0/0	0/0/0	0/0/0	1/1/1
Ave % rust			0	0	0	0	0	1
Std bearing corrosion, DI, 67 hrs, % Rust	D1743 mod		0/0/1	0/0/0.5	1/5/10			5/1/10
Ave % rust			0.3	0.2	5.3			5.3
Emcor (DI Water), Rating	D6138	2/2	1/1	0/1	0/0	0/1	0/0	0/0

Table 24 - Packages steel corrosion results

In this particular base grease, all of the S/P Packs showed less protection against copper corrosion than the ZDDP- containing packages [see Table 25]. This is not surprising in light of the positive impact seen above with ZDDP and the negative impact due to the more active sulfur found in the S/P packages. It is interesting to note that the only S/P package that contains AO shows more protection than the other S/P packages (which do not contain AO).

Test	ASTM	Base Grease	ZDDP Pack 1	ZDDP Pack 2	S/P Pack 1	S/P Pack 2	S/P Pack 3	S/P Pack 4
Copper corrosion, 100C, 24 hrs	D4048	3a	1b	1b	3a	2e	3a	3b

Table 25 - Packages copper corrosion results

Unfortunately, the unadditized base grease used for testing the packages had a very low pressure loss result in the D942 testing and no significant differences were seen between packages in this test as shown in Table 26. More severe conditions would be needed to be able to differentiate the response.

Test	ASTM	Base Grease	ZDDP Pack 1	ZDDP Pack 2	S/P Pack 1	S/P Pack 2	S/P Pack 3	S/P Pack 4
Bomb oxidation (100 hr), psi loss	D942	4.3	2.9	3.4	3.5	2.8	4.5	2.8

Table 26 - Packages oxidation results

As seen in Figure 17, both ZDDP packages showed a significant increase in thermal stability of the grease compared to the base grease by itself. In Figure 18, the S/P packages also seem to have an impact on the grease thickener it is less distinct with the region of the thermogram associated with base oil being almost unchanged. How this impacts the performance of the grease, especially at high temperatures, is unknown at this time.

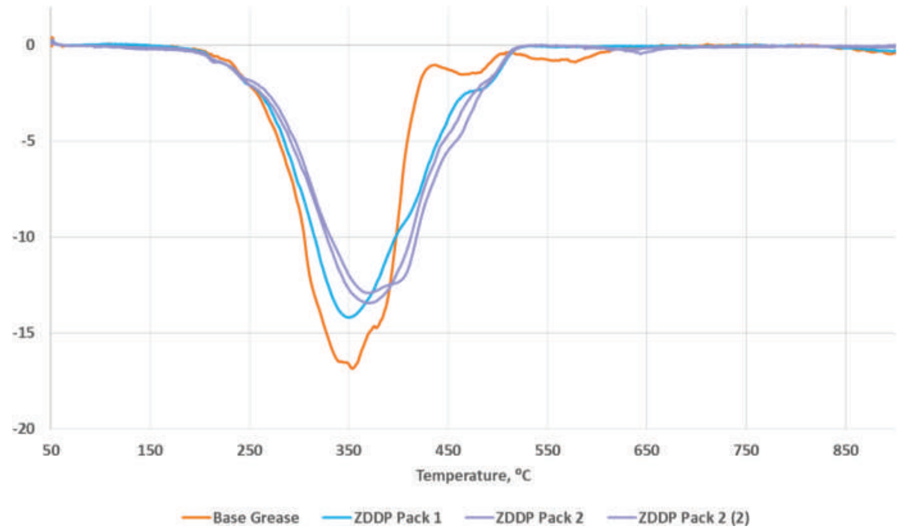

Figure 147 – ZDDP Packages TGA results

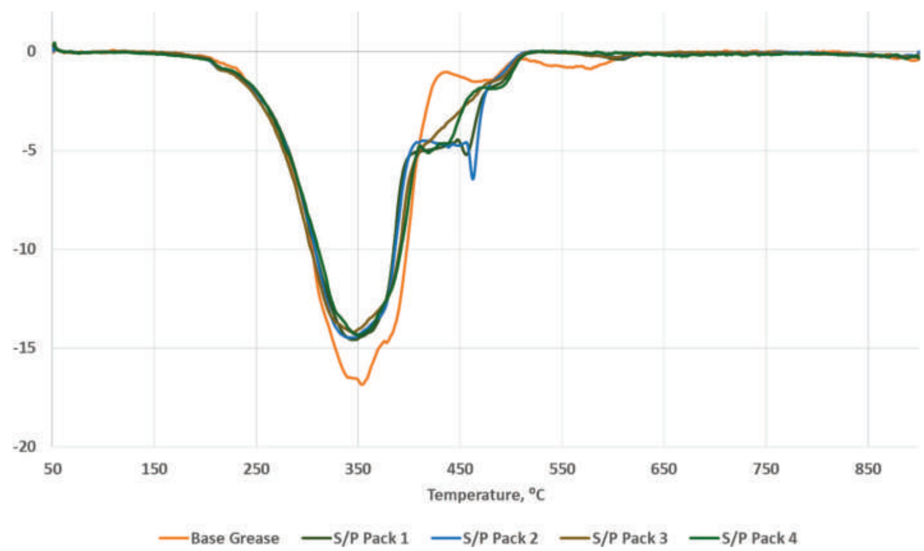

Figure 158 - S/P Packages TGA results

High temperature rheology shows similar results with differentiation between ZDDP and S/P packages. There are some small differences between ZDDP Pack 1 and 2 (Figure 19) that may be due to the inclusion of a high level of AO in ZDDP Pack 2, but both show good consistency and stability through the dropping point range and maintain a signal up to the end of test. This is different than what is seen in Figure 20 in which the results of all four S/P packages are seen to be similar with a loss of signal corresponding to the approximate temperature at which the dropping point was measured (~200ºC). Interestingly, the AO-containing S/P package shows a similar trend toward a more liquid nature in the lower temperature ranges (140ºC to 190ºC) as the AO-containing ZDDP package did.

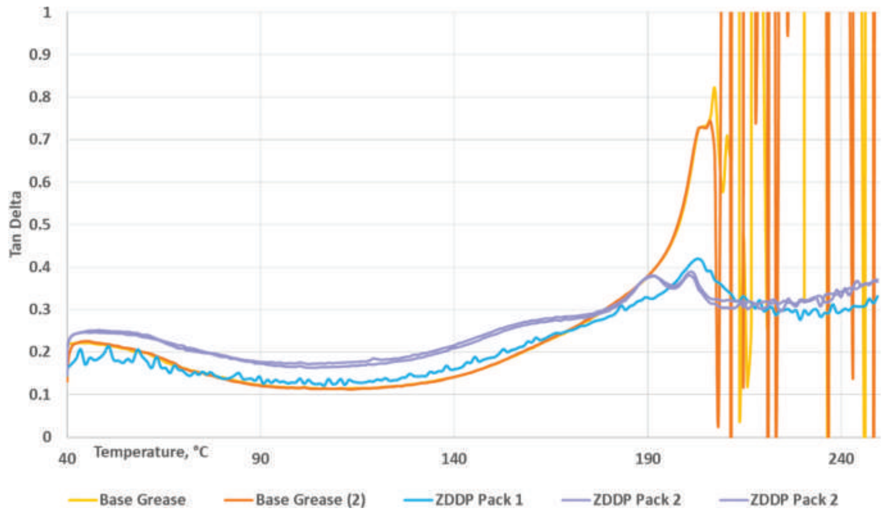

Figure 19 - ZDDP Packages high temperature rheology results

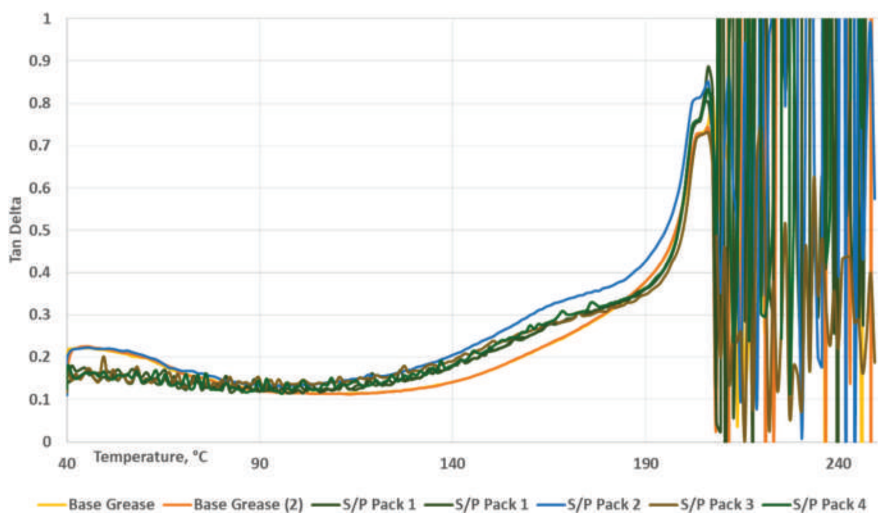

Figure 20 - S/P Packages high temperature rheology results

It is interesting to see the differences in response to extreme pressure protection between packages that all contain the same nominal amount of sulfur as seen in Table 27. This highlights the differences between activities of sulfur and the interaction of ZDDP and other components of the packages. In general, the higher activity S/P packages give better EP but worse AW protection, whereas the ZDDP-containing packages sacrifice a little EP protection for better AW. The exception for this grease is S/P Pack 3 which shows high EP while maintaining a low wear scar.

Test	ASTM	Base Grease	ZDDP Pack 1	ZDDP Pack 2	S/P Pack 1	S/P Pack 2	S/P Pack 3	S/P Pack 4
4 Ball EP, Weld Point	**D 2596**	**180**	**240**	**230**	**280**	**270**	**270**	**270**
4 Ball Wear(40kg, 75C, 1200 rpm, 1 hr), mm	**D 2266**	**0.67**	**0.53**	**0.45**	**0.68**	**0.58**	**0.52**	**1.06**

Table 27 - Packages EP & AW results

The results for fretting wear (Table 28) were somewhat surprising in view of the relatively lack of significant impact from the individual components studied above. Each pack showed a significant improvement on the fretting wear of the base grease alone. The increased treat rate of individual components as well as the presence of some phosphate antiwear additives not studied above may account for the improvement in many cases. The ZDDP Pack 2 showed the best results with an average of 14 mg wear while each of the S/P packages were roughly equal at 19 to 24 mg wear.

Test	ASTM	Base Grease	ZDDP Pack 1	ZDDP Pack 2	S/P Pack 1	S/P Pack 2	S/P Pack 3	S/P Pack 4
Fretting wear, mg	**D4710**	**36.7**	**25.7**	**15.1 13.0**	**20.0**	**21.8**	**19.3**	**23.7**

Table 28 - Packages fretting wear results

The friction testing by HFRR (Figure 21) showed a wide spread of results with the two ZDDP-containing packages showing the same fluctuations in the mid-temperature range representative of the tribofilm formation in that region. Both end up with relatively high COF values near the base grease likely due to thick films formed by the relatively high concentration of ZDDP in both formulations. The S/P packages showed a split with S/P Packs 1 and 4 ending up with friction levels higher than the base grease while S/P Packs 2 and 3 ended with relatively low COF values below 0.12. This is likely due to the different phosphorus films formed and the interactions with the active sulfur sources present in each. Interestingly, this roughly correlates with the wear scar data shown above indicating that the type of films formed with the S/P packages are more likely the smooth films associated with polyphosphates that appear to protect from wear while also reducing friction. The tribofilms associated with ZDDP are typically thicker, rougher films which, while protecting against wear, also tend to raise friction.

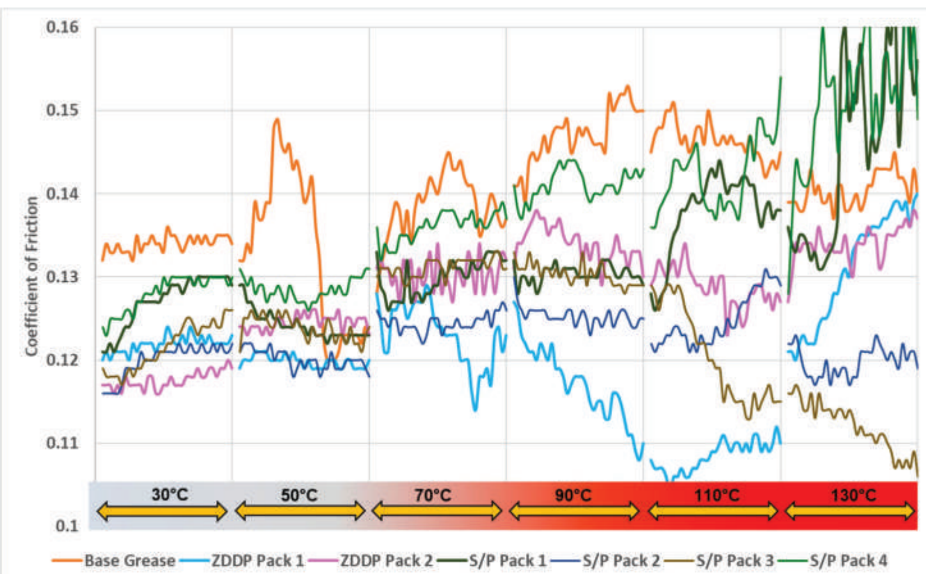

Figure 21 - Packages HFRR results

Summary and Conclusions

ZDDP – ZDDP is typically used in grease as an antiwear agent that can also bring some benefits as a secondary antioxidant through its role as peroxide decomposer. Testing in this study confirmed those benefits in 4 ball wear and oxidation testing with no significant differences seen between types. Thicker tribolayers formed by ZDDP also seemed to contribute to improvements in 4 ball EP testing, and to a lesser extent in the fretting wear test, in both of which the mixed ZDDP showed significantly better performance. Protection was also seen in both steel and copper corrosion. The thicker tribolayer also contributed to higher friction by HFRR. Finally, evidence was seen of stabilization of the grease thickener structure at higher temperatures in both TGA and high temperature rheology.

Sulfur – As expected, the role of sulfur in protecting under extreme pressure was confirmed with an accompanying detriment in wear protection. Surprisingly, both sulfur sources also seemed to provide some protection against steel and copper corrosion over the base grease alone. The sulfurized olefin also was shown to provide the expected oxidation benefits in the pressure vessel oxidation testing but both sulfur sources showed minimal improvement to the grease structure at high temperature unless used in combination with ZDDP. Interactions with ZDDP had an impact on performance due to apparent competition for the surface. These interactions need to be taken into account when formulating with both component types.

AO/Borate – While the expected benefits in oxidative and thermal stability were seen by dropping point, TGA, high temperature rheology and oxidation testing, the borated dispersant was also seen to improve steel corrosion and possibly impact the wear protection negatively.

Packages – The packages tested showed overall some of the benefits of well-formulated packages that could bring additional protection over the use of individual components. This testing also emphasizes the point that packages need to be chosen with overall performance of the finished grease in mind and that there is no "one-size-fits-all" package each having strengths and weaknesses in a particular grease. Overall, the ZDDP containing packages showed good EP/AW balance while helping with copper corrosion, oxidation and high temperature performance. The S/P based packages gave improved EP performance that sometimes sacrificed antiwear protection, showed better steel corrosion protection in some cases while overall lacking copper passivation, and in general did not perform as well at higher temperatures.

