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Fretting Wear Study:Effect of the Addition of Azelaic-A and Azelaic-B into Lithium Complex Greases

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Abstract

The study presented will demonstrate the effectiveness of two newly developed azelaic acid based products, Azelaic-A and Azelaic-B, designed as complexing agents in lithium complex grease to reduce fretting wear. The performance of Azelaic-A and Azelaic-B will be compared against traditional lithium complexing agents dimethyl sebacate and adipic acid. The performance of Azelaic-A, Azelaic-B, dimethyl sebacate and adipic acid complexing agents will be evaluated based upon their performance in the Penetration Test (ASTM D217), Dropping Point (ASTM D2265), Four Ball Wear (ASTM D2266), Oil Separation (ASTM D6184) and Fretting Wear (ASTM D4170) commonly used to evaluate lithium complex greases. The data will demonstrate that the incorporation of Azelaic-A and Azelaic-B as the complexing agent will significantly improve the fretting wear properties of the lithium complex grease and the data will highlight the performance improvement compared to the common complexing agents dimethyl sebacate and adipic acid.

Introduction

Lithium and lithium complex greases account for 77 percent of all grease made according to the NLGI 2013 Grease Production Survey (1). The use of diacids such as adipic acid (C6), azelaic acid (C9) and dimethyl sebacate (C10) in the grease thickener has been common practice in the industry for many years (2) (3). Emery Oleochemicals has been a long standing supplier of azelaic acid to the lubricating industry for many decades. Over the course of time, Emery Oleochemicals has continued to develop and reformulate its azelaic acid portfolio to better serve the lubrication community. Emery Oleochemicals has developed new azelaic acid formulations for lithium complex greases that are designed to reduce fretting wear.

To reduce fretting wear with lithium complex greases, the common industry practice is to introduce anti- friction, anti-wear and/or extreme pressure additives into lubricating greases. The addition of these additives, such as molybdenum disulfide, tungsten disulfide and graphene, are solely designed to improve performance and to reduce wear due to extreme pressure or fretting. (4) (5) (6) (7) (8) (9) In this study, Azelaic-A and Azelaic-B based lithium complex greases were prepared without the addition of any anti- wear additives to demonstrate their beneficial properties.

Equipment
The grease samples were prepared in 100Lb and 10Lb grease kettles that have electrical heating jackets. The kettles are open top and equipped with counter rotating mixing paddles. Milling of the grease which homogenizes and disperses the thickener was performed using a Morehouse grease mill.

Test Methods

- *ASTM D217* Cone penetration of lubricating grease was run for 0, 60 and 10000 strokes to measure the greases stability and dispersion of soap.

- *ASTM D 6184* Screen bleed test was run to determine how well the grease thickener was able to hold the oil. The grease was packed in a 60-mesh wire cone then suspended in a beaker for 30 hours at 100°C. The amount of oil lost was reported as a percentage of the total grease sample.

- Titration test was performed to measure the free remaining lithium hydroxide in the soap.

- FTIR scan of the soap was performed to confirm completion of reaction.

- *ASTM D 4170* Fretting wear protection. The grease sample was used to lubricate two thrust bearings loaded to 550 pounds and oscillated at 1800 cycles/minute for 22 hours at room temperature. The average loss in weight of the bearings was measured and reported in the units of milligrams (mg) of loss.

- *ASTM D2265* The dropping point of the lubricating grease was measured to determine the temperature at which the grease de-gels. The grease sample was heated in a drop point cup until the sample melts and a drop runs out and falls from the bottom of the cup.

- *ASTM D 2266* Four Ball Wear. The grease sample was used to lubricate three hard steel balls that are locked in place. A fourth ball was locked in place and rotated at 1200 rpm at 75°C for 60 minutes while pressing against the three other balls. The wear scar on each of the three balls was measured and the average scar diameter was reported as the measure of the wear (mm of wear).

The following test equipment has been used for the above describes tests :

Digital Penetrometer Koehler Model # K95560
Bruker Tensor 27 FTIR Spectrometer
Koehler Aluminum Block for Dropping Point

Procedure

- Added 40% total 750 Coastal Pale Oil (naphthenic based oil) and 12-OH stearic acid to kettle and heated to 85°C (185°F) or until fatty acid had completely dissolved.
- When temperature reached 85°C (185°F) and with the fats dissolved slowly added slurry of hydrated lithium hydroxide and water.
- Adjusted temperature to 121°C (250°F) and maintained the temperature for 30 minutes.
- Shut off the heat and added in the complexing agents slowly. The complexing agent was mixed in for 20-30 minutes.
- Added in slowly 2nd addition of slurry of hydrated lithium hydroxide and water.
- Applied heating and adjusted the temperature to 160°C (320°F) and maintained for 30 minutes. Take a sample at this point for soap titration and FTIR scan.
- Continued heating the sample to 210°C (410°F). As the grease temperature increased, slowly added 30% oil.
- After reaching 210°C (410°F), the heating was discontinued. Continued stirring and added 10% oil to aid in cooling the sample.
- When the temperature has cooled to below 82°C (180°F), the grease was milled. Added additional base oil as required until the sample was within the NLGI 2 grade penetration.

Discussion/Results

Emery Oleochemicals has developed several new azelaic acid formulations (Azelaic-A and Azelaic-B) that are designed to reduce fretting wear when incorporated into lithium complex greases. In this study, the performances of Azelaic-A and Azelaic-B were compared to adipic acid and dimethyl sebacate as complexing agents in lithium complex grease formulations. The results of the evaluation are described below.

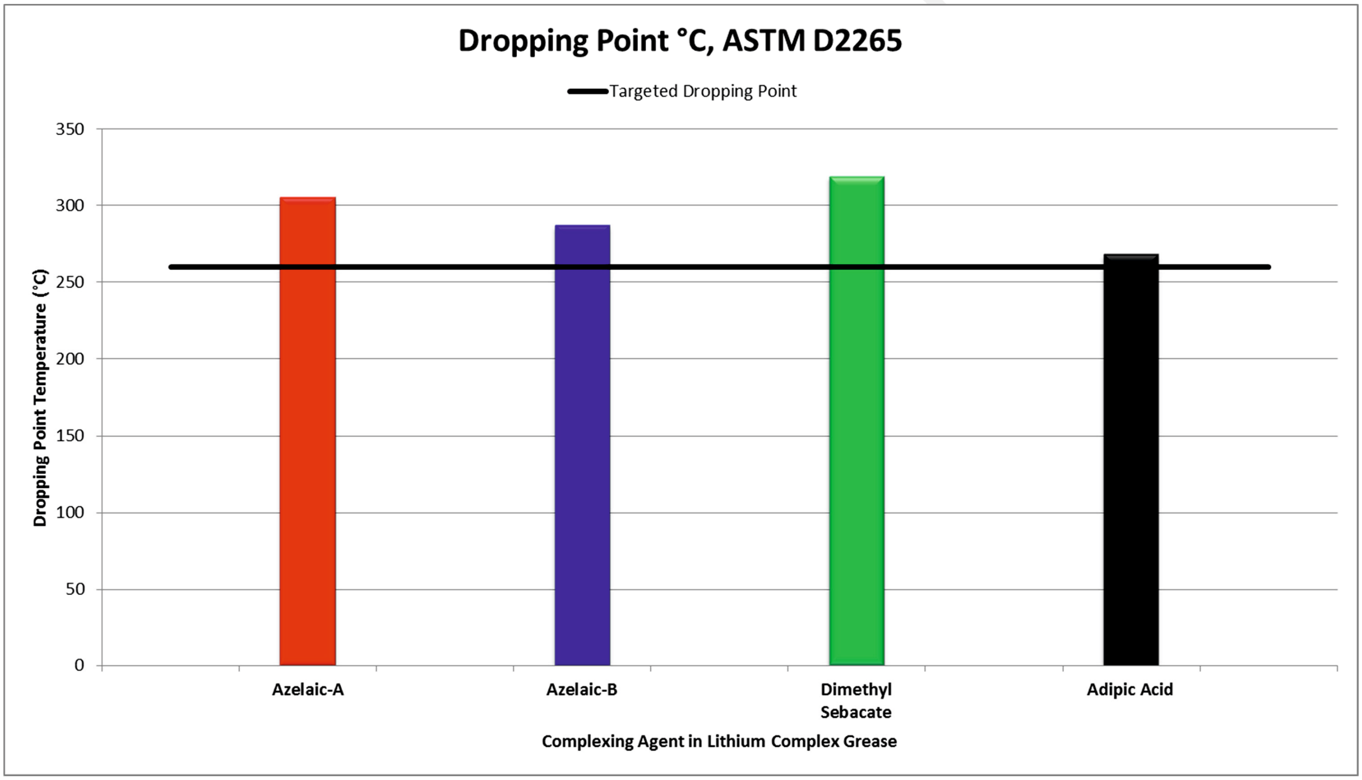
The lithium complex greases prepared for this study were cooked in an open top kettle until the reaction was deemed complete. The reaction progress was monitored by FTIR. The method involves collecting "soap" samples at different times of the cooking process and analyzing by FTIR. The reaction is complete when the carbonyl absorption band at ~1700 -1750 cm^{-1} shifted to ~1575cm^{-1}.