Additional work is needed in many areas. Some performance areas seemed to show a benefit (or detriment) but the results were not statistically significant. Additional testing in those areas would be beneficial to confirm initial findings and hypotheses. The high temperature work with TGA and rheology shows interesting differences that can be linked to additive componentry but this area needs further study to correlate these findings to bearing response at high temperature. Finally, it would be of interest to compare some of the key findings from this study to responses in a lithium complex grease and to look at the effect of slight differences in straight lithium bases by changing alkalinity, base oil, or manufacturing process.

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Standardization in greases in India – Lithium based greases

NAGAMANI.T, BIS

Standardization is pre-historical activity, which was evident by the sharp tools used by primitive human race and are identified in various excavations. From 1800's efforts to standardize various tools and machinery were evident in the modern world. In 1898, American industry has institutionalized standardization, by creating American section of International Association of Testing Materials, which dealt with railways. Later the organization was changed into American Society of Testing and Materials. Subsequently other national bodies and in 1947, International Organization for Standardization (ISO) have been established. Indian Standards Institute (ISI) was also established in 1947, in India.

Standardization is the process of formulating and applying rules for an orderly approach to a specific activity for the benefit and with the cooperation of all concerned, and in particular for the promotion of optimum overall economy taking due account of functional conditions and safety requirements. It is based on the consolidated results of science, technique and experience. It determines not only the basis for the present but also for future development, while keeping pace with technological developments world over. The evolution of the concept of standardization has helped in codifying the existing knowledge and in bridging the international barriers, it being a dynamic activity.

Standard[1)] is as a document, established by consensus and approved by a recognized body that provides, for common and repeated use, rules, guidelines or characteristics for activities or their results, aimed at the achievement of the optimum degree of order in a given context.

Standards helps in controlling varieties, improving quality, and streamlining a process/ product with minimum failures and facilitates trade.

National Standardization of greases

Bureau of Indian Standards, the National Standards Body of India (NSB) formulates Indian Standards under the activity of Standard Formulation, while other activities include conformity assessment schemes (product certification, systems certification, etc), laboratory testing, training to industry/ regulators/laboratories in this sector, enquiry point of WTO-TBT notifications, etc. Around 20,400 Indian standards have been published by BIS with the help of more than 15000 experts spanning all over the country and under 16 Division Councils, having 335 Sectional Committees for various industrial sectors.

Lubricants and their related products Sectional Committee, PCD25 under Petroleum, Coal and related products Division Council (PCDC) formulates Indian Standards for for terminology; lubricants, bio lubricants, lubricating oils and their related products like hydraulic fluids, corrosion preventives, quenching and cutting oils and codes of practice for storage, handling, transport and application. This Committee has three Subcommittees, of which Automotive and Industrial Greases Subcommittee, PCD 25:3 deals with Indian Standards for greases. As on date, 17 Indian Standards have been published on various greases. Most of these standards were recently revised and updated in line with Indian industry requirements as well keeping in mind the international scenario.

Standardization of Lithium based greases

Originally, IS 1002:1956 - Specification for multipurpose grease (with 3 amendments) used to cover all the very wide coverage such as greases for industrial and automobile applications, greases with lithium base as well as lime soap formulations, which was subsequently revised in 1985 and 1993.

Lithium is a soft silvery white alkali metal, which is highly reactive, flammable and need to store in mineral oil. Lithium and its compounds are used in glass, ceramics, lubricating greases, flux additives for iron, aluminium & steel production, lithium batteries and lithium ion batteries.

Along with lithium based greases, other soap based greases like calcium, sodium, aluminium/aluminium complex, polyurea, etc., are also used by various industries. However, Lithium based greases are most popular among industries due to its long life, high viscocity and water resistance and heat resistance performances. With these properties, lithium based greases are known as multipurpose greases, as they are applicable for more than one application, in a system, i.e., a lithium grease can be used for chassis and wheel bearing applications in a vehicle. Earlier, a calcium based grease was used for chassis and a sodium based grease for wheel bearing applications[2)].

While reviewing the standard (IS 1002), in 1970's, the then Committee decided that separate specifications for various soap based greases be published. Lithium based greases are widely used for multipurpose applications and hence IS 7623 was published in 1974, which was applicable for both industrial and automotive applications. Further, in 1980's, while reviewing this specification for lithium base grease, it was felt that it is better to have a separate specification of lithium base grease for automotive purposes in order to take care of the various consumers interests. Thus IS 12203 has been published in 1987.

Latest modifications

World is moving towards greener fuels and green technologies. This in a way has led to increased utilization of electric vehicles, which are using lithium/ lithium ion batteries. With the increasing consumption of lithium to manufacture lithium ion batteries for powering/ fuelling automotive vehicles, the cost of lithium has increased many folds. Now a days, high performance greases with different additives are available, that can replace lithium based greases. Therefore, the technical Committee, PCD25, has now decided to revise IS 7623 and IS 12203, giving scope to use other soap based greases, but meeting the requirements of these laid down specifications.

Recently **IS 7623** has been revised, extending its usage applicable for other soap based greases. Accordingly the scope and title have been modified. The requirement for the property of resistant to water wash, at 80°C, percent loss by mass, for Grade II & III of both Regular type (Table 1, Sl no viii) and Extra Pressure (EP) type (Table 2, Sl no v) has been decreased to 10. This modification enables usage of other soap based greases, in place of lithium greases. A new parameter of elastomer compatibility has also been included. With these modifications, the standard is revised and published as 'IS 7623:2019 Multipurpose Industrial greases – Specification (third revision).

Similarly, in IS 12203, the requirements of free organic acidity, Elastomer NBRL compatibility, Life performance of wheel bearing and Low temperature torque modified as well scope has been extended to include other soap based greases. The title of the draft has been modified as 'Multipurpose automotive greases – Specification'

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Tribological Performance of Novel Molybdenum Dithiocarbamate (HBHS-MoDTC) in Greases Studied by Four-Ball, SRV Testers and Mini-Traction Machine (MTM)

Baojie Wu[1], Aili Ma[2], Zhibin Li[1], Ruiming "Ray" Zhang[3] and Junbing Yao[2]

[1] TIANJIN BRANCH, SINOPEC LUBRICANT CO., LTD.
5 Chemical Street, Hangu District, Tianjin, China

[2] VANDERBILT (BEIJING) TRADING, LTD.
No. 8 Hangfeng Road, Fengtai District, Beijing, China

[3] VANDERBILT CHEMICALS, LLC.
30 Winfield Street, Norwalk, CT 06856, USA

ABSTRACT: Four-ball, Oscillating Friction and Wear (SRV) testers and Mini-Traction Machine (MTM) were employed to evaluate the tribological performances of novel liquid MoDTC with Highly Branched Alkyl Groups and Highly Sulfurized Core (HBHS-MoDTC) in lithium complex, polyurea and calcium sulfonate complex greases. The experimental data indicate that, HBHS-MoDTC exhibits excellent anti-wear and/or friction-reducing properties in these greases in all three different tribological contact geometries represented by each tester, especially when it is measured at higher temperatures. MTM was run at different speed, Slide/Roll Ratio (SRR), and different temperature to observe HBHS-MoDTC's friction behavior in lithium complex grease. MTM data indicate that, high speed, high Slide/Roll Ratio (SRR), and high temperature, activate HBHS-MoDTC's friction-reducing function more prominently, i.e., HBHS-MoDTC is a very potent additive to improve grease's tribological performance under high speed, high SRR and high temperature conditions.

KEYWORDS: Grease, Molybdenum Dithiocarbamate, Friction, Wear, Friction Modifier, Mini-Traction Machine

1 INTRODUCTION

Environmental protection, energy-saving and high efficiency are the key drivers for lubricant upgrading. Molybdenum dithiocarbamate (MoDTC) is a well-established phosphorus-free additive technology known to reduce friction, improve energy efficiency and prevent wear for lubricating oil and grease. In the mixed to boundary lubrication regime, use of the MoDTC additive results in avery low friction coefficient of around 0.05 making it a very effective friction modifier and an essential component of current lubricants, such as in engine oil and CVJ grease[1-7]. Its effectiveness in friction reduction comes primarily from forming a MoS_2-containing tribofilm on the rubbing surfaces. The layer-lattice structure of the MoS_2 contributes to low friction. In MoS_2, there is powerful covalent bonding between atomic species, but between lattice layers there is only very weak Van der Waals attraction. The weak Van der Waals forces between MoS_2 layers maintain easy shear within the molecule and are responsible for the low-friction properties [8].

MoDTC compounds can vary chemically due to differences in degree of sulfurization and types of amines used in preparation. These subtle chemical differences of different MoDTC types have much effect on its tribological performance and its compatibility with base oils. Recent research shows that [9], as a lubricant additive, the MoDTC with highly branched alkyl groups and highly sulfurized core (HBHS-MoDTC), exhibits the extra performances as follows:

(1) Improved low-temperature solubility in highly hydro-treated mineral oil and poly-alpha-olefin (PAO);
(2) Better friction-reducing (FR) performance at low treat level, and lower activation temperature; and
(3) Better FR retention capability and the formation of stronger tribochemical film.

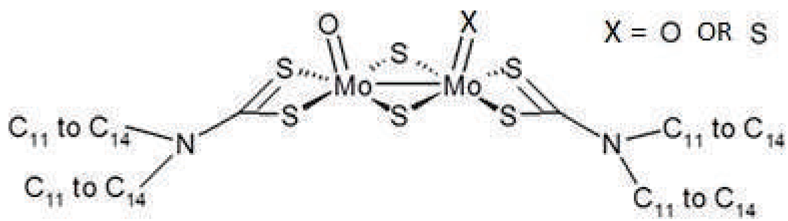
In this paper, the friction performances of HBHS-MoDTC in lubricants, especially in greases, are investigated, and also the favorable tribological conditions are discussed.

2 EXPERIMENTAL / MATERIALS AND METHODS

2.1 Base Oil, Greases and Additives

The lubricating oils used in this study are 150N Group II base oil. The lubricating base greases used include a lithium complex grease, a polyurea grease and a complex calcium sulfonate grease. All three base greases were obtained from real production batches.

The MoDTC with Highly Branched and Symmetrical amine and Highly Sulfurized core is designated as HBHS-MoDTC. This liquid HBHS-MoDTC additive contains 10.2% of Molybdenum and 11.4% of Sulfur with the atomic ratio of S/M 3.35 (compared to S/M 3.00 in traditional MoDTC). The chemical structure of HBHS-MoDTC can be described as follows:



2.2 Four-Ball Friction and Wear Test

The four-ball friction and wear test method of standard ASTM D2266 for grease and D4172 for oil were used to evaluate additive performance in lubricating oil and greases. Experimental conditions were: 20, 30 and 40 kgf load, 1200 rpm speed, 60 minutes, and 75ºC. 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.

2.4 MTM Stribeck Curve

Mini Traction Machine (MTM) was used to evaluate frictional characteristics of lubricants in boundary and mixed lubrication regime (Stribeck Curve) with "Ball on Disc" configuration. MTM consists of a rotating 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. The test conditions: 35N load (Equivalent to 1GPa Hertzian point contact load), 50% Slide to Roll Ratio (SRR), Stribeck curves generated at 40ºC, 60ºC, 80ºC, 100ºC, 120ºC and 140ºC, Mean speed 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. The operation scheme of MTM is illustrated as in Figure 1.

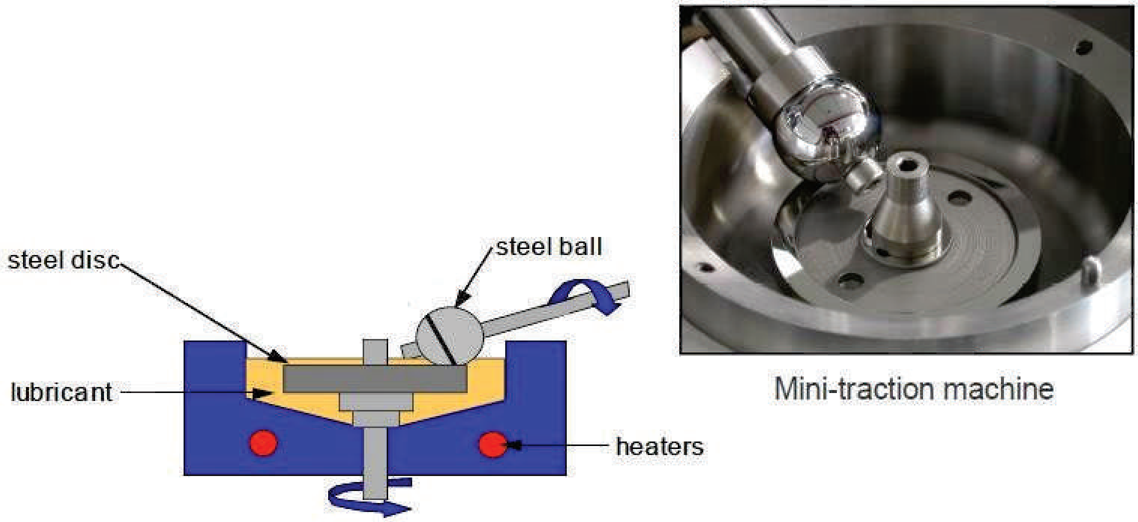


Figure 1. MTM work scheme

2.5 MTM Step Test

High speed can help lubricating oil wedging effectively into the tribological contacts, and therefore improving the lubrication status, even reaching the hydrodynamic lubrication regime. But for highly viscous, semi-solid greases, it is always a great challenge in tribological design whether the grease can effectively wedge into the frictional contacts or not, especially under high speed. We tried to run MTM Stribeck test for grease, according to the test profile above for oil, but the tests failed, due to jump-up high friction caused by starvation of the grease between ball and disc under high speed. Obviously, it is very difficult for MTM to run the grease Stribeck test under short-time contact and continuously changing speed. Thus, we ran MTM step test to evaluate grease's friction properties with and without HBHS-MoDTC under specific tribological conditions, such as different temperature, speed and slide/roll ratio (SRR).

The MTM step test conditions: 35N load, temperatures of 60ºC and 120ºC, 50% SRR (half Sliding and half Rolling) and 200% SRR (pure sliding), speeds of 100mm/s, 500mm/s, 650mm/s and 800mm/s, and the test duration of 60 minutes.

2.6 SRV Test

According to the ASTM D5707 test method, the lubricating grease's coefficient of friction under high-frequency and linear-oscillation motion was determined using an Oscillating Friction and Wear (SRV) test machine at a test load of 200 N, frequency of 50 Hz, stroke amplitude of 1.00 mm, duration of 60 minutes, and temperatures of 50ºC and 80ºC.

3 RESULTS AND DISCUSSION

3.1 Tribological performance in base oil by four-ball test

HBHS-MoDTC was added into the 150N Group II base oil, and the tribological performance was evaluated under different loads by four-ball friction and wear tests. The experimental results are given in Table 1.

Table 1. The EP, AW and FR Performance of HBHS-MoDTC in Group II Base Oil by Four-Ball Test

	Wear scar diameter, mm			Average friction coefficient			Last non-seizure load, kgf
	20 kgf	30 kgf	40 kgf	20 kgf	30 kgf	40 kgf	
150N Group II base oil	0.599	0.666	fail	0.117	0.108	fail	34
+ 0.8% HBHS-MoDTC	0.469	0.504	0.514	0.074	0.079	0.073	80

It can be seen from Table 1 that, HBHS-MoDTC possesses excellent friction-reducing (FR), good anti- wear (AW) performance in the base oil, and also increases the last non-seizure load of the oil, whichmeans the strength of the tribochemical film produced on the rubbing surfaces.

3.2 Tribological performance in base oil by MTM

0.8% HBHS-MoDTC was added into the 150N Group II base oil, and the frictional properties under slide/roll conditions were evaluated using Mini Traction Machine (MTM) at 40ºC, 60ºC, 80ºC, 100ºC, 120ºC and 140ºC. The Stribeck curves at 60ºC and 120ºC are given in Figure 2 as the representativesat low and high temperatures.

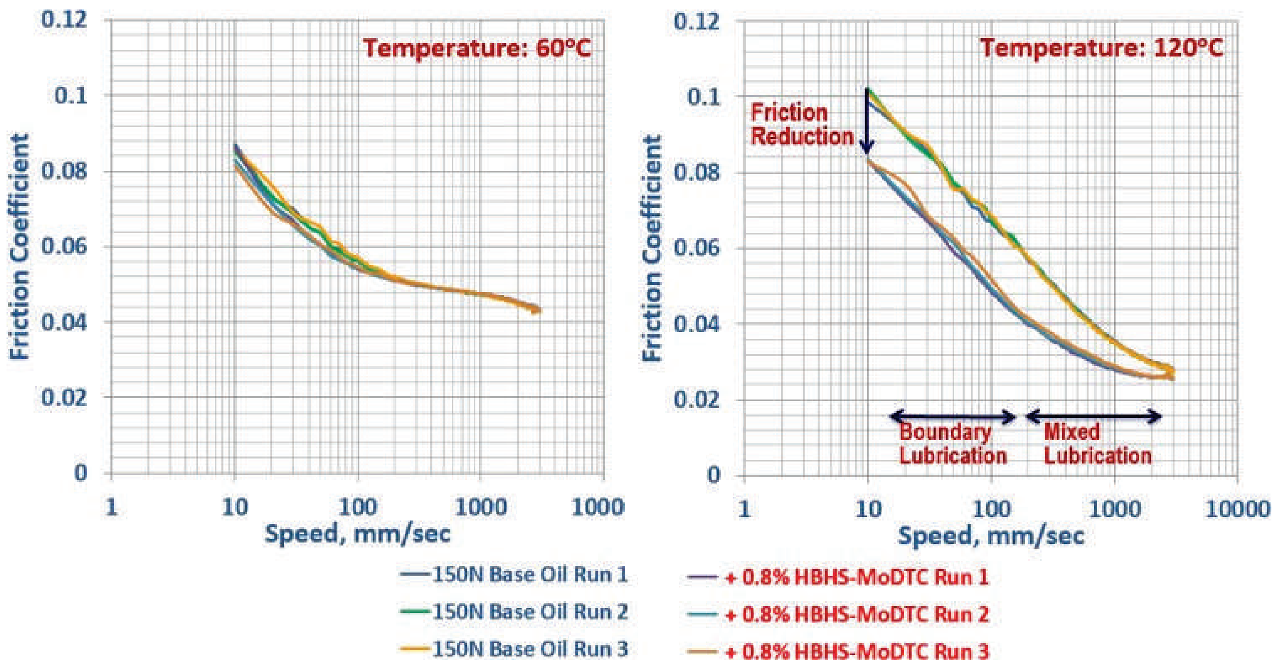


Figure 2. MTM Stribeck curve of the base oil with and without HBHS-MoDTC at 60ºC and 120ºC

From Figure 2, it can be found that the temperature is a key factor for HBHS-MoDTC to develop its FR performance in the oil. At low temperature (60ºC), we cannot identify an obvious FR characteristic by HBHS-MoDTC, but at high temperature (120ºC), HBHS-MoDTC exhibits excellent FR properties under both mixed lubrication (1000-100 mm/s) and boundary lubrication (100-10 mm/s).

3.3 Tribological performance in greases by Four-Ball test

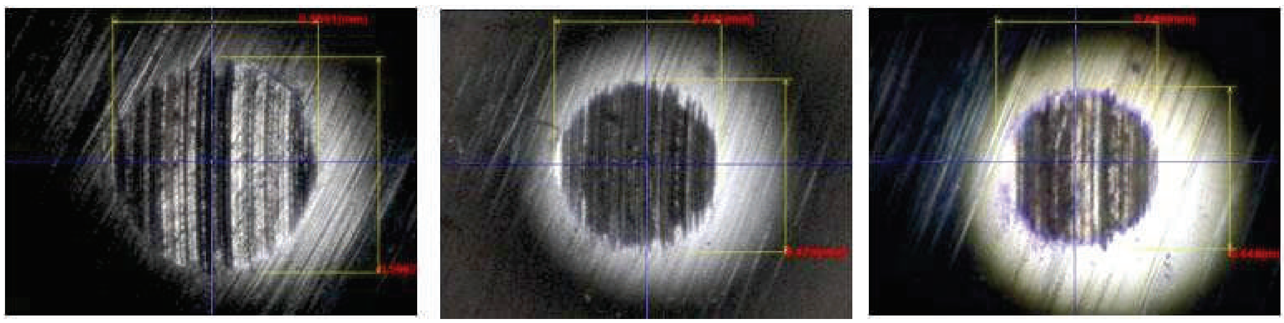
HBHS-MoDTC was added into lithium complex, polyurea and calcium sulfonate complex base greases, and the tribological performance was evaluated by four-ball friction and wear tests. The experimental results are given in Table 2.

Table 2. The EP, AW and FR Performance of HBHS-MoDTC in Greases by Four-Ball Test

	Friction and Wear Test (40Kgf, 1200 rpm, 75ºC, 60 min)		EP Test	
	Wear Scar, mm	Average Friction Coefficient	LNSL, Kgf	Weld load, Kgf
Lithium Complex Base Grease	0.588	0.099	82	250
+ 1.0% HBHS-MoDTC	**0.469**	0.081	109	250
+ 2.0% HBHS-MoDTC	**0.445**	**0.074**	114	250

Polyurea Base Grease	0.647	0.094	104	200
+ 1.0% HBHS-MoDTC	**0.524**	**0.072**	100	200
+ 2.0% HBHS-MoDTC	**0.515**	**0.071**	100	200
Calcium Sulfonate Complex Base Grease	0.375	0.098	100	315
+ 1.0% HBHS-MoDTC	0.348	**0.076**	109	400
+ 2.0% HBHS-MoDTC	0.367	0.082	126	400

It shows in Table 2 that, HBHS-MoDTC exhibits excellent FR performance in all the three greases with at least 20% friction reduction, and good AW performance in the complex lithium grease and the polyurea grease. Anyway, HBHS-MoDTC does not obviously improve the EP performance of thethree greases. The wear scar and the friction curves for the complex Li grease with and without HBHS-MoDTC are illustrated in Figure 3 and 4, in which HBHS-MoDTC's antiwear and friction-reducing (FR) properties can be observed.



Base grease Base + 1.0% HBHS-MoDTC Base + 2.0% HBHS-MoDTC

Figure 3. Wear scars by complex lithium grease by four-ball test

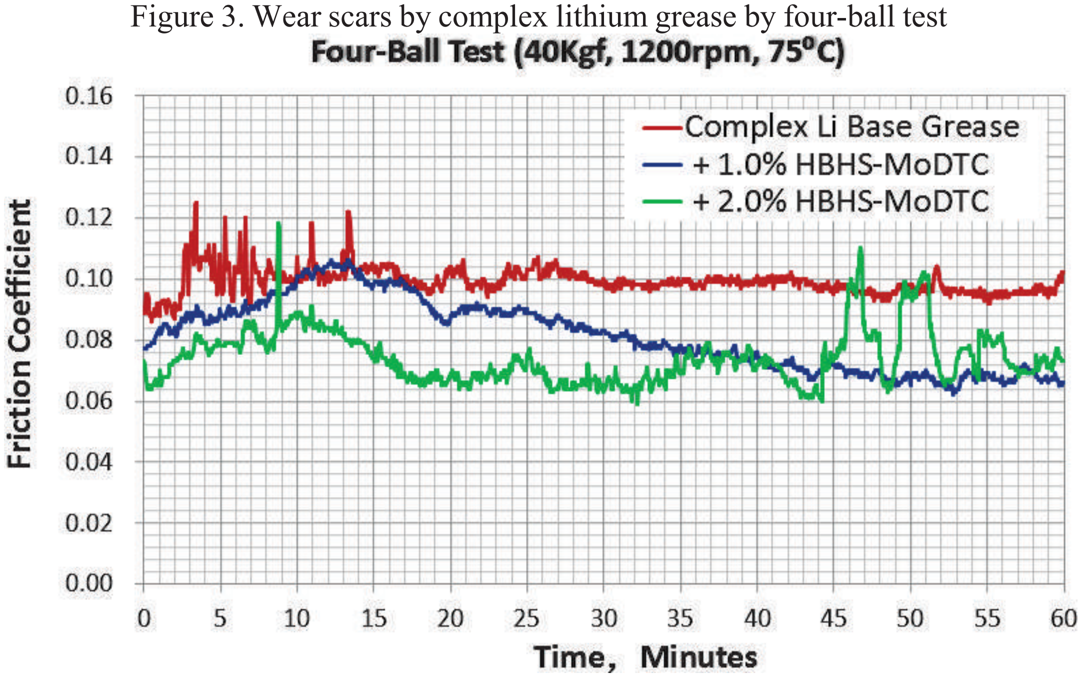


Figure 4. The FR performance of the complex Li grease with and without HBHS-MoDTC by four-ball test

The friction curves by the polyurea greases with and without HBHS-MoDTC are also illustrated inFigure 5, in which the excellent friction-reducing performance of HBHS-MoDTC is demonstrated.

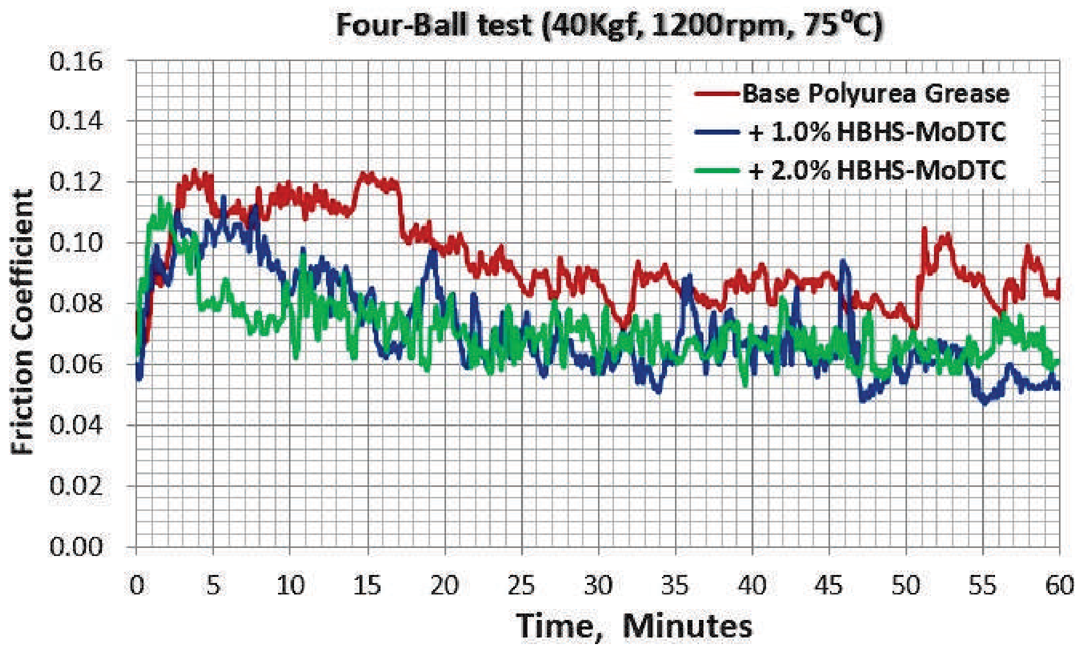


Figure 5. The FR performance of the polyurea grease with and without HBHS-MoDTC by four-ball test

3.4 SRV grease test

1.0% and 2.0% HBHS-MoDTC were added separately into lithium complex, polyurea and calcium sulfonate complex base greases, and the friction behaviors were evaluated by the SRV test at 50°C and 80°C. The friction curve of the lithium complex grease with and without HBHS-MoDTC are illustrated in Figure 6.

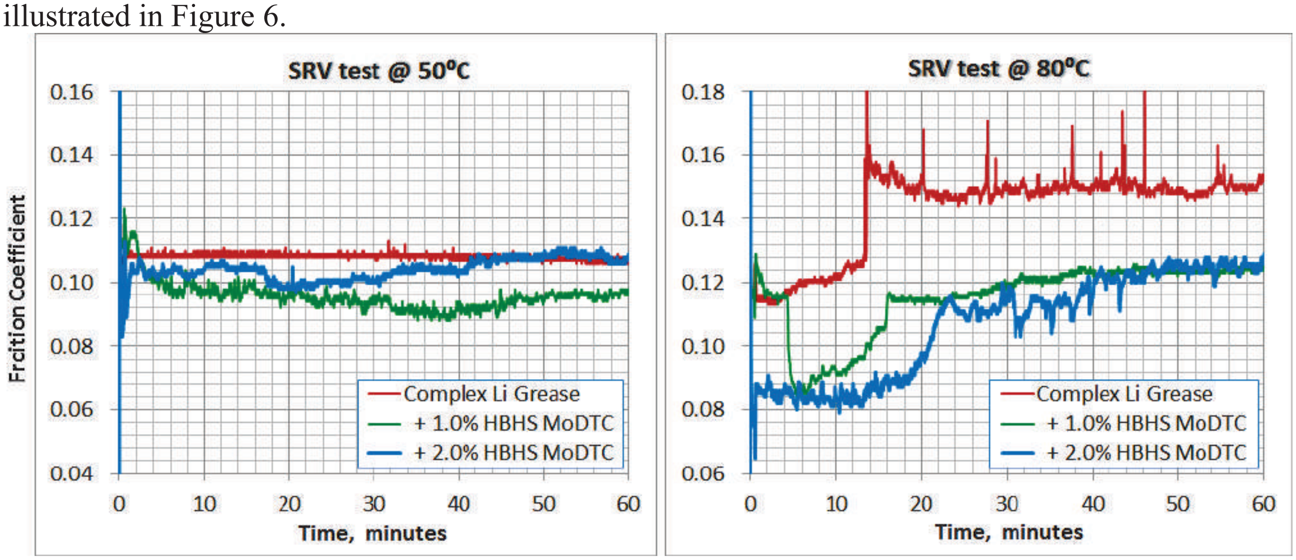


Figure 6. The friction curves of the complex Li grease with and without HBHS-MoDTC by SRV test

From Figure 6, it could be found that, in the complex lithium grease, at low temperature, i.e., 50°C, HBHS-MoDTC exhibits certain friction-reducing properties, but not significantly. However, under higher temperature, i.e., 80°C, HBHS-MoDTC demonstrates excellent friction-reducing capacities.

The friction curve of the polyurea grease with and without HBHS-MoDTC at both 50°C and 80°Care illustrated in Figure 7.