Dropping Point Results

The dropping point was measured following the procedure described in the ASTM D2265 Standard Test Method for Dropping Point of Lubricating Grease Over Wide Temperature Range. In this study, a dropping point of greater than or equal to 260°C was targeted. The lithium complex grease formulations were adjusted until the grease dropping point met or exceeded

260°C. The data shown in **Figure 1** demonstrates that the greases prepared in this study met the defined specifications.

Figure 1 Dropping Point Data Results of Lithium Complex Greases Containing Azelaic Acid-A or Azelaic-B Compared to Dimethyl Sebacate and Adipic Acid



Cone Penetration Results

The consistency (hardness) of the greases prepared for this study was measured following the procedure described in the ASTM D217-10 Standard Test Methods for Cone Penetration of Lubricating Grease. For this study, the targeted consistency number was that of NLGI No. 2 grease. The cone penetration test was measured on the unworked grease (0 strokes) and after the grease was worked for 60 and 10,000 (10K) strokes, respectively. The unworked grease penetration data showed that the majority of the grease samples met the consistency criteria of NLGI No. 2 grease and the remaining met the criteria of NLGI No. 3 grease, see **Figure 2**. After the greases were worked for 60 strokes, the grease penetration data showed that most of the grease samples met the consistency criteria of NLGI No. 2 grade grease. The remaining few met the criteria of NLGI No. 3 grade greases, see **Figure 3**. After the greases were worked for 10K strokes, the cone penetration data showed that all the greases formulated in this study met the criteria of NLGI No.2 grade grease, see **Figure 4**.

Figure 2 Unworked Penetration Results of Lithium Complex Greases Containing Azelaic Acid-A or Azelaic-B Compared to Dimethyl Sebacate and Adipic Acid

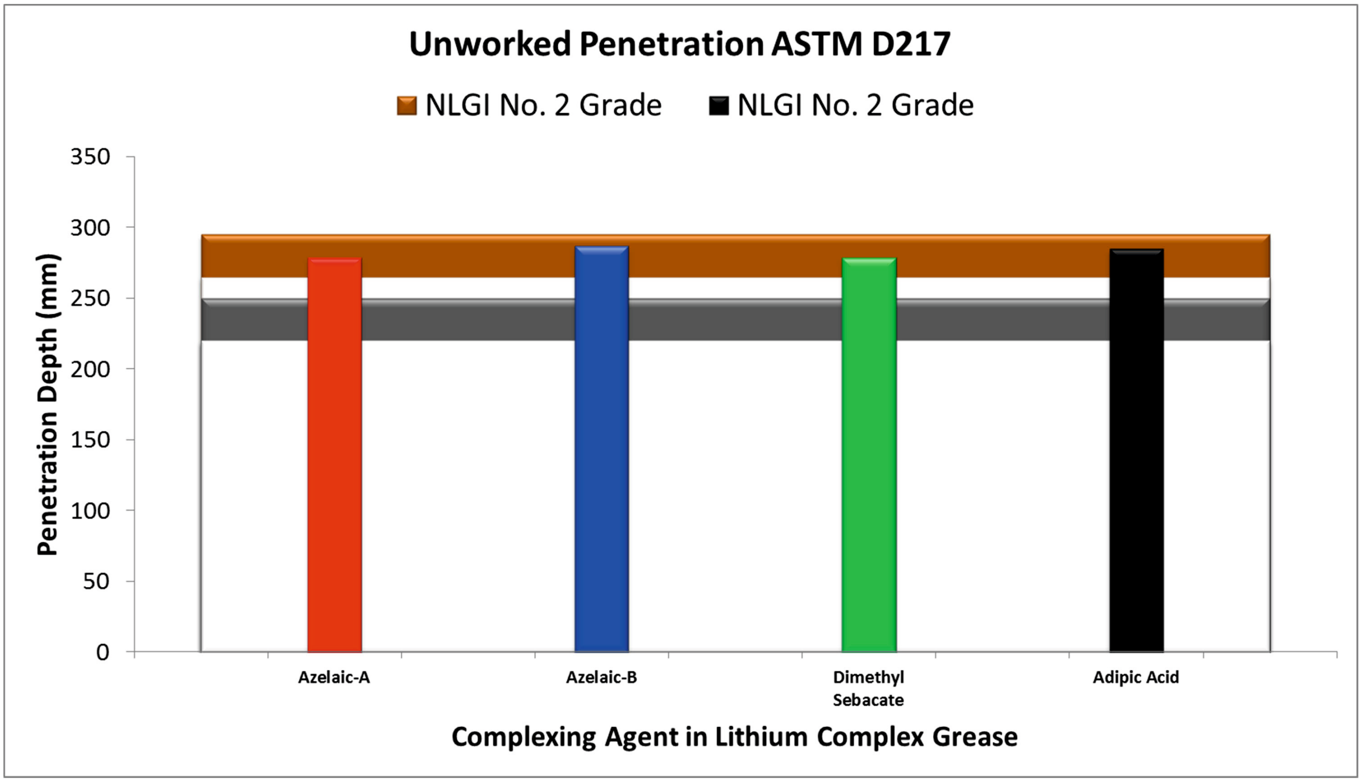


Figure 3 Worked Penetration Results, 60 Strokes Results of Lithium Complex Greases Containing Azelaic Acid-A or Azelaic-B Compared to Dimethyl Sebacate and Adipic Acid