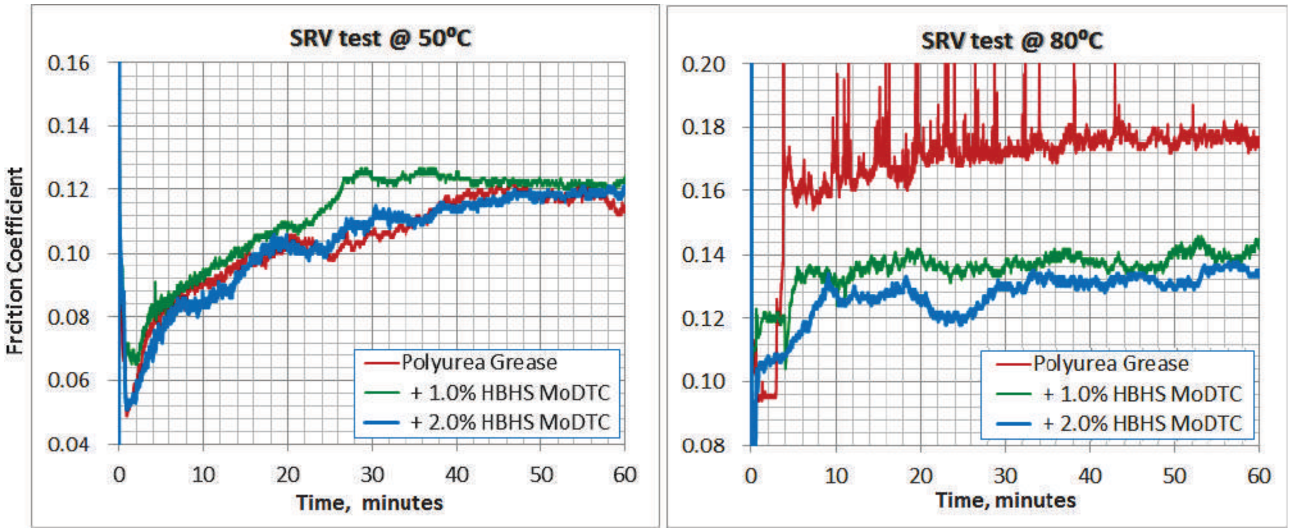


Figure 7. The friction curves of the polyurea grease with and without HBHS-MoDTC by SRV test

It could be found from Figure 7 that, in the polyurea grease, at low temperature, i.e., 50ºC, HBHS-MoDTC does not exhibit friction-reducing properties, and even makes the friction a little worse at low treat level compared to the base grease alone. However, under higher temperature, i.e., 80ºC, HBHS-MoDTC demonstrates outstanding friction-reducing capacities, and the friction-reducing efficiency can even be high as about 40%.

The friction curve of the calcium sulfonate complex grease with and without HBHS-MoDTC at both50ºC and 80ºC are illustrated in Figure 8.

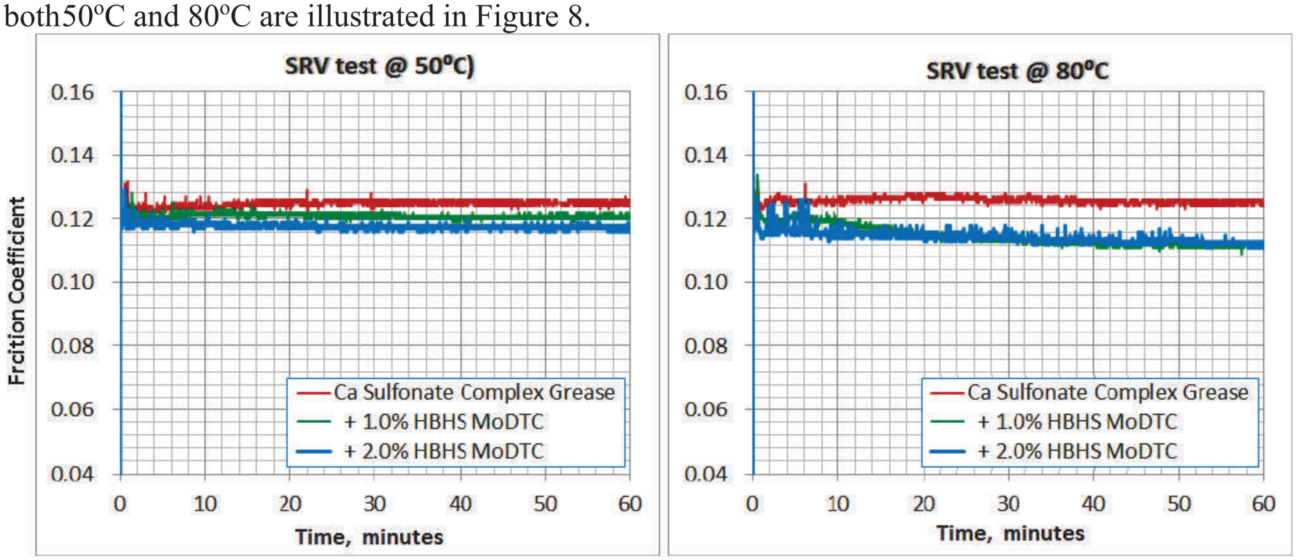


Figure 8. The friction curves of the calcium sulfonate complex grease with and without HBHS-MoDTC by SRV test

From Figure 8, it could be found that, in the calcium sulfonate complex grease, at both 50ºC and 80ºC, HBHS-MoDTC can exhibit certain friction-reducing properties, but not significantly. However, under higher temperature, i.e., 80ºC, HBHS-MoDTC's friction-reducing ability is much better than at 50ºC.

From all the SRV friction data, it could be easily concluded that, the temperature plays a significant role for HBHS-MoDTC to develop its friction-modifying performance in greases under boundary lubrication, and higher temperature promotes the friction-reducing capability of HBHS-MoDTC.

3.5 MTM step test for grease

The starvation of the grease between ball and disc under short-time contact and continuously changed speed, will result in jump-up high friction, which makes it almost impossible to run grease Stribeck test, We therefore designed a series of timed step tests under different temperature, speed and SRR conditions, to evaluate the effects of temperature, speed and SRR on the friction- reducing performance in the complex lithium grease containing 2.0% HSHB-MoDTC. The effect of temperature under the given contact conditions is illustrated in Figure 9.

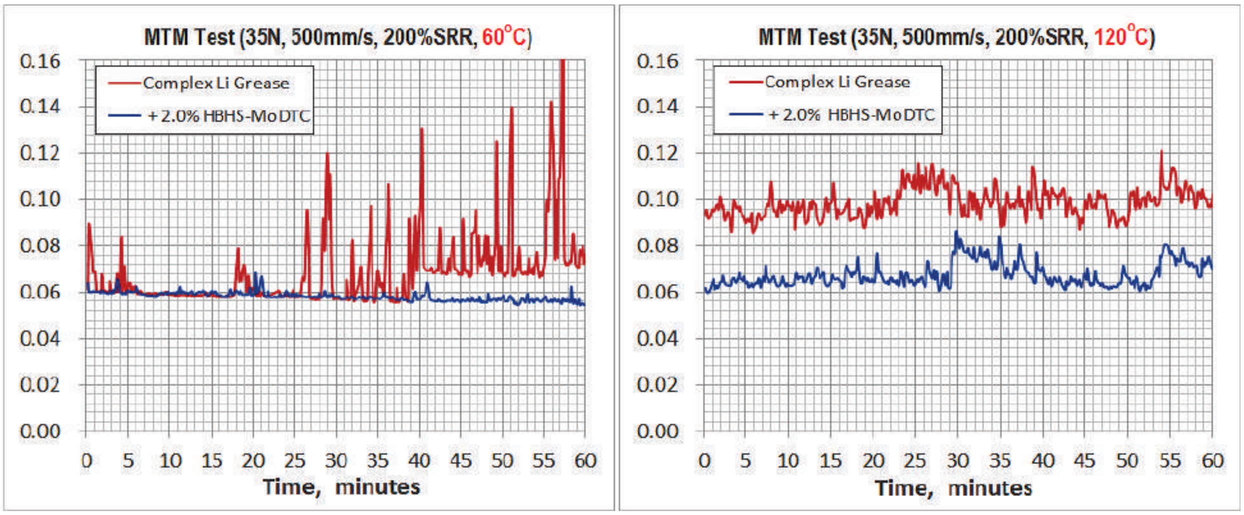


Figure 9. The effect of temperature on the FR performance of the complex Li grease with and without HBHS-MoDTC by MTM step test

From Figures 9, it can be found that, HBHS-MoDTC does not reduce the friction at low temperature (60ºC), although it does eliminate the very sharp spikes in friction, but at high temperature (120ºC), HBHS-MoDTC reduce the friction significantly. Thus again, same as in Figure 3 and 6, it was observed that the temperature plays a crucial role for HBHS-MoDTC to develop itsFR performance in lubricants.

The effect of speed is illustrated in Figure 10, in which it can be found that, the speed is also an important factor for HBHS-MoDTC to perform friction-reducing properties. For the given contact conditions, at low speed (100 mm/s), HBHS-MoDTC does not reduce the friction in the complex lithium grease, but at high speed (800 mm/s), HBHS-MoDTC functions well in the grease as a friction modifier.

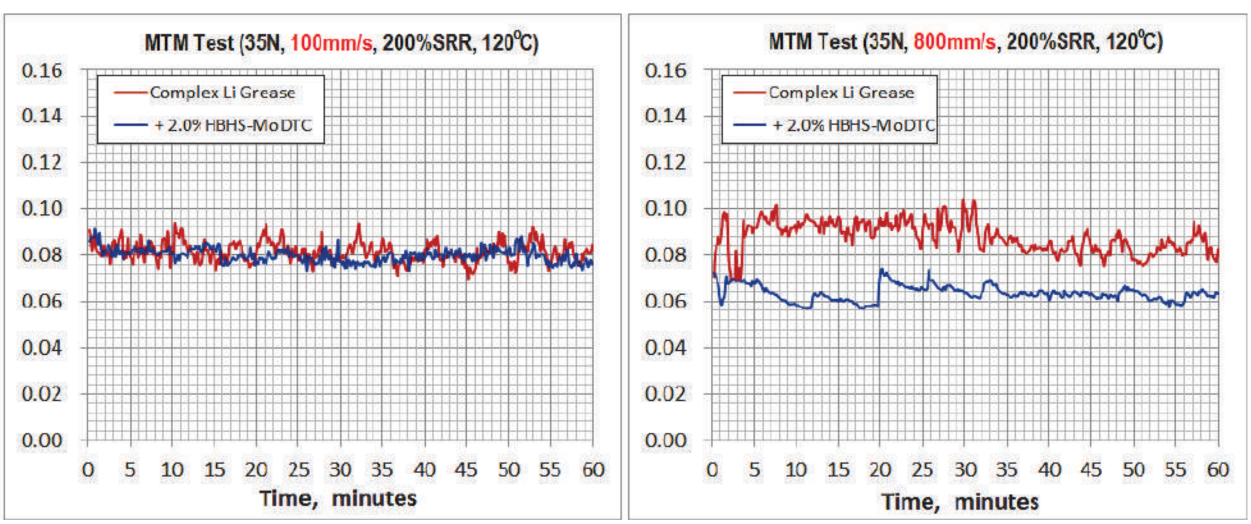


Figure 10. The effect of speed on the FR performance of the complex Li greasewith and without HBHS-MoDTC by MTM step test

The effect of the slide/roll ratio (SRR) on the friction behavior of the greases with and without HBHS-MoDTC was also evaluated by MTM step test, and the data is illustrated in Figure 11. It canbe found from Figure 11 that, for the given contact conditions, under 50% SRR (half sliding and half rolling), HBHS-MoDTC exhibits almost no friction-reducing capacities, but under 200% SRR (pure sliding), HBHS-MoDTC works well in decreasing the friction coefficient in the grease. Thus, sliding is another favorable factor for HBHS-MoDTC to develop good friction-reducing performance in the lubricant.

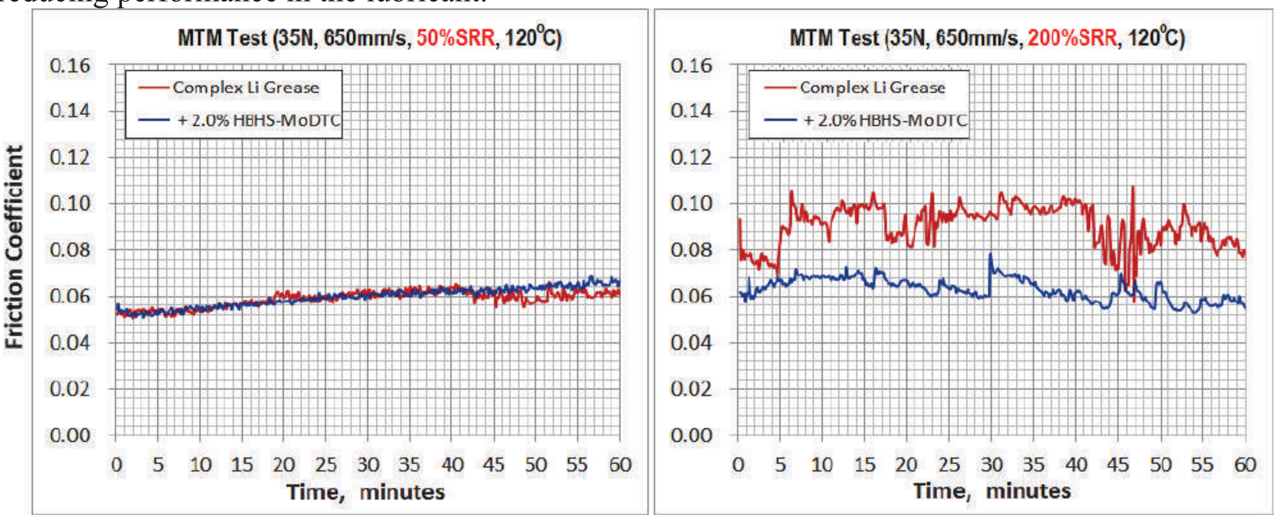


Figure 11. The effect of SRR on the FR performance of the complex Li greasewith and without HBHS-MoDTC by MTM step test

A series of MTM step tests for the greases with and without HBHS-MoDTC were conducted to further understand the effect of speed, SRR and temperature on HBHS-MoDTC's friction behaviors, and all the data is given in Table 3.

Table 3. The Effect of Speed, SRR and Temperature on of HBHS-MoDTC'sFriction-Reducing Properties in Complex Lithium Grease by MTM Step Test

Speed mm/s	SRR %	Temp. °C	Average Friction Cofficient: Complex Li Grease	Average Friction Cofficient: +2.0% HBHS-MoDTC	Friction Reduction, %
100	50	60	0.0553	0.0588	- 6.33%
		120	0.0421	0.0427	- 0.06%
	200	60	0.0791	0.0815	- 3.03%
		120	0.0818	0.0780	4.65%
500 (Test Twice)	50	60	0.0613 (0.0592, 0.0634)	0.0644 (0.0646, 0.0641)	- 0.51%
		120	0.0552 (0.0490, 0.0613)	0.0550 (00570, 0.0531)	0.36%
	200	60	0.0646 (0.0692, 0.0600)	0.0633 (0.0581, 0.0684)	2.01%
		120	0.0961 (0.0992, 0.0929)	0.0709 (0.0678, 0.0740)	26.22%
650	50	60	0.0634	0.0668	-5.36%
		120	0.0591	0.0602	- 1.86%
	200	60	0.0583	0.0538	7.72%
		120	0.0895	0.0627	29.94%
800	50	60	0.0687	0.0594	13.54%
		120	0.0735	0.0548	25.44%
	200	60	0.0698	0.0643	7.88%
		120	0.0876	0.0640	26.94%

For a more visual representation, the data in Table 3 is illustrated by bar the chart in Figure 12, so that the statistical finding of the effects of speed, SRR and temperature on HBHS-MoDTC's anti-friction capabilities in grease can be concluded.