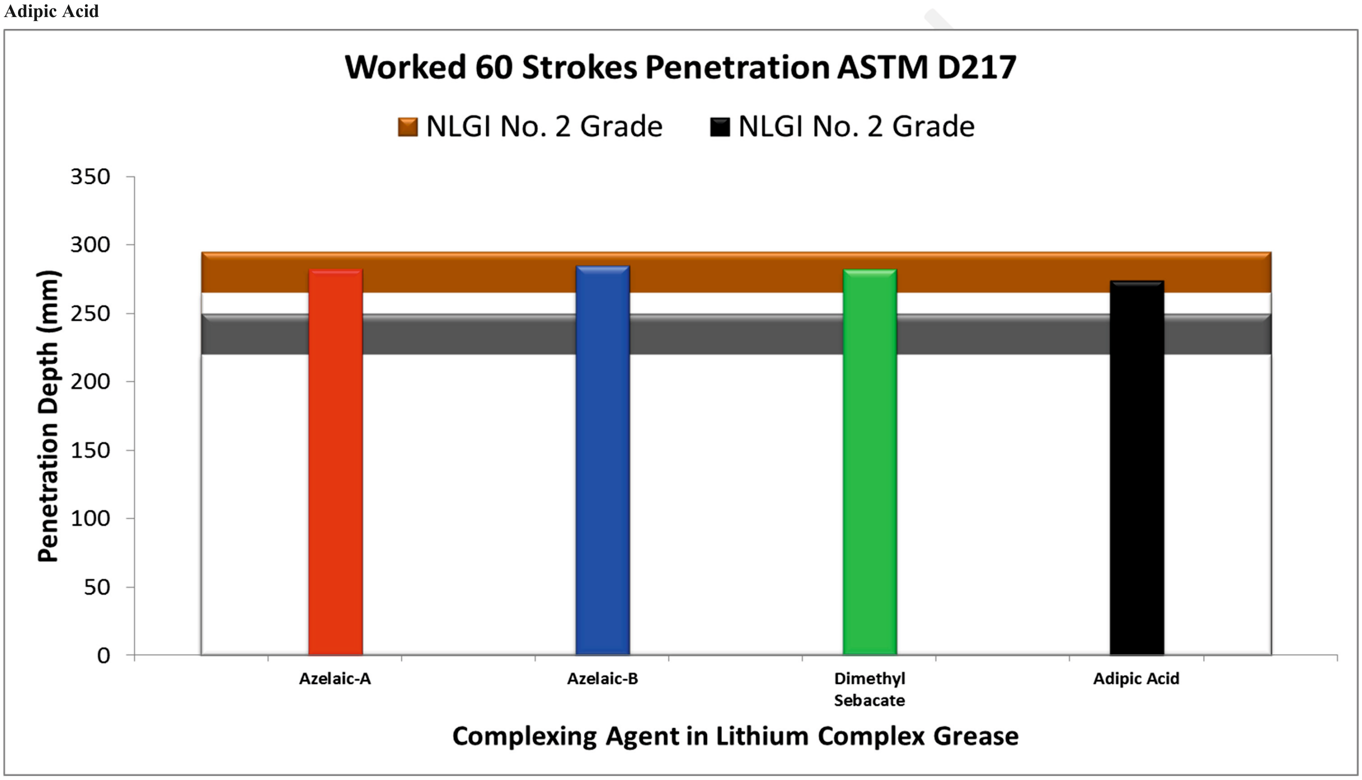
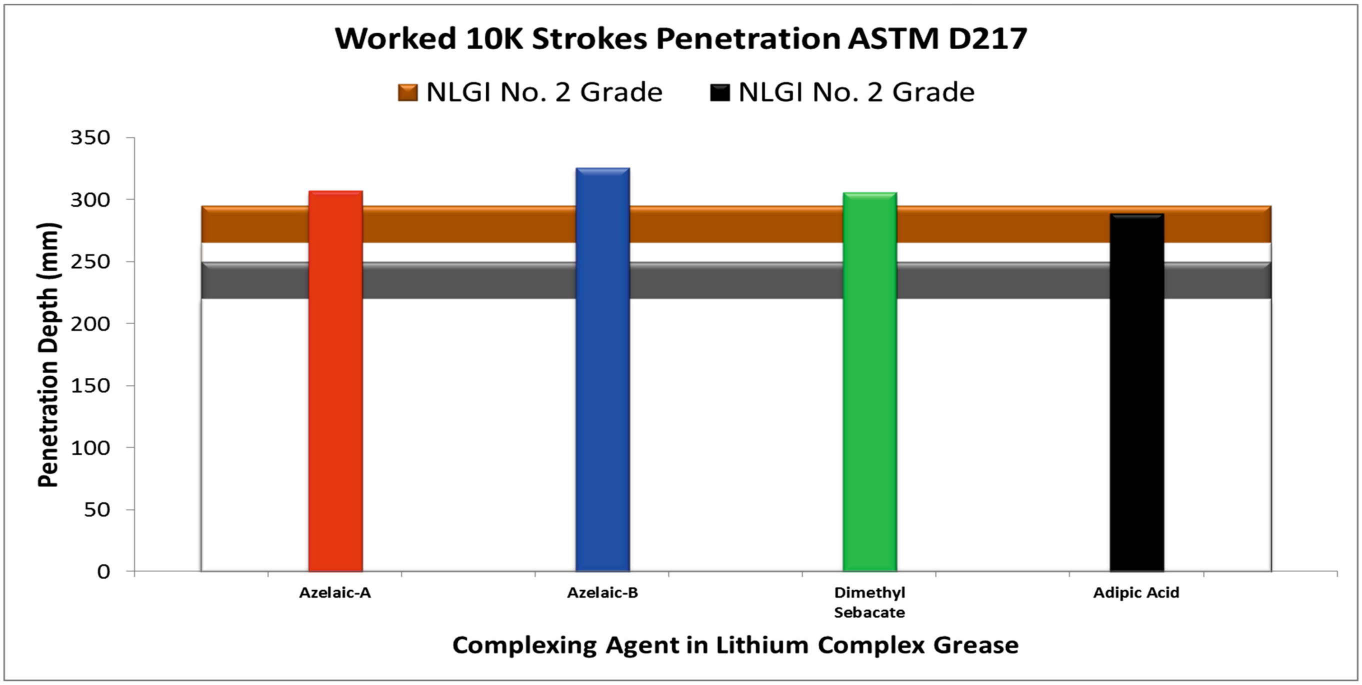


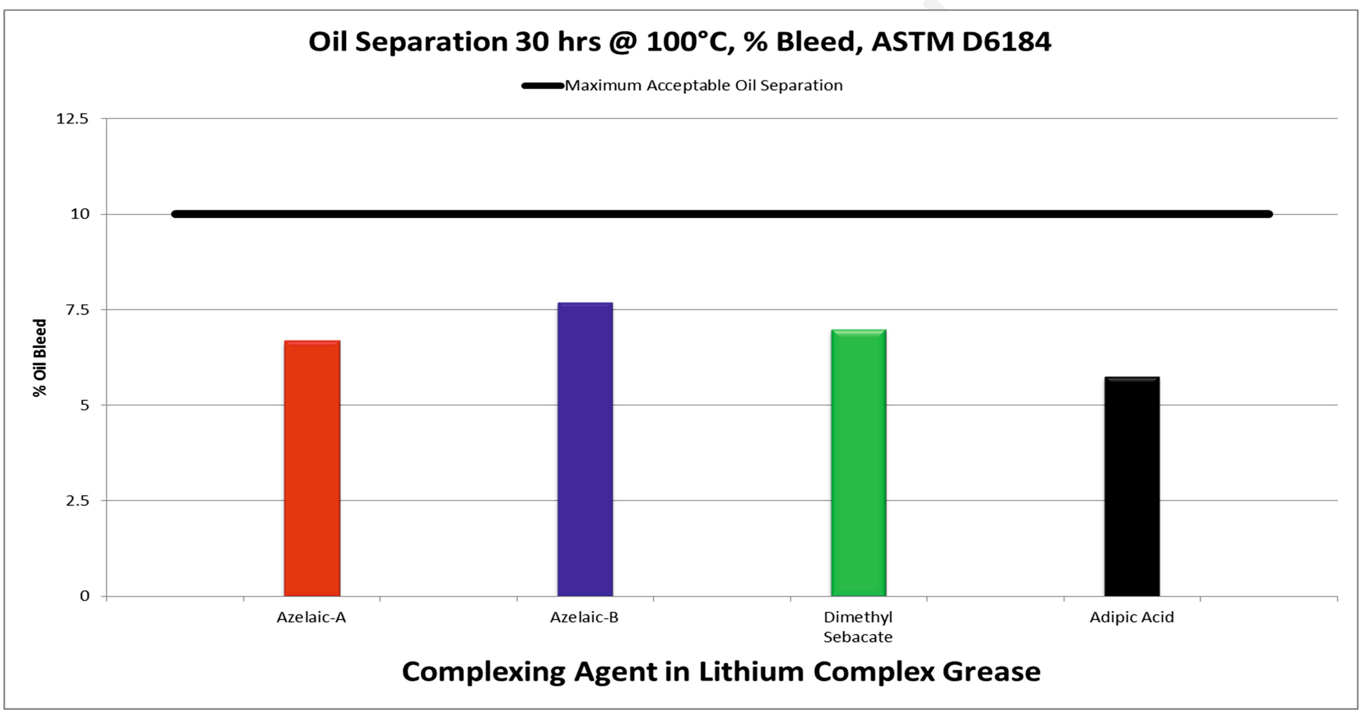
Figure 4 Worked Penetration Results, 10,000 Strokes Results of Lithium Complex Greases Containing Azelaic Acid-A or Azelaic-B Compared to Dimethyl Sebacate and Adipic Acid



Oil Separation

The oil separation of the greases prepared for this study was measured following the procedure described in the ASTM D6184-14 Standard Test Methods for Oil Separation from Lubricating Grease (Conical Sieve Method). The grease was packed in a 60-mesh wire cone and suspended in a beaker for 30 hours at 100°C. The amount of oil lost was reported as a percentage of the total grease sample. The reference greases prepared with azelaic acid complexing agent exhibited quite similar oil bleed as compared to the greases prepared with the sebacic acid derived complexing agent and adipic acid , see **Figure 5.**

Figure 5 Oil Separation Test Results of Lithium Complex Greases Containing Azelaic Acid-A or Azelaic-B Compared to Dimethyl Sebacate and Adipic Acid



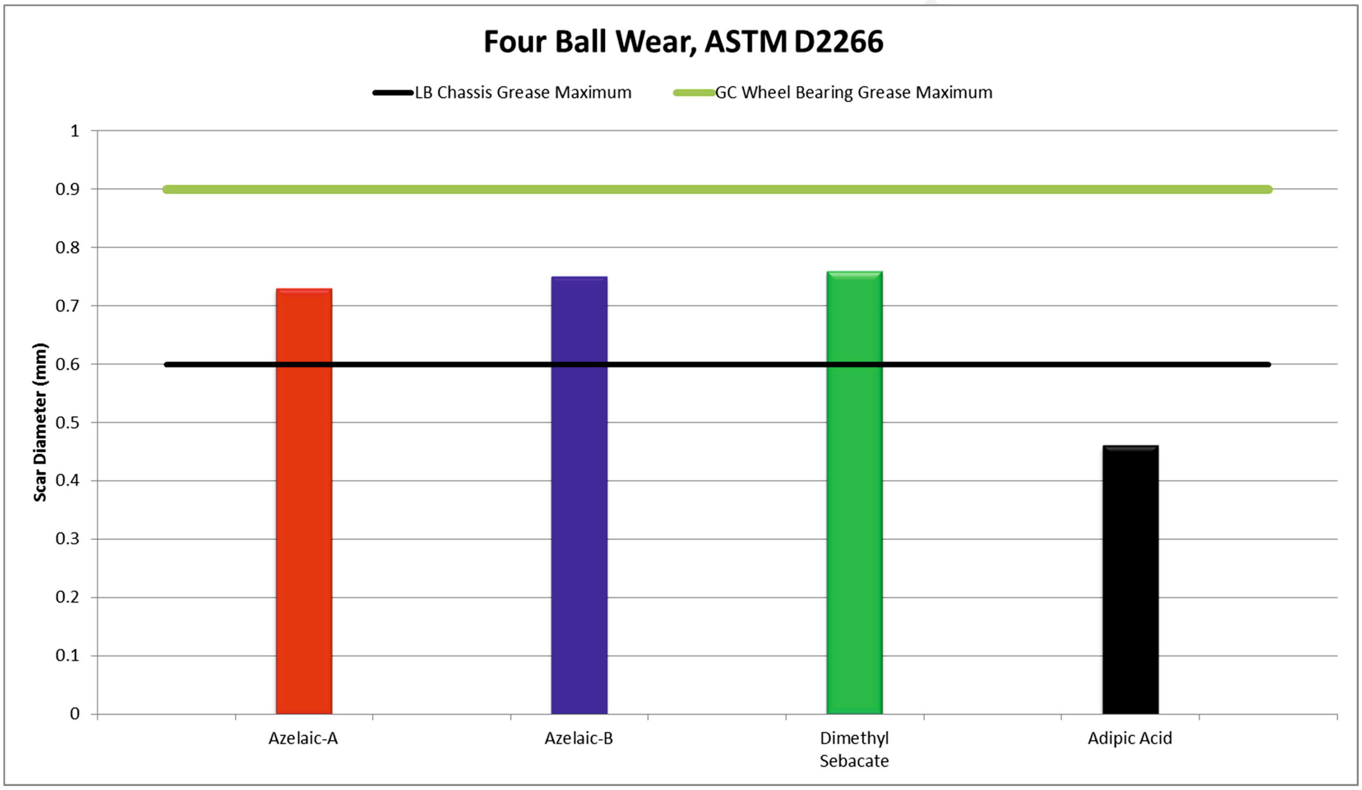
Four-Ball Wear

The ability to prevent wear (erosion of bearing surface) by the greases prepared in this study was measured following the procedure described in the ASTM D2266-01 Standard Test Methods for Wear Preventive Characteristic of Lubricating Grease (Four-Ball Method). The four ball wear specifications for LB Chassis Grease and GC Wheel Bearing Grease classifications are 0.9 mm and 0.6 mm maximum scar diameter, respectively.

The performance of the Azelaic-A and Azelaic-B in the four ball wear test was similar to the performance of those obtained when dimethyl sebacate was used as the complexing agent. The results of the four- ball wear analysis are shown in **Figure 6**. All greases in the study exhibited scar diameters of less than

0.9 millimeter in the four-ball wear test. Therefore, the greases would meet the specification for GC Wheel Bearing Grease as described in ASTM D4950. It should be noted that the four ball wear result for Azelaic-A and Azelaic-B was only slightly higher than that observed for the adipic acid complexing agent.

Figure 6 4-Ball Wear Results of Lithium Complex Greases Containing Azelaic Acid-A or Azelaic-B Compared to Dimethyl Sebacate and Adipic Acid