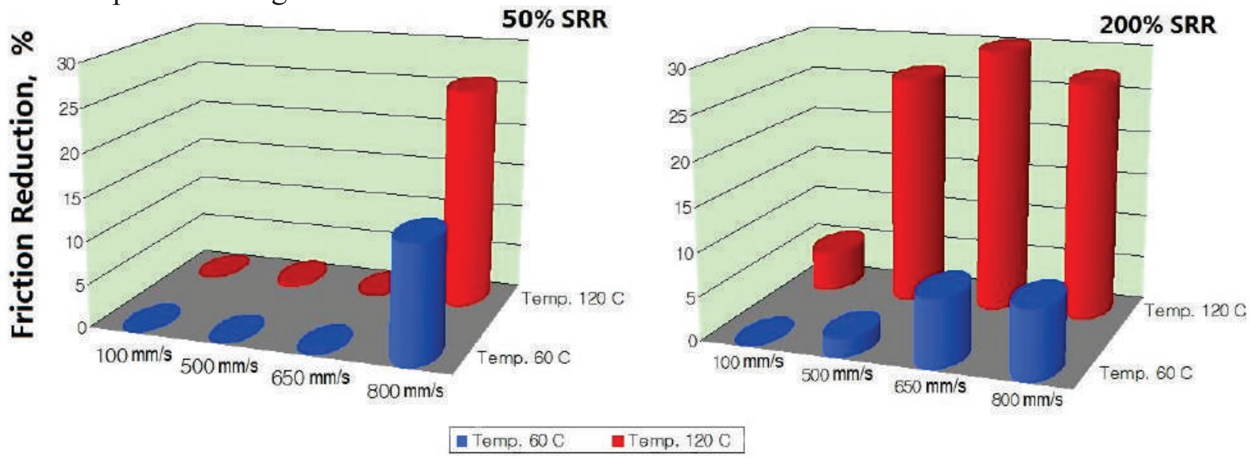


Figure 12. The effects of speed, SRR and temperature on the FR performance of the complex Li grease containing HBHS-MoDTC by MTM step test

It can be found from Figure 12 that, high speed, high SRR and high temperature significantly promote the friction-reducing (FR) performance of HBHS-MoDTC in the grease. It seems that high speed, high SRR and high temperature will produce a favorable tribochemical micro-atmosphere for MoDTC to form an MoS_2 film under boundary lubrication. These three factors, high speed, high SRR and high temperature, can help MoDTC jointly in grease, but even the single factor can also exerts its own contribution to MoDTC's friction modification. For example, it can be seen that from Figure 12, even under low temperature, if with high speed and/or high SRR, MoDTC can also work effectively in the grease as friction modifier.

4 CONCLUSIONS

(1) Four-ball tests showed, Liquid MoDTC with Highly Branched Alkyl Groups and Highly Sulfurized Core (HBHS-MoDTC), exhibits excellent Antiwear (AW) and Friction-Reducing (FR)performance in lubricating base oil.

(2) Four-ball tests also indicated, HBHS-MoDTC possesses excellent friction-reducing performancein complex Li grease, polyurea grease and complex Ca sulfonate grease, and good anti-wear performance in complex Li grease and polyurea grease.

(3) SRV grease tests proved that HBHS-MoDTC functions effectively as friction modifiers in all thethree greases under moderately high temperature.

(4) MTM Stribeck curve test indicates, HBHS-MoDTC can reduced the base oil's friction under boundary and mixed lubrications at high temperature.

(5) MTM timed grease step tests indicated, high speed, high SRR and high temperature significantly promote the friction-reducing (FR) performance of HBHS-MoDTC in grease.

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Development of High Performance Antiwear/ EP grease additives: Study of IF-WS2 Formulated Additives performance in Lithium, Lithium complex, Aluminum complex and Polyurea greases.

Dr. Manish Patel, Director of Technical Sales India & Americas, Dr. George Diloyan, CEO/CTO, NIS Nanotech Industrial Solutions, 2323 Randolph Ave, Avenel, NJ, 07001. & Dr. Raj Shah, Director, Koehler InstrumentCompany, Long Island

Abstract

India has flourished in recent years, and its rapidly developing economy has opened new doors to manufacturers and e-Commerce companies and has led to the blossoming of nanotechnology.

With the growth of nanotechnology, the lubricant market is simultaneously being brought up to prominence. Lubricants have achieved superior performance by using an entirely new class of additives: submicron Inorganic Fullerene-like Tungsten Disulfide, or IF-WS_2 for short. Tungsten Disulfide is often referred to as the most lubricious substance on earth. WS_2 superior lubricity and anti-friction properties are multiplied thanks to IF-WS_2 particles' unique morphology and submicron (nano) size. The particles are Fullerene-like, meaning they are nearly spherical.

Nanotech Industrial Solutions Inc. is the exclusive producer of submicron spherical IF-WS_2 particles on a commercial scale, and various highly concentrated dispersions, based on IF-WS_2.NIS supplies its products globally through two manufacturing facilities: from its HQ in Avenel,NJ, and Yavne, Israel.

In today's highly competitive market demands automotive and heavy-duty industries to increase efficiency, reduce downtime and emission. Core components of various mechanisms are exposed to extreme conditions: temperature, load, and vibration. To meet industry requirements the use of the high-performance additive for lubricant and grease production, that can protect equipment under extreme conditions, has significant importance.

Industries widely use solid particles to enhance its tribological properties such as extreme pressure (EP), wear and friction. Micron size and platelet/lamellar structure particles of WS2, MoS2, and PTFE have been known as a good lubricious solid and widely used in industrial applications. Novel fullerene-like inorganic nanoparticles of tungsten disulfide (IF-WS2) have a close caged (spherical) structure and are considered to be excellent Antiwear, antifriction and EP additives. Due to particle's nanosize the treat rates are the order of magnitude lower than for conventional platelet particles. The unique spherical shape of IF-WS2 nanoparticles with a hollow core allows withstanding high impacts (up to 35 GPa) by absorbing shock, increase EP properties and reduce wear and coefficient of friction up to 2 times.

This paper shows a comparative study of IF-WS2, MoS2 and PTFE particles in mineral and full synthetic Lithium complex greases. Extreme pressure (EP), Antiwear (AW) and antifriction (AF) properties, as well as other physical properties of greases, have been reported.

Introduction

Tribological properties such as antifriction, anti-wear and EP (Extreme Pressure) properties in greases play a very important role in industrial applications such as mining, automotive, steel production, etc. There are many additives in the market that are reducing wear and friction (i.e., MoDTP, MoDTC, ZnDTP, 2H-MoS2) and increasing EP properties (i.e., heavy metals, sulfur, phosphorous).

Anti-wear characteristics of ZnDTP (Zinc dialkyl-dithiophosphate) are attributed to the formation of phosphate films that can react with abrasive iron oxides [1]. On the other hand, MoDTC (molybdenum dialkyl-dithiocarbamate) has been used primarily as a friction modifier due to the formation of MoS2 at high Hertzian pressure points. MoDTP (molybdenum dialkyl-dithiophosphate) possesses combined anti-wear and friction reduction properties [2]. Both MoDTP and MoDTC require the presence of temperature and friction in order to start the generation of MoS2 layers. 2H-MoS2 particles (Figure 1a [3]) are platelet shape micron size particles that in the presence of shear stress exfoliate layers of MoS2 thus reducing friction.

IF-WS2 nanoparticles (Figure 1b) are novel spherical particles that were invented in 1992 by Professor Reshef Tenne in the Weizmann Institute of Science. These particles currently are produced on a commercial scale and are available in various forms of dispersions (water, paste, oil). In this paper, the commercially available paste dispersion of IF-WS2 nanoparticles has been tested in LiX grease. Wear, friction, and EP characteristic along with other physical properties have been evaluated.

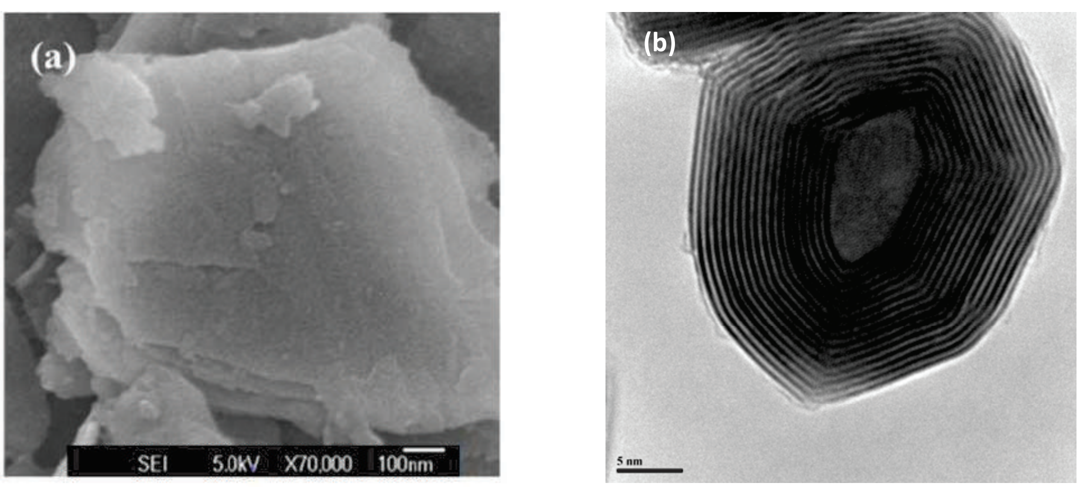
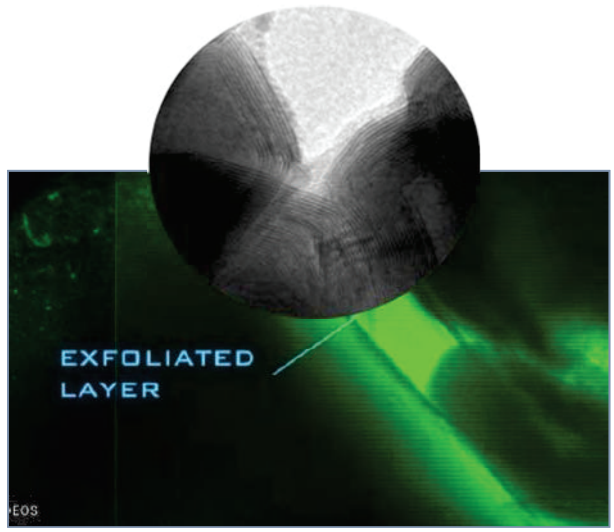
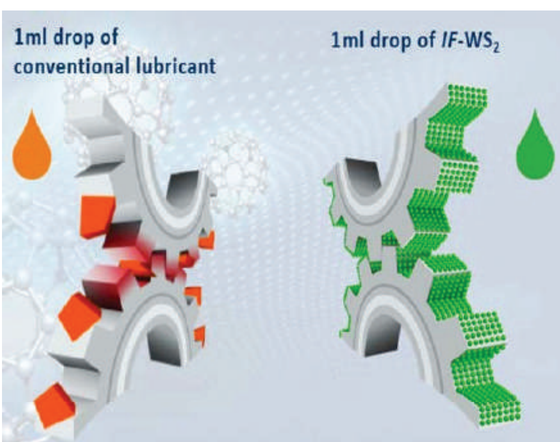


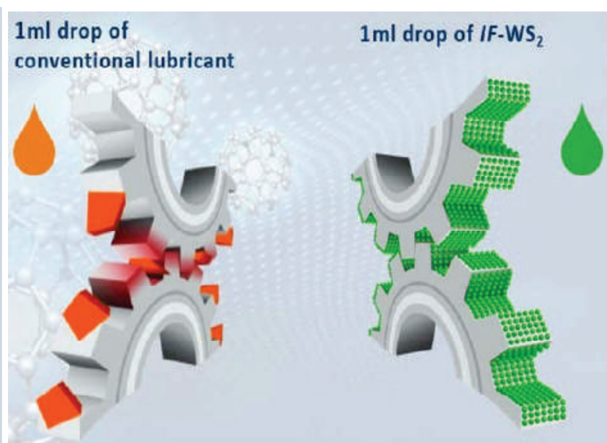
Fig. 1. SEM image of 2H-MoS2 micron size particle [3] (a) and closed-caged nanoparticle of IF-WS2 (b)

Due to their morphology and size, *IF*-WS2 nanoparticles provide excellent shock absorbing properties along with antiwear, anti-spalling and pitting, [4] friction reducing, and extreme pressure properties. Figure 2 depicts the mechanisms of IF-WS2 nanoparticles and their behavior under various conditions: static and dynamic loads, shock, shear, etc. Due to the Nano range of the primary particle size (30-280nm), the surface area is significantly large thus the treat rate of *IF*-WS2 in applications varies from 0.15% to 1%. In comparison 2H-MoS2 is mostly used between 3% - 10% accompanied with active sulfur to get decent EP characteristics (above 315kgf ASTM D2596).



- IF-WS2 particles have dozens of concentric LAYERS, like an onion
- The **layers** exfoliate under pressure, forming a PROTECTIVE TRIBOFILM on the contacting surfaces





Nanoparticles of IF-WS2 have a Very High Surface Area to Volume Ratio IF-WS2 particles stick to the work surface SMOOTH, and HEAL it.

At nanoscale IF-WS2 particles possess increased Strength and Enhanced Thermo- physical Properties, reducing heat generated due to friction and wear.

Figure 2: Mechanism of *IF-WS2* performance

Below is the summary of mechanism that describes the operation of IF-WS2.

- Spherical nanoparticle with a hollow core act as a damper at applications with high loads and impact
- Nano-sized particles smooth a surface, covering roughness irregularities and asperities
- The spherical geometry allows nanoparticles to play a role of nano ball bearings, creating a roller friction
- Multi-layer onion-like structures of IF WS2 nanoparticles start exfoliating under high pressures and create a thin protective film on the friction surface.

The study conducted by O. Tevet et al. shows mechanisms of *IF* –WS2 nanoparticle's operation [5].For the experiment a golden nanoparticle was deposited on a surface of *IF* – WS2 nanoparticle, to play a role of the marker. The study showed that rotating mechanism predominant under loads up to 0.7 GPa, sliding under uniaxial compression between 0.6 and 1.1 GPa and exfoliation at compressions above 1.1 GPa. All the tests were conducted under low shear rate: low speed (quasi-static) 10^{-7} m/sec.

Remarkable tribological results of IF –WS2 particles results shown in some earlier tests were not always repeatable while testing the materials by various matrices. It was found that proper/stable dispersion was not the only requirement to achieve excellent tribological. Stable dispersion provides a homogeneous distribution of particles and shelf life. However, certain surfactants may restrict IF –WS2 particles to be delivered to metal surface thus reducing performance [4].

A new challenging task faced the researchers: developing a way of converting the powder into liquid-type material with enhanced stability and performance.The efforts of researchers and engineers resulted in 2^d generation of dispersions of *IF*-WS2 nanoparticles combining the best knowledge of nature of nanoparticles with advancedmanufacturing techniques, resulting in a new level of stability 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 operating conditions. Thedifference 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 the particular application.Basically, IF –WS2 particles, compare to other solids, have multiple mechanisms of operation. Layer exfoliation/release, that is mono or multilayer WS2 that provides antiwear protection, occursdue to shear force, shock/impact and normal load. During WS2 layer exfoliation/release, friction decreases and released layer/layers adhere to the surface, by chemo-mechanical interlock, and creates a protective layer on a surface.