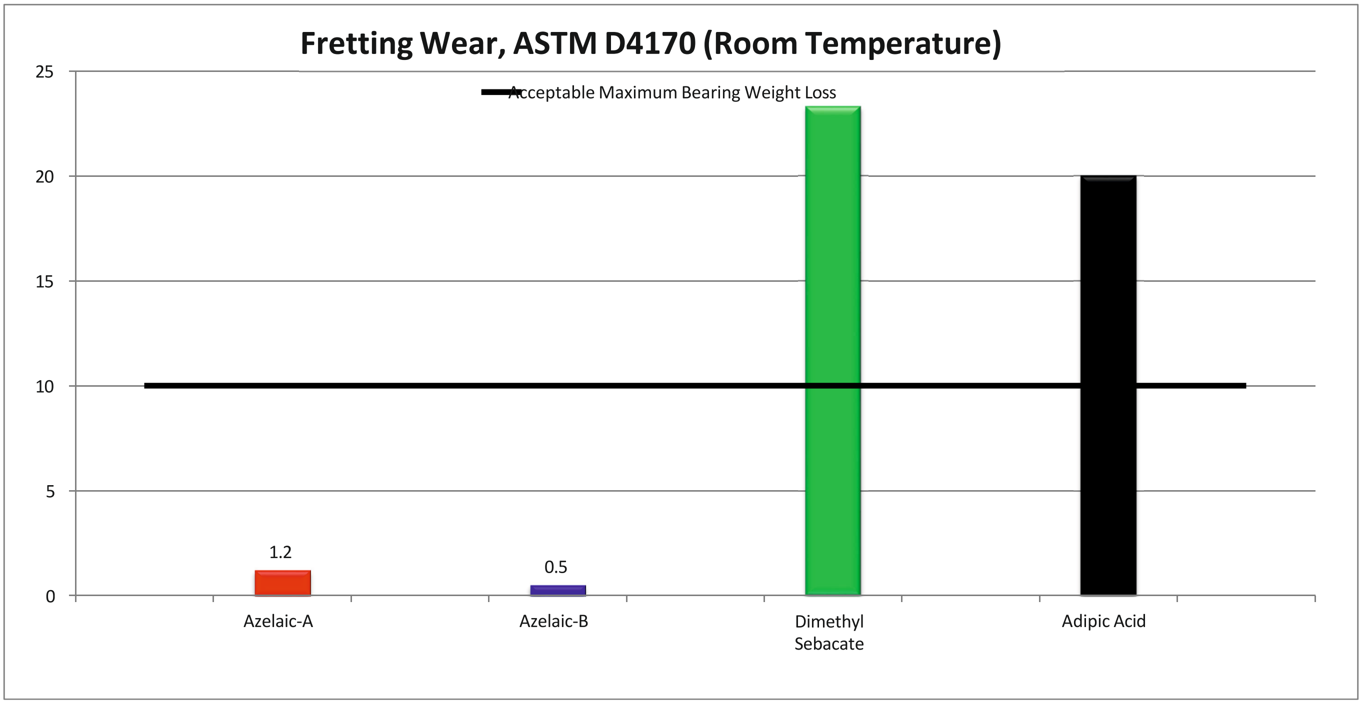


Fretting Wear

The ability to prevent wear (erosion of bearing surface) by the greases prepared in this study was measured following the procedure described in the ASTM D4170-10 Standard Test Methods for Fretting Wear Protection by Lubricating Greases. The results of the fretting wear analysis are discussed below. The industry standard for the acceptable fretting wear is less than 10 mg of bearing weight loss for both LB Chassis and GC Wheel Bearing grease classifications.

The greases containing Azelaic-A and Azelaic-B as the complexing agent considerably outperformed the dimethyl sebacate and adipic acid complexing agents in the fretting wear test. The observed bearing weight loss for Azelaic-A and Azelaic-B were 1.2 milligrams and 0.5 milligrams, respectively, compare to 23.3 milligrams for the dimethyl sebacate and 20 milligrams for the adipic acid containing grease, see **Figure 7**.

Figure 7 Fretting Wear Results of Lithium Complex Greases Containing Azelaic Acid-A or Azelaic-B Compared to Dimethyl Sebacate and Adipic Acid



Conclusion

The evaluation of lithium complexing greases prepared from various traditional complexing agents (, adipic acid and dimethyl sebacate) and Emery Oleochemicals' experimental complexing agents Azelaic- A and Azelaic-B provides strong evidence of the benefits of incorporating Azelaic-A and Azelaic-B into lithium complex grease formulations. The data demonstrates that Azelaic-A and Azelaic-B can be easily formulated into a lithium complex grease and match the grease properties that are typical of common lithium complex greases. The Azelaic-A and Azelaic-B greases evaluated in this study possess fretting wear, four ball wear, oil separation, penetration and dropping point properties that are easily acceptable as GC Wheel Bearing grease throughout the grease industry. With modest adjustments to the formulation, the Azelaic-A and Azelaic-B could meet the specifications of LB/GC grease commonly targeted and used in the lubrication industry. The anti-fretting power of Azelic-A and Azelaic-B compared to dimethyl sebacate and adipic acid will provide more options for grease formulators to address fretting wear issues. In addition to the high performance of Azelaic-A and Azelaic-B , these complexing agents also offer a sustainable and cost effective solution to reduce fretting wear. These products are developed from rapidly renewable resources utilizing Emery Oleochemicals manufacturing capabilities and experience as supplier of oleochemicals to the grease industry for decades. Based upon the results of this study, Emery Oleochemicals has developed EMEROX® 1177 and EMEROX® 1122 to serve the lubricating grease industry based upon the proprietary Azelaic-A and Azelaic-B product compositions.

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The Future of Aluminium Complex Greases

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Introduction

The grease thickener components not only transform the liquid lubricant into consistent lubricant, but also alter their properties. The gelling component of greases are mostly soaps (fatty acid salt - normal or complex), but they can be different chemical structure materials too (organic and ionic-non ionic polyureas, organoclay, well-dispersed silica acid, etc.) [1].

Aluminium complex greases began to appear in the mid-1960s, and a number of patents were issued over the next several years covering various modifications. Most of the efforts were in the areas of improved water resistance, and thermal and mechanical stability. Out of the aluminium complex greases one type is currently dominant in the world, which contains aluminium stearate and benzoate (Figure 1). The importance of the aluminium complex greases shows a trend to decline in the past decades. However, there were attempts for better understanding of the soap formation and to broaden the application areas.

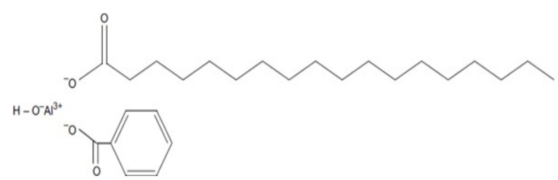


Figure 1
Aluminium stearate and –benzoate complex

Main properties of the aluminium complex greases include high dropping point and thus high maximal application temperature; excellent water resistance with a slight hardening of consistency in the presence of water; good working, mechanical and shear stability; very good oxidation stability; excellent pumpability and thus easy handling and applicability in central lubrication systems and bulk storage; wide operating temperature range; chemical resistance; good compatibility with a wide range of other greases. Its reversibility or ability to retain consistency after repeated heating and cooling, is unique as well [2][3].

Moreover, high quality aluminium complex greases can be formulated relatively easily on different types of base oils, which is being a current development focus.

These properties enable their application in steel mill applications. In addition, their non-toxicity also enables their applicability in the food industry (NSF category H1 grease maybe produced), as well as in the formulation of biodegradable, environmentally sound lubricating greases or any other highly specialized areas which require the use of lubrication by greases [4].

There are different methods to produce aluminium complex greases. In case of 2 step process method is known (Figure2). This is a more complex and long process which may be difficult to handle/manage. In the first step, an aluminium containing compound which is a reaction product of aluminium and isopropyl alcohol is reacted with fatty acid thus aluminiumand long carbon chain containing material is formed. In this step, the alcohol component of the feedstock is released, so ventilation of the system is essential. In the second step, the reaction product of the first step is reacted with benzoic acid to make the aluminium complex grease.

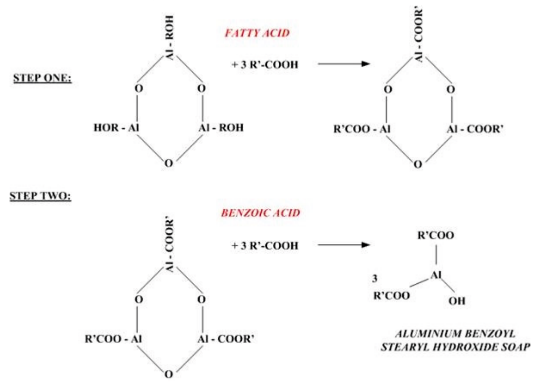
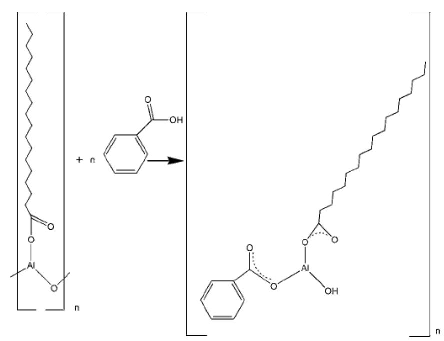


Figure2
Aluminium complex grease production via 2 step method

In case of the 1 step aluminium complex grease production procedure, the thickener agent feedstock is easy to handle (only slight pre-warming may be necessary), and it is a relatively short and easy to handle process as well (Figure 3) [5]. In the process the aluminium thickeneris reacted with benzoic acid and aluminium complex soap is formed. Because there is only a trace or no amount of alcohol is in the precursor, there is no need for ventilation of the system, which can also mean cost reduction.