It is very important to note that in order to utilize IF –WS2 particles' benefit, it is required to provide particle to surface delivery mechanisms. It is important to use proper surfactants and synergistic additives that can provide: stable dispersion, surface delivery and avoid surface competition.

Experimental

The grease selected for our current study was a Lithium, Lithium complex, Aluminum complex and Polyurea base grease were obtained from a commercial batch of a grease manufacturer. *IF*-WS2 based concentrate in paste form (EMX) was used at various treat rates between 1% and 3%. 2H-MoS2 micron-sized platelet-shaped particles of MoS2 were used at concentration range 3-5%. Sub-micron solid dispersion in PAO30 oil was used in treat rates: 3wt%, and 5 wt% respectively. EMX and 2H-MoS2 were mixed in the LiX grease followed by homogenization in the FlakTec Speed Mixer shown in Figure 3. Wear scars were measured in an optical microscope, and 3D images were obtained via RTec profilometer (RTec Instruments).

All samples after milling were evaluated for grease consistency following ASTM D217 standard test procedures and dropping point following ASTM D2265. Table 1 shows a description of each sample evaluated.

Table 1. Sample description

Sample Number	Sample Description
Sample 1	Li base grease
Sample 2	Li base + 1.5% IFWS2
Sample 3	Li base+ 2.5 % IFWS2
Sample 4	Li base + 3% IFWS2
Sample 5	Li base + 1 % MoS2 + 2% IFWS2
Sample 6	Li Base + 5% MoS2
Sample 7	LiX base grease
Sample 8	LiX base + 1% IFWS2
Sample 9	LiX base+ 2 % IFWS2
Sample 10	LiX base + 3% IFWS2
Sample 11	LiX base + 3 % MoS2 + 2% IFWS2
Sample 12	LiX Base + 5% MoS2
Sample 13	AlX base Grease
Sample 14	AlX base Grease + 2% IFWS2
Sample 15	AlX base Grease + 2.5% IFWS2
Sample 16	AlX base Grease + 3% IFWS2
Sample 17	AlX base Grease + 5% IFWS2

Sample 18	AlX base Grease + 3% MoS2
Sample 19	AlX base Grease + 3% MoS2 + 2% IFWS2
Sample 20	Polyurea base grease
Sample 21	PU + 1% IFWS2
Sample 22	PU + 2$ IFWS2
Sample 23	PU + 3% IFWS2
Sample 24	PU + 3% IFWS2 + 1 % MoS2

Figure 3: High Speed grease mixer:

Since *IF*-WS2 powder after synthesis process comes in agglomerated form, where agglomerates areseveral microns in size, the de-agglomeration and dispersion procedures have been conducted. Figure 4c shows TEM micrographs of *IF*-WS2 agglomerates, aggregates, and primary particle. Where on the edge of the aggregate can be seen the spherical shape of *IF*-WS2 primary particles? Inorder to make sure that all *IF*-WS2 particles were in the primary size range (30-280nm), ready to use IF-WS2 based concentrate (EMX) has been used for this study.

Table 2 shows the list of standard tests that been conducted for each sample and parameters monitored.

Table 2. List of tests conducted on samples

#	Test Name	Description
1	ASTM D2266	Four-Ball Wear
2	ASTM D2266	Coefficient of Friction
3	ASTM 2596	Four Ball EP
4	ASTM D01092	Low temperature mobility

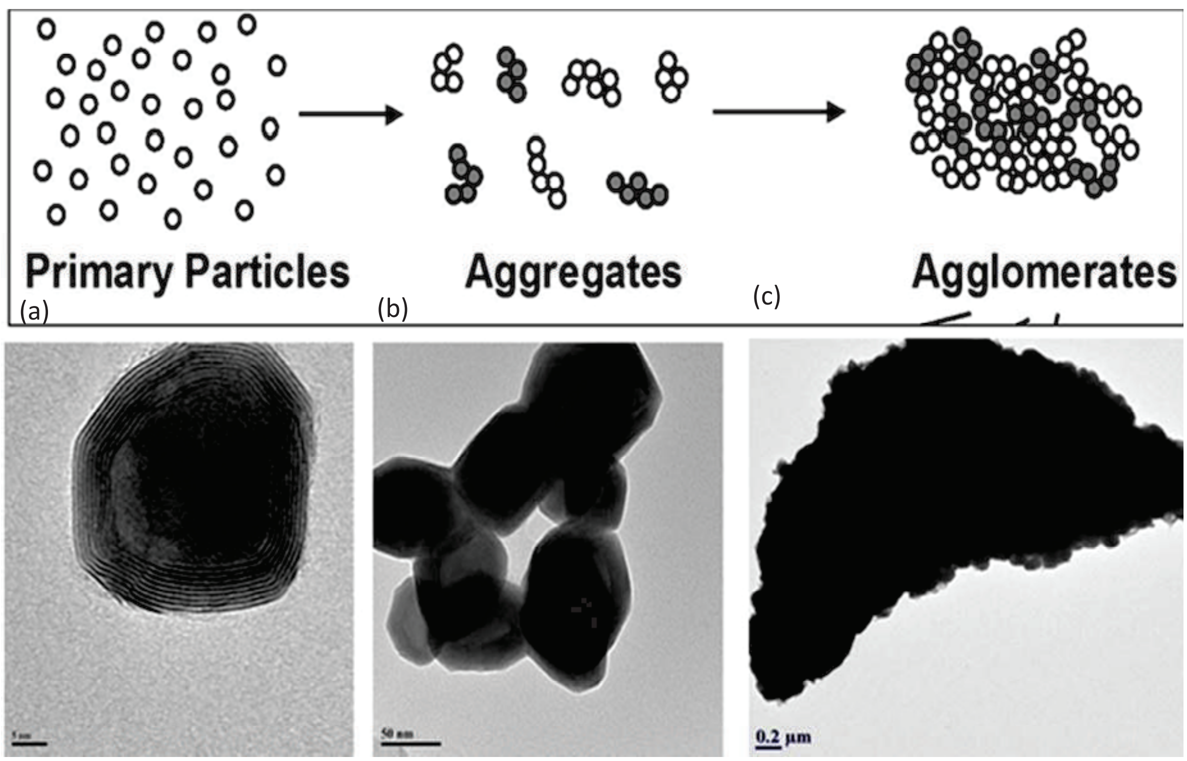


Figure 4. *IF*-WS2 primary particle (a), aggregate (b) and agglomerate (c)

The tackiness tester is another Koehler Instrument that tests the consistency of greases.

Results and Discussion

The grease formulations evaluated in this study showed excellent tribological properties. Results in table 3 below show that the Li, LiX, AlX and PU greases with *IF*-WS2 particles even at low percentages increase the performance in extreme pressure and wear. 2H-MoS2 particles showed good antifriction properties and increased EP properties, however, increased wear at higher treat rates.

Low friction, wear and increased EP properties of *IF*-WS2 based dispersion could be explained by the multi-functional mechanism of *IF*-WS2 particles. Due to spherical morphology of IF-WS2 they behave differently under various tribological conditions. The mechanism can change from rolling, to sliding and to exfoliation under various loads, shear and shock. On the other hand 2H-MoS2 platelets reduce friction predominantly under shear/sliding motion. And due to platelet structure and big particle size (about 1.5-3 μm) could be abrasive, especially high-speed applications.

Figures 5-8 shows wear, friction and weld point data for all tested samples.

Table 3 Property summary of Li and LiX grease samples

Lithium Grease Treated with IFWS2 Additive

Test Name	Description	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
ASTM D2266	Four Ball wear, mm	0.863	0.697	0.605	0.6	0.677	0.673
ASTM D2266	Coefficient of Friction	0.0976	0.0943	0.0691	0.0651	0.0683	0.0735
ASTM 2596	Four Ball EP, kg weld point	160	250	500	620	620	250

Lithium Complex Grease Treated with IFWS2 Additive

Test Name	Description	Sample 7	Sample 8	Sample 9	Sample 10	Sample 11	Sample 12
ASTM D2266	Four Ball wear, mm	0.795	0.398	0.422	0.397	0.425	0.623
ASTM D2266	Coefficient of Friction	0.1054	0.075	0.0792	0.0708	0.0623	0.0782
ASTM 2596	Four Ball EP, kg weld point	200	400	620	850	800	315

Figures 5, 6 and 7 show wear, CoF and weld point data for all tested samples

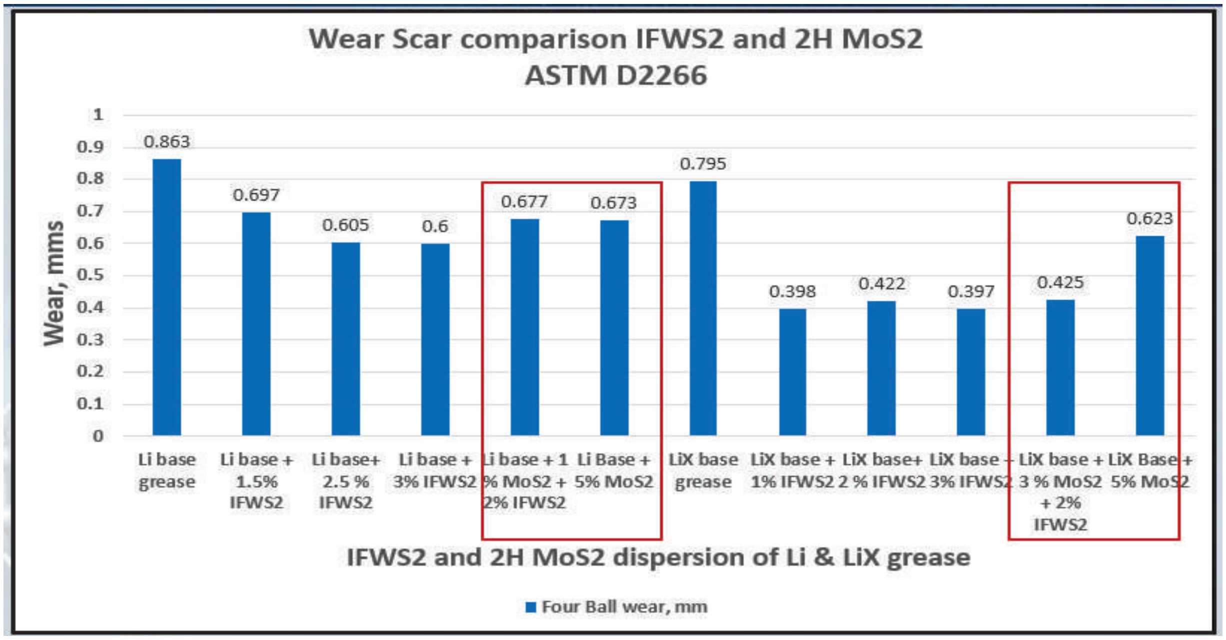


Figure 5: Wear scar comparison of IF-WS2 and 2H MoS2 disperse in Li & LiX greas

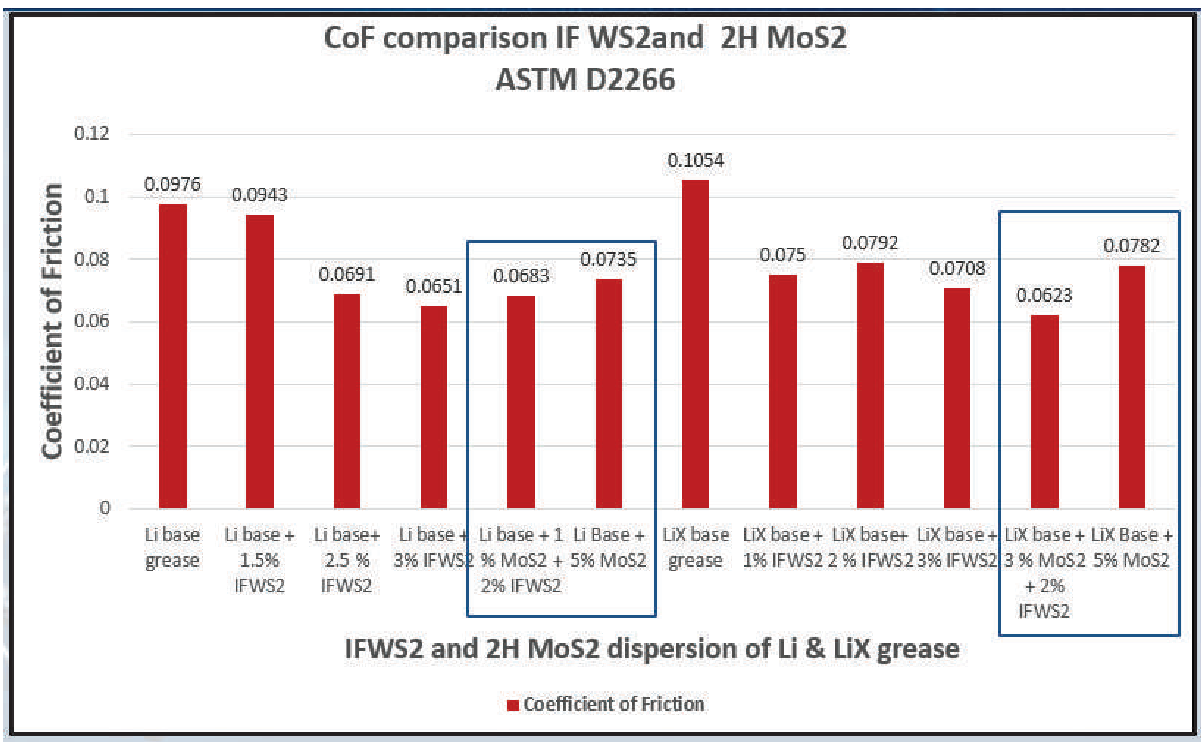


Figure 6: CoF comparison of IFWS2 and 2H MoS2 disperse Li & LiX grease

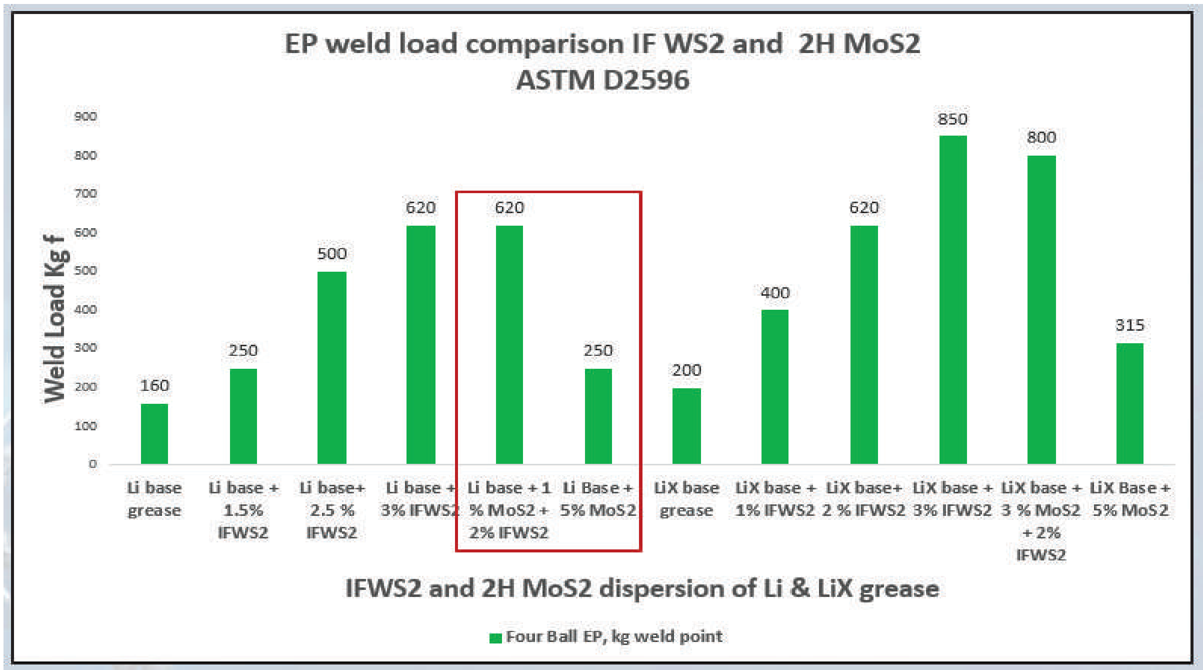


Figure 7: Ep Weld load comparison of IF WS2 and 2H MoS2 dispersed in Li and LiX grease.