Figure 3



Aluminium complex grease production via 1 step method

Because of the increasing need for better performance, there is a growing need for high performance, specially designed and formulated lubricants based on special base fluids. Thisis already changing the lubrication market and thus the lubrication industry itself. If the lubricant manufacturers would like to keep up with the trends, they have to find and offer solutions for these needs for the benefit of their customers. However it lags behind a bit when it is about change, this tendency also applies for the grease industry, too.

Experimental

Objectives

Our main objective is the continuous development and to meet the challenges of the future. Therefore we continuously explore the possibilities of lubricating greases and grease thickener formulation for special needs and applications, based on paraffinic base oils and based on biodegradable base oils. We are experimenting continuously to find the optimal maximum yield vs. maximum performance combinations in the formulation of aluminium complex lubricating greases. On the course of this, we investigated the possibilities of the formulation of excellent performance aluminium complex greases on different oil bases, from Group I. to Group V. and vegetable oils as well.

Feedstocks

During the experiments, we used different types of base oils, such as mineral oils with different characteristic (naphthenic, Group I. to Group III.), different synthetic bases (ester, polyalphaolefin, polyisobuthylene) and organic oil (rapeseed oil), too.

As thickener component we used aluminium containing thickener agent which contained approximately 50w/w% aluminium stearate thickener dissolved in Group I. base oil. To make the aluminium complex structure, technical grade benzoic acid was used.

Sample production

The samples were produced in a laboratory scale open grease kettle. The whole quantity of base oil mixture was poured into the kettle. After that stirring and heating has been started. At about 60°C, powdered benzoic acid and in some cases excess fatty component was added. After the acids were dissolved, the pre warmed thickener component had been added at 70– 80°C. After this the mixture has been heated to 150°C at first, for saponification. Then the temperature has been increased to the maximum of about 200–220°C, mainly depending on the type of base oil used. After reaching the maximum temperature, the grease has been

cooled immediately. After cooling, finishing operations, such as milling and deaeration had been done.

Analytical methods

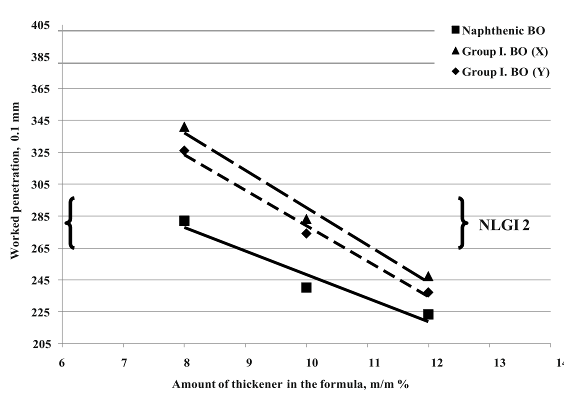
The analytic methods used for determining the properties of the grease samples were standardized (ISO, DIN, ASTM) methods commonly used in the grease industry.

Results and discussion

Formulation on different base oils

In the first stage of our experiments the effect of changing the base oil types were investigated. During this our goal was to formulate greases with NLGI grade 2 consistency greases on different types of base fluids.

It can be seen on Figure 4, that for the formulation of NLGI grade 2 grease in case of different base oils, different amount of soap (thickener and benzoic acid) were needed.



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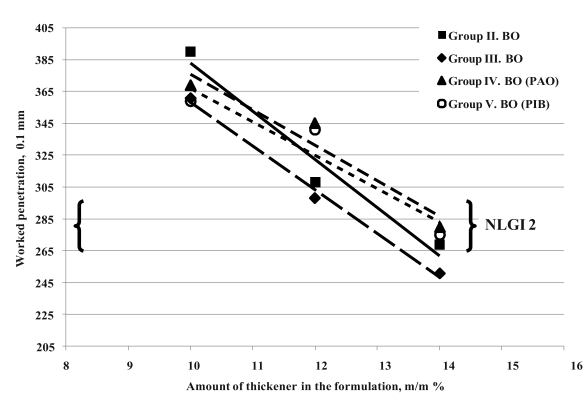

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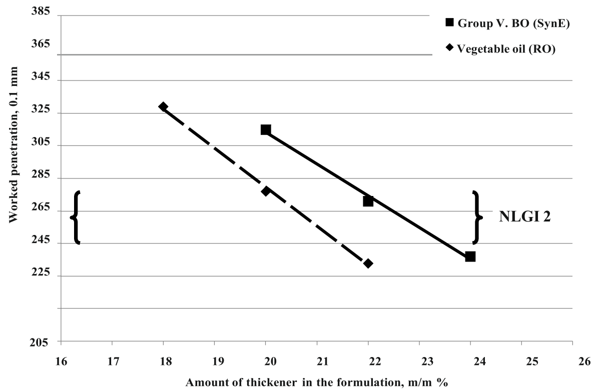

c,

X – SN base oil with medium viscosity, high paraffin content, low naphthenic aromatic content

Y – SN base oil with higher viscosity, higher naphthenic and aromatic content;

PAO – Polyalphaolefin;

PIB – Polyisobuthylene;

SynE – Synthetic ester;

RO – Rapeseed oil

Figure 4
Worked penetration of the grease samples formulated on different types of base fluids as a function of the necessary amount of thickener agent
Thickener component has approx. 50w/w% active material content

Table 2
Formulation of NLGI 2 lubricating grease on Group I. and Naphthenic base oils

Sample name		**1**	**2**	**3**
Type of base oil		**Naph-thenic**	**Group I. (X)**	**Group I. (Y)**
Molar ratio (Al stearate:BA)		**1:1**	**1:1**	**1:1**
Type of thickener		**mineral oil based**	**mineral oil based**	**mineral oil based**
Amount of thickener, %		**8**	**10**	**10**
Visual		yellow-brown	yellow-brown	yellow
Penetration at 25°C, 0.1 mm	ISO 2137	277	269	266
Worked penetration at 25°C, 0.1 mm	ISO 2137	282	283	274
Penetration change after 10,000 double strokes, 0.1 mm	ISO 2137	44	49	36
Penetration change after 100,000 double strokes, 0.1 mm	ISO 2137	66	68	71
Water wash out, %	ASTM D 1264	0.5	2	0.7
Flow pressure at -30°C, mbar	DIN 51805	1463	over 2100	over 2100
Oil separation at 100°C over 24h, %	IP 121	6.8	6.9	3.2

Thickener component has approx. 50w/w% active material content X – SN base oil with medium viscosity, high paraffin content, low naphthenic aromatic content; Y – SN base oil with higher viscosity, higher naphthenic and aromatic content; BA – Benzoic acid In case of applying naphthenic base oil only 8% of thickener component was enough to reach NLGI 2 grade. In case of Group I base oils 10% was needed. But when applying highly paraffinic (or similar structure) Group II-V. base oils to reach the required grade 13-14% of thickener had to be applied. Furthermore working with synthetic ester and vegetable oil, the thickener component had to be applied above 20%.

Table 3

Formulation of NLGI 2 lubricating grease on Group II.-IV. base oils

Sample name		**4**	**5**	**6**
Type of base oil		**Group II.**	**Group III.**	**Group IV. (PAO)**
Molar ratio (Al stearate:BA)		**1:1**	**1:1**	**1:1**
Type of thickener		**mineral oil based**	**mineral oil based**	**mineral oil based**
Amount of thickener, %		**14**	**12**	**14**
Visual		yellow	yellow	light yellow
Penetration at 25°C, 0.1 mm	ISO 2137	258	272	245
Worked penetration at 25°C, 0.1 mm	ISO 2137	269	298	280
Penetration change after 10,000 double strokes, 0.1 mm	ISO 2137	41	60	55
Penetration change after 100,000 double strokes, 0.1 mm	ISO 2137	77	82	71
Water wash out, %	ASTM D 1264	0.9	1.5	1.9
Flow pressure at -30°C, mbar	DIN 51805	2043	over 2100	872
Oil separation at 100°C over 24h, %	IP 121	0.9	4.8	2.8

Thickener component has approx. 50w/w% active material contentPAO – Polyalphaolefin; BA – Benzoic acid

These results are shown in Table 2-4 also, with alongside further properties which had been measured. The results shown in Figure 4-5, and also in Table 2-4 show that by increasing the soap content, the desired consistency grade with acceptable properties can be made. However in case some of the utilized base fluids, this increase of the soap components is not tooeconomical because of the relatively high price of the components.