Table 4 Property summary of AlX and PU grease samples

Aluminum Complex Grease Treated with IFWS2 Additive								
Test Name	Description	Sample 13	Sample 14	Sample 15	Sample 16	Sample 17	Sample 18	Sample 19
ASTM D2266	Four Ball wear, mm	0.475	0.677	0.792	0.452	0.448	0.758	0.710
ASTM D2266	Coefficient of Friction	0.0798	0.0731	0.0821	0.0626	0.0599	0.1120	0.0726
ASTM 2596	Four Ball EP, kg weld point	160	400	500	500	620	200	500

Poly Urea Grease Treated with IFWS2 Additive						
Test Name	Description	Sample 20	Sample 21	Sample 22	Sample 23	Sample 24
ASTM D2266	Four Ball wear, mm	0.425	0.34	0.32	0.35	0.39
ASTM D2266	Coefficient of Friction	0.0517	0.0358	0.0559	0.0433	0.0420
ASTM 2596	Four Ball EP, kg weld point	250	315	400	500	620

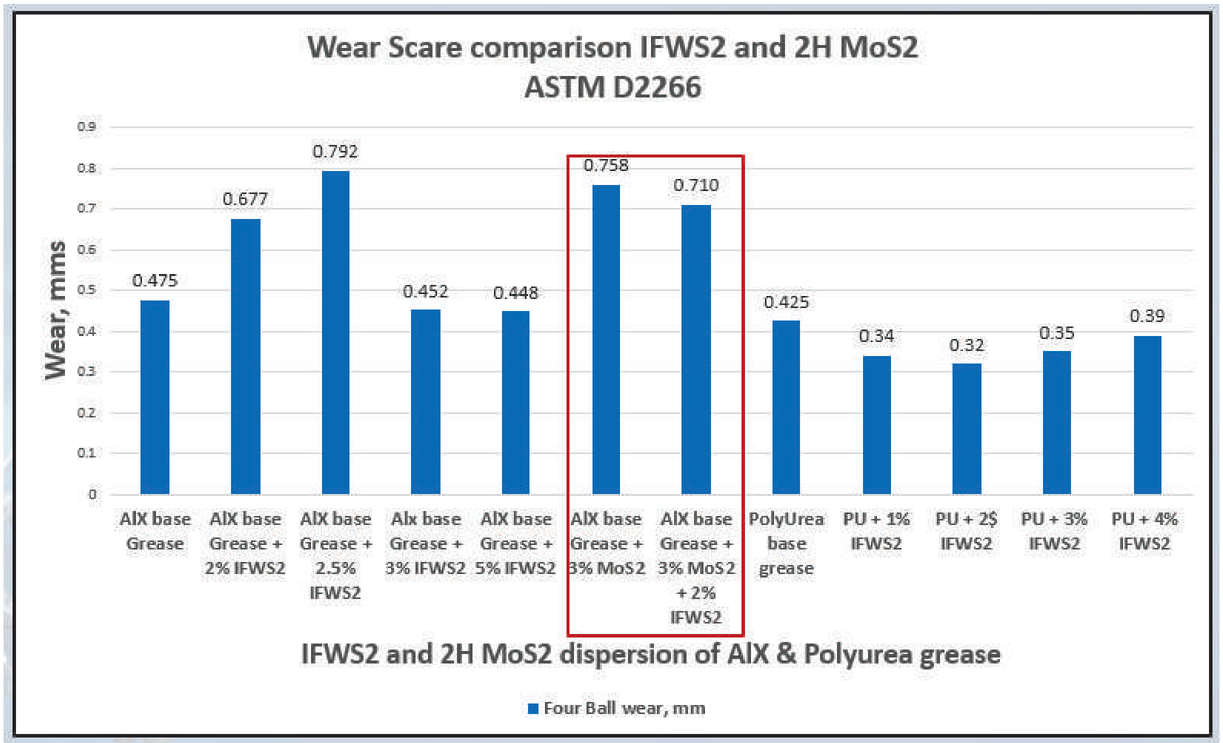


Figure 8: Wear scar comparison of IF-WS2 and 2H MoS2 disperse in AlX & PU grease

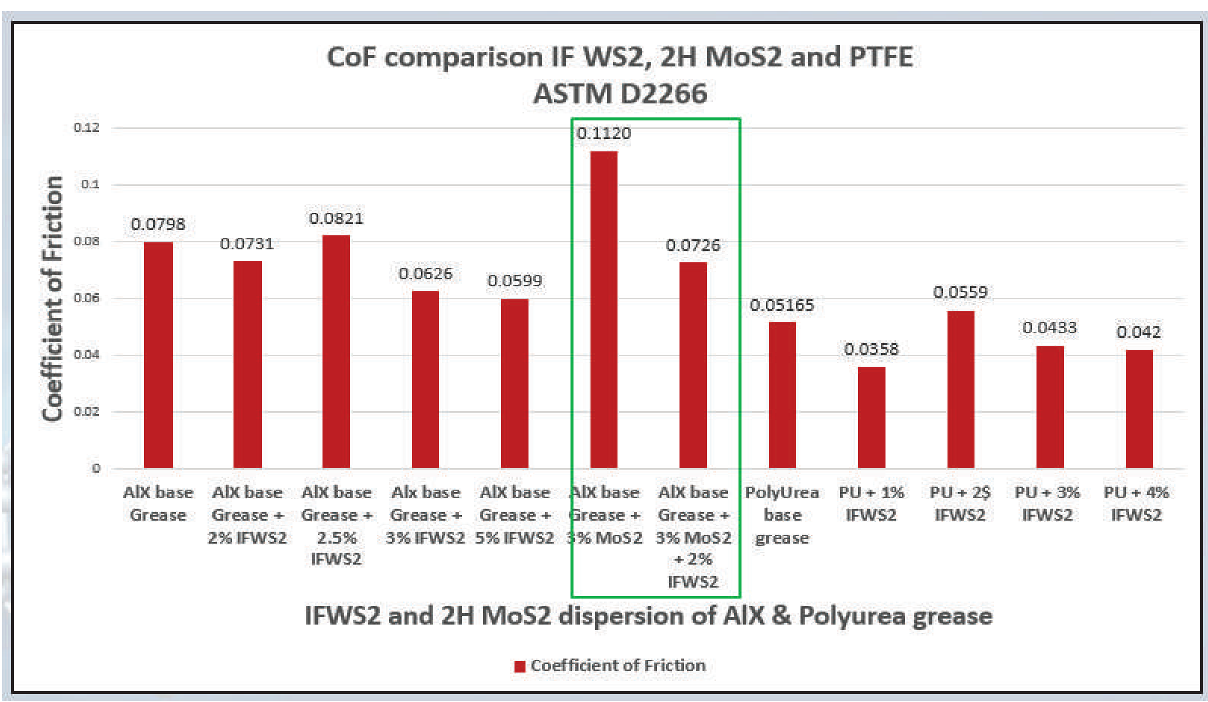


Figure 9: CoF comparison of IF-WS2 and 2H MoS2 disperse in AlX & PU grease

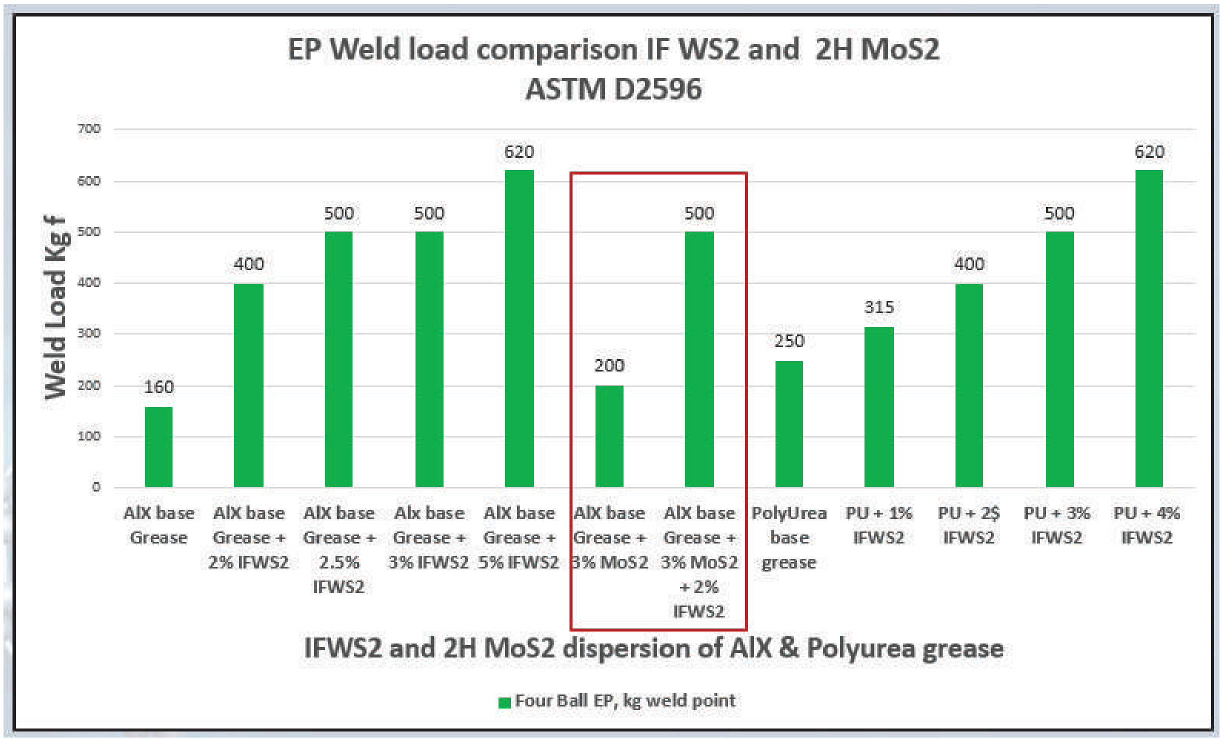


Figure 10: EP Weld load comparison of IF-WS2 and 2H MoS2 disperse in AlX & PU grease

Sample Description	Four Ball wear, mm	Coefficient of Friction	Four Ball EP, kg weld point
Li base + 3% IF-WS_2	**0.6**	**0.0651**	**620**
Li Base + 5% MoS_2	**0.673**	**0.0735**	**250**
Li base + 1 % MoS_2 + 2% IF-WS_2	**0.677**	**0.0683**	**620**
LiX base + 3% $IFWS_2$	0.397	0.0708	850
LiX Base + 5% MoS_2	0.623	0.0782	315
LiX base + 3 % MoS_2 + 2% IF-WS_2	0.425	0.0623	800
Alx base grease + 3% IF-WS_2	0.452	0.0626	500
AlX base grease + 3% MoS_2	0.758	0.1120	200
AlX base Grease + 3% MoS_2 + 2% IF-WS_2	0.710	0.0726	500

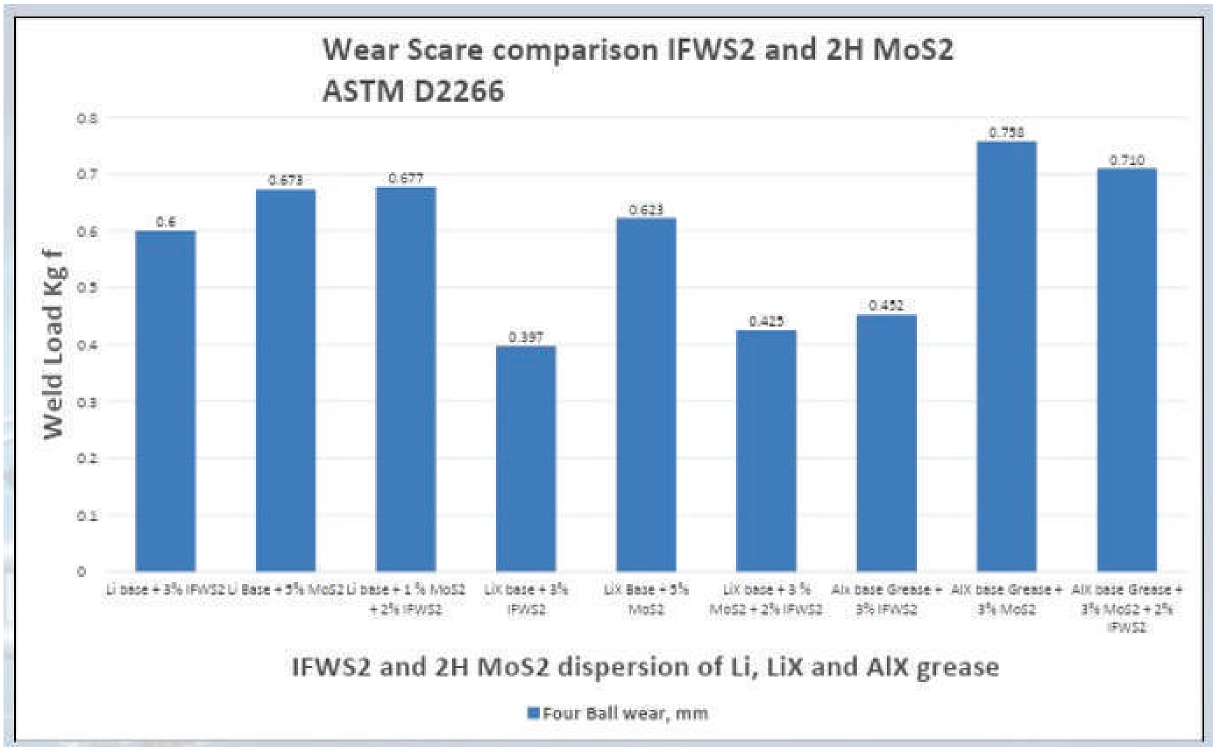


Figure 11: Wear scar comparison of IF-WS2 and 2H MoS2 disperse in Li, LiX & AlX grease