Table 4
Formulation of NLGI 2 lubricating grease on Group V. and vegetable oil

Sample name		**7**	**8**	**9**
Type of base oil		**Group V. (SynE)**	**Group V. (PIB)**	**Rapeseed oil**
Molar ratio (Al stearate:BA)		**1:1**	**1:1**	**1:1**
Type of thickener		**mineral oil based**	**mineral oil based**	**mineral oil based**
Amount of thickener, %		**14**	**22**	**20**
Visual		yellow-brown	light yellow	yellow-brown
Penetration at 25°C, 0.1 mm	ISO 2137	252	268	245
Worked penetration at 25°C, 0.1 mm	ISO 2137	291	281	297
Penetration change after 10,000 double strokes, 0.1 mm	ISO 2137	-38	61	-43
Penetration change after 100,000 double strokes, 0.1 mm	ISO 2137	-25	73	-36
Water wash out, %	ASTM D 1264	0.5	2.1	0
Flow pressure at -30°C, mbar	DIN 51805	1055	over 2100	over 2100
Oil separation at 100°C/24h, %	IP 121	1.2	1.4	0.9

Thickener agent has approx. 50w/w% active material content
PIB – Polyisobuthylene; SynE – Synthetic ester; BA – Benzoic acid

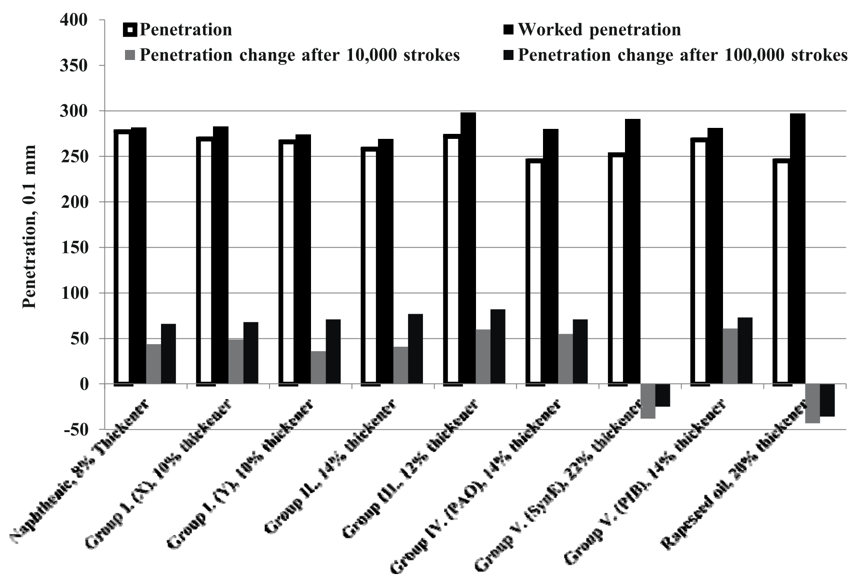

Figure 5
Penetration and mechanical stability

Thickener agent has approx. 50w/w% active material content; X – SN base oil with medium viscosity, high paraffin content, low naphthenic aromatic content; Y – SN base oil with higher viscosity, higher naphthenic and aromatic content; PAO – Polyalphaolefin; PIB – Polyisobuthylene; SynE – Synthetic ester

Changing the molar ratio

In the second stage of our experiments the effect of changing the molar ratio of the feedstocks were investigated. Because of the special structure (one cyclic and one paraffin component) of the aluminium complex grease, it can be tailored for different base oils relatively easily.

Table5
Modification of the molar ratio of the soap components

Sample name		**6A**	**6B**
Type of base oil		**PAO**	**PAO**
Molar ratio (SA:Al:BA)		**1:1:1**	**1.2:1:0.8**
Type of thickener		**mineral oil based**	**mineral oil based**
Amount of thickener, %		**14**	**10**
Amount of excess stearic acid, %		**-**	**~1**
Visual		yellow	yellow
Penetration at 25°C, 0.1 mm	ISO 2137	245	266
Worked penetration at 25°C, 0.1 mm	ISO 2137	280	289
Penetration change after 10,000 double strokes, 0.1 mm	ISO 2137	55	66
Penetration change after 100,000 double strokes, 0.1 mm	ISO 2137	92	105
Water wash out, %	ASTM D 1264	1.9	1.6
Flow pressure at -30°C, mbar	DIN 51805	2.8	8.8
Oil separation at 100°C over 24h, %	IP 121	872	787

Thickener agent has approx. 50w/w% active material content
PAO – Polyalphaolefin; SA – Stearic acid; Al - Aluminium, BA – Benzoic acid

Based on this idea the molar ratio of the cyclic component (benzoic acid) and the paraffin component (carbon chain of the stearic acid) has been changed to produce a more paraffin heavy grease structure. Based on the results (Table 5) it was determined that with the modification of the molar ratio with lower amount of thickener similar grease can be produced. This means that the thickener can be tailored well to the applied base oil, and not only with the use of excessive amount of thickener, but only with a small amount of excessivefatty acid, which is much cheaper. Thus this formulation method can mean economical benefitand can lead to extra profit.

Utilization of different fatty acids

As it was presented above, with the use of a small amount of excessive fatty acid, the desired consistency grade grease can be produced with such good performance as withincreasing the soap content. In the third stage of our experiments the effect of the use of different fatty acids were investigated.

The results are shown in Table 6-8 and Figure 6. It was investigated that if the different chemical formulas (ligand, unsaturation etc.) and the excess of the fatty acids had effect to grease properties. In these experiments we applied different amounts of excess fatty acids, namely distilled stearic acid (mixture of highly saturated C16 and mainly C18 carbon chains), 12 hydroxystearic acid (widely used in grease production) and oleic acid (unsaturated C18 chains).

Table 6
Formulation with excess stearic acid

Sample name		**6A**	**6C**	**6D**
Type of base oil		**PAO**	**PAO**	**PAO**
Type of thickener		**mineral oil based**	**mineral oil based**	**mineral oil based**
Amount of thickener, %		**14**	**12**	**10**
Amount of excess fatty acid, %		**-**	**0.7**	**1.4**
Type of excess fatty acid		**-**	**DSA**	**DSA**
Visual		yellow	yellow	yellow
Penetration at 25°C, 0.1 mm	ISO 2137	245	248	270
Worked penetration at 25°C, 0.1 mm	ISO 2137	280	287	293
Penetration change after 10,000 double strokes, 0.1 mm	ISO 2137	55	33	39
Penetration change after 100,000 double strokes, 0.1 mm	ISO 2137	92	87	110
Water wash out, %	ASTM D 1264	1.9	0.5	1.1
Flow pressure at -30°C, mbar	DIN 51805	2.8	4.8	5.6
Oil separation at 100°C over 24h, %	IP 121	872	894	950

Thickener component has approx. 50w/w% active material content
PAO – Polyalphaolefin; DSA – Distilled stearic acid

Table 7
Formulation with excess 12 hydroxystearic acid

Sample name		**6A**	**6E**	**6F**
Type of base oil		**PAO**	**PAO**	**PAO**
Type of thickener		**mineral oil based**	**mineral oil based**	**mineral oil based**
Amount of thickener, %		**14**	**12**	**10**
Amount of excess fatty acid, %		**-**	**0.7**	**1.4**
Type of excess fatty acid		**-**	**12HSA**	**12HSA**
Visual		yellow	yellow	yellow
Penetration at 25°C, 0.1 mm	ISO 2137	245	257	295
Worked penetration at 25°C, 0.1 mm	ISO 2137	280	278	330
Penetration change after 10,000 double strokes, 0.1 mm	ISO 2137	55	57	61
Penetration change after 100,000 double strokes, 0.1 mm	ISO 2137	92	154	138
Water wash out, %	ASTM D 1264	1.9	0.8	2.1
Flow pressure at -30°C, mbar	DIN 51805	2.8	5.6	3.4
Oil separation at 100°C over 24h, %	IP 121	872	878	935

Thickener component has approx. 50w/w% active material content
PAO – Polyalphaolefin; 12HSA – 12 hydroxystearic acid

It was concluded that applying the thickener component in 10-12% with applying different types of excess fatty acids, proper NLGI 2 grade greases could be produced with relatively same, very good performance levels. This means that the performance of the grease is not necessarily depends on the price or availability of the utilized fatty component.

Table 8
Formulation with excess oleic acid

Sample name		**6A**	**6G**	**6H**
Type of base oil		**PAO**	**PAO**	**PAO**
Type of thickener		**mineral oil based**	**mineral oil based**	**mineral oil based**
Amount of thickener, %		**14**	**12**	**10**
Amount of excess fatty acid, %		**-**	**0.7**	**1.4**
Type of excess fatty acid		**-**	**OA**	**OA**
Visual		yellow	yellow	yellow
Penetration at 25°C, 0.1 mm	ISO 2137	245	255	244
Worked penetration at 25°C, 0.1 mm	ISO 2137	280	278	264
Penetration change after 10,000 double strokes, 0.1 mm	ISO 2137	55	70	51
Penetration change after 100,000 double strokes, 0.1 mm	ISO 2137	92	116	101
Water wash out, %	ASTM D 1264	1.9	0.9	1.3
Flow pressure at -30°C, mbar	DIN 51805	2.8	2.5	2.7
Oil separation at 100°C over 24h, %	IP 121	872	995	934

Thickener component has approx. 50w/w% active material content
PAO – Polyalphaolefin; OA – oleic acid

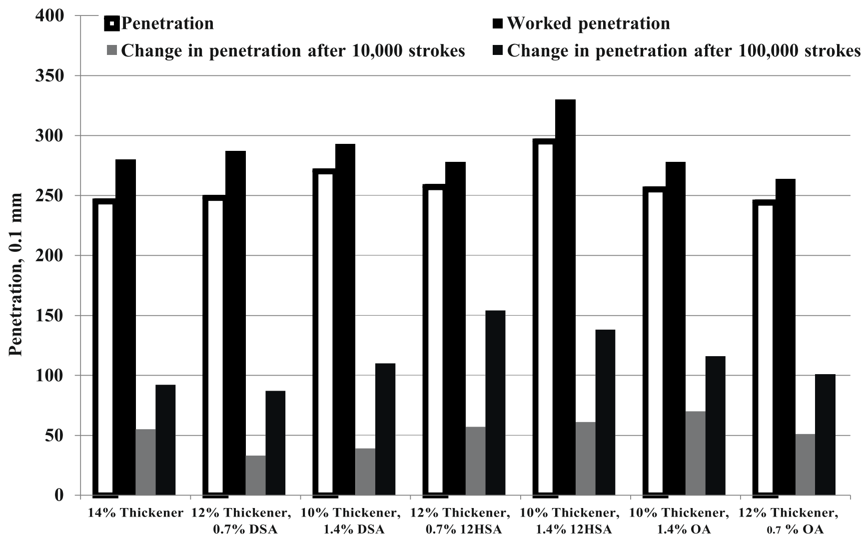

Figure 6
Penetration and mechanical stability of grease as a function of the applied amount of thickener and excess fatty component
Thickener component has approx. 50w/w% active material content; DSA – Distilled stearic acid; 12HSA – 12 hydroxystearic acid; OA – oleic acid

Conclusions

It can be concluded that the aluminium complex lubricating grease have a bright future in special areas, where there is a need for high dropping point, high water resistance, wide operating temperature range and chemical resistance. Such areas are steel industry, food industry, any application which requires lubrication and a chemically active environment.

During our experimental work, we determined that aluminium complex greases are easily made in a one step process with the utilization of aluminium stearate containing thickener compositions and moreover it is relatively easy to formulate lubricating greases, evenspecialities on different base oil types with excellent properties.

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Performance Evaluation of Antimony/Zinc Diamyl Dithiocarbamate as Grease Additive

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ABSTRACT: The Extreme-Pressure (EP), antiwear (AW), friction-reducing (FR) and antioxidation (AO) performances of antimony/zinc mixed metal diamyl dithiocarbamate (Sb/ZnDTC) as a grease additive are evaluated. The four-ball tests show that, the Sb/ZnDTC a mixed metal organic salt, exhibits excellent EP, good AW, but no FR performances in lubricating base oil. Whereas it exhibits good EP, but no obvious AW and FR capacities in lithium complex, polyurea and calcium sulfonate complex greases. The combination of Sb/ZnDTC and molybdenum dialkyl dithiocarbamate (MoDTC), a known AW and FR additive, could give a balanced overall performance in grease with high EP and excellent FR/AW characteristics. The MTM (Mini Traction Machine) Stribeck curves indicate, Sb/ZnDTC could effectively reduce the friction coefficients under boundary and mixed lubrication regimes in calcium sulfonate complex grease, especially at high temperature. In addition, the PDSC (Pressure Differential Scanning Calorimetry) oxidation test proves that Sb/ZnDTC is an excellent antioxidant in greases as a hydroperoxide decomposer.

KEYWORDS: Grease, Dithiocarbamate, Antimony, Zinc, Extreme-Pressure, Antioxidant

1 INTRODUCTION

Antimony, same as phosphorus, belongs to the Group VA in the periodic table of the elements, possesses some extreme-pressure (EP) and antiwear properties too. Extreme Pressure (EP) performances, especially the Timken OK loading capacity, of greases and oils have long been enhanced by the use of antimony dithiocarbamate (SbDTC)[1-6]. However, it is very important to try to limit the amount of antimony into the environment, due to the environmental and health concerns over its toxicity as a heavy metal element. It is a challenge to utilize low amount of antimony dithiocarbamate in lubricating oils and greases to achieve high EP performances. Very meaningfully, the *in situ* (in one kettle) preparation of zinc dialkyl dithiocarbamate (ZnDTC) in the preparation of antimony dithiocarbamate (SbDTC) has allowed for the significant reduction of the SbDTC needed while maintaining the necessary EP properties of the grease composition as determined by the Timken OK load test[7][8]. The *in situ* synthesis of this di-metal salt of dithiocarbamate (Sb/ZnDTC) from a secondary amine, carbon disulfide and antimony (III) oxide, Sb_2O_3, and zinc (II) oxide, ZnO can be describe as follows:

$$R_2NH + CS_2 + Sb_2O_3 + ZnO \longrightarrow Sb(S_2CNR_2)_3 + [Zn(S_2CNR_2)_2]_2 + H_2O$$

The EU Classification of Xn (harmful) N (dangerous for the environment) for concentration of Antimony (Sb) is: Sb ≥ 25 %, Xn, N, R20/22-51/53; 2.5 % ≤ Sb < 25 %, Xn, R20/22-52/53; and 0.25 % ≤ Sb < 2.5 %, Xn, R20/22. So it is very important for the concentration level of antimony in grease to be less than 0.25%. Reduced antimony content in greases without the loss of EP capability or the need for sulfurized olefin or ester with strong odor could be achieved by this synthesis method. The Sb/ZnDTC by this *in situ* (in one kettle) synthesis can guarantee an excellent EP performance, when Sb is less than 0.25% in greases. The comparison between the bi-metal salt of dithiocarbamate by *in situ* synthesis