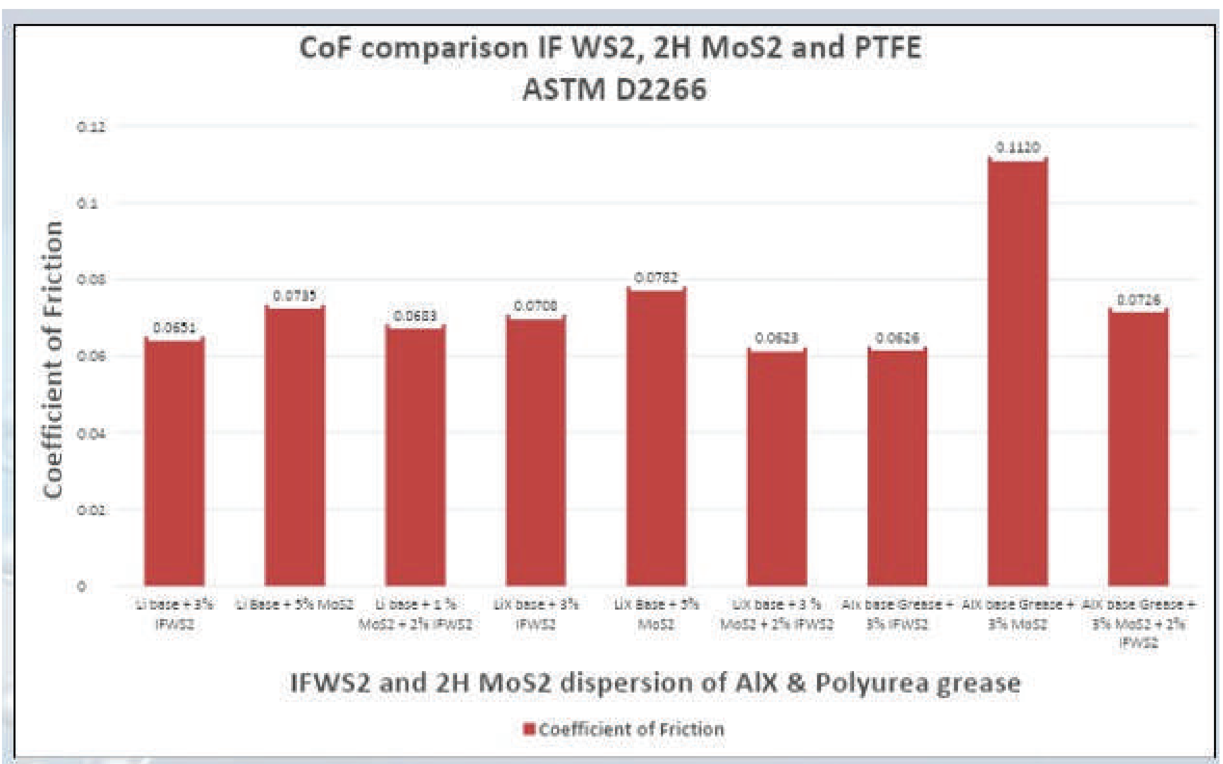


Figure 12: CoF comparison of IF-WS2 and 2H MoS2 disperse in Li, LiX & AlX grease

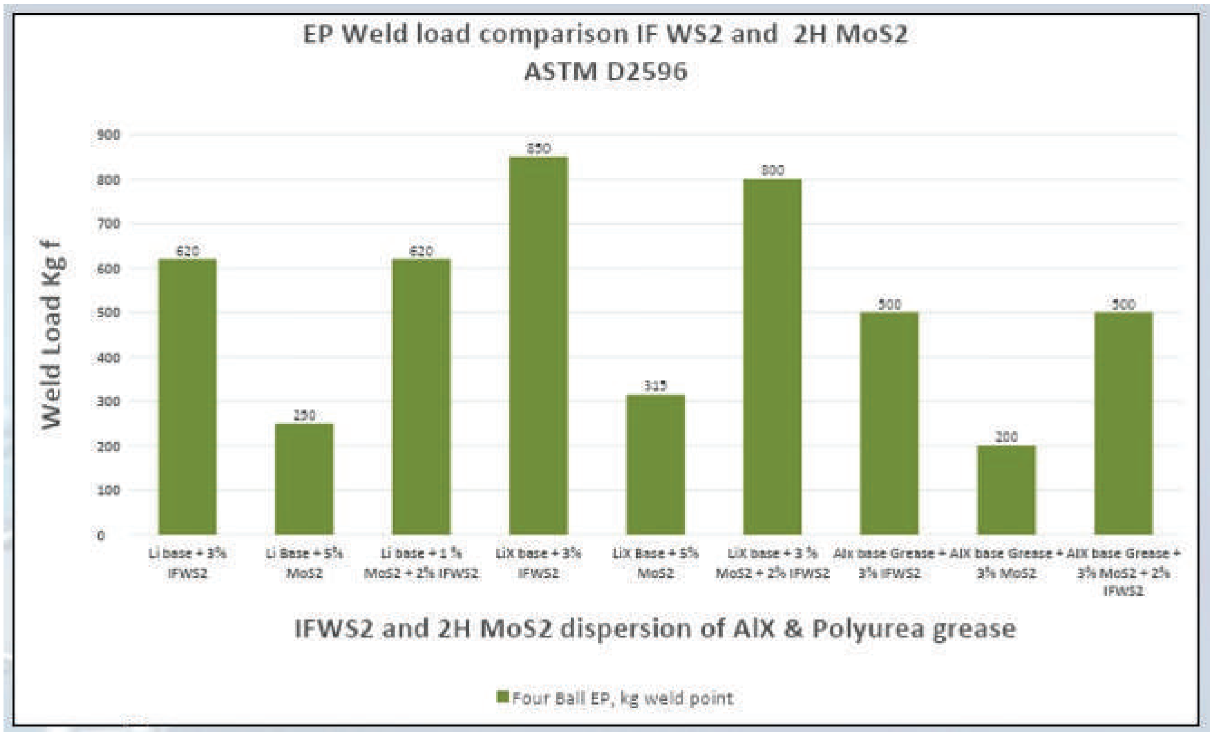


Figure 13: Weld load comparison of IF-WS2 and 2H MoS2 disperse in Li, LiX & AlX grease

Figure 14: 1%, 2% and 3% of IF-WS2 treat rate on blue, grease and brown grease.

Dark color of IF-WS2 additive does not significantly affect the color of grease. It might make it one shade darker, but done not turn it to black.

We have studied low temperature mobility of LiX synthetic grease NLGI Grade 1.5 at Koehler Instrument K95300. Low temperature mobility tests the flow properties of greases at low temperatures. This test was performed under ASTM D01092 method and detail information about use and preparation is shown in below slide.

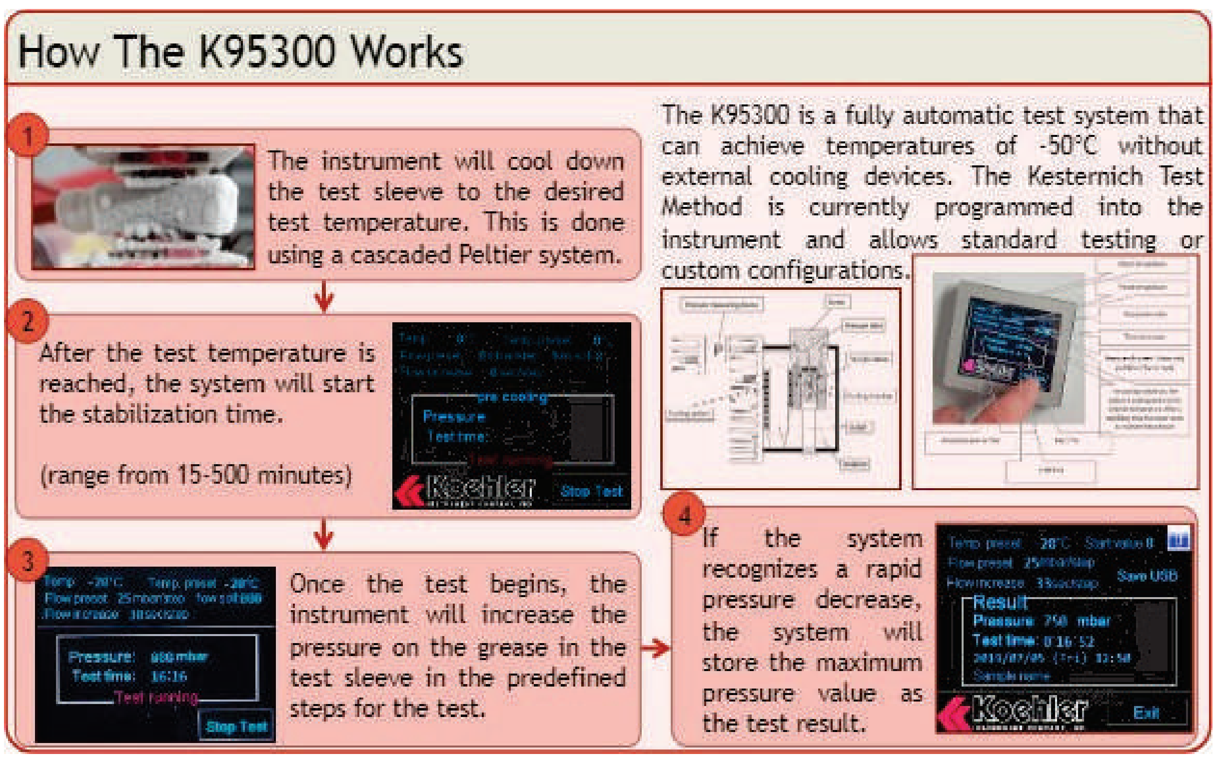


Figure 15: How K95300 works

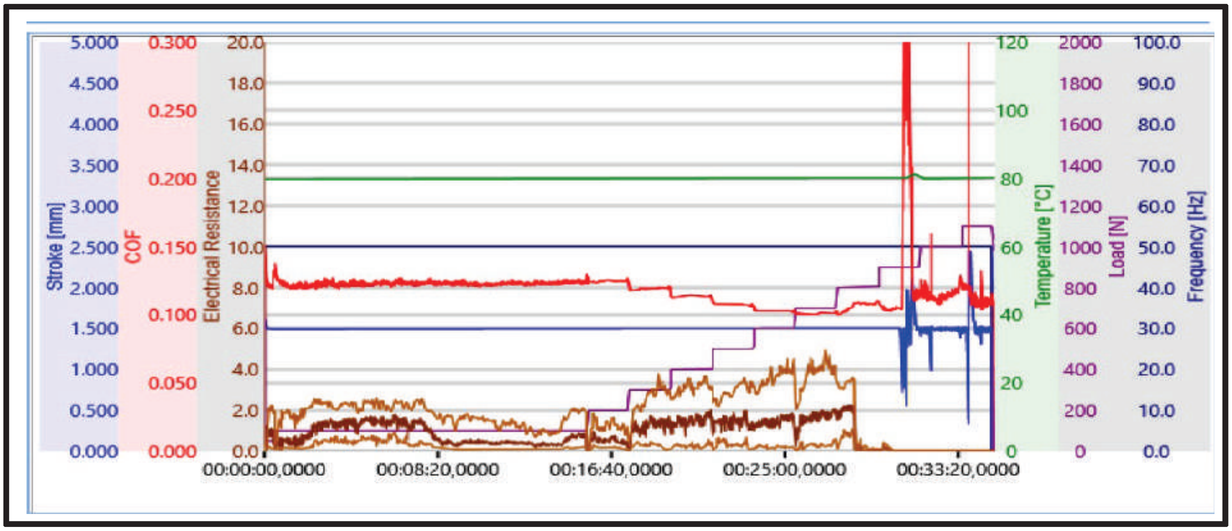


Figure 16: Result chart of test.

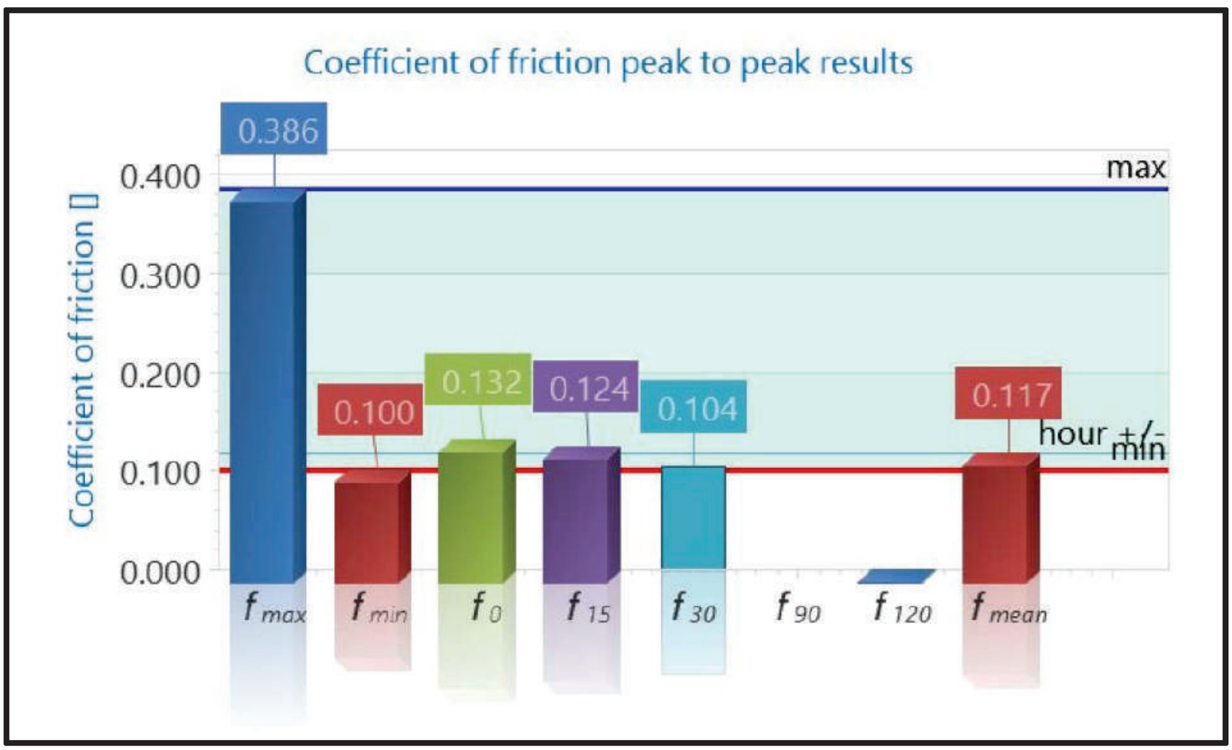


Figure 5: Chart of CoF peak to peak results

IF-WS2 additive did meet low temperature mobility property.

Conclusion

The work done here has compared IF-WS2 spherical particles' based concentrate, micron-sized platelet form 2H-MoS2 particles and submicron PTFE particles in LiX (lithium complex) grease formulation. By using some basic tribological tests (4-ball EP (ASTM D2596), 4-Ball Wear (ASTM D2266), and Timken (ASTM D2509)), it has been shown that *IF*-WS2 dispersion significantly improves tribological properties of greases compare to platelet *2H*-MoS2. Other physical propertiesof the grease such as dropping point or cone penetration were not affected.
We have compared performance of grease additive based on NIS' unique submicron Inorganic Fullerene-like Tungsten Disulfide particles and much larger (micron-sized) platelet MoS2 particles based additives in commercially available Li, LiX, and Polyurea formulation. IF-WS2 additive in grease works more as a complete tribological package. IF-WS2 near spherical particles increase Extreme Pressure properties, while reducing wear and Coefficient of Friction. In contrast to superior IF-WS2particles, 2H MoS2 demonstrates lower antiwear properties at a higher treat rate. Other physical properties (such as dropping point, cone penetration or low-temperature performance) were not significantly affected. Low concentration of IF-WS2 additive provide higher weld load in comparison to 2H-MoS2 additives. This translates into bigger savings for grease manufacturers. NIS is currently testing IF-WS2 additives in other types of greases, including Wire rope grease, biodegradable WR grease, fully synthetic grease, and high-performance open-gear grease.

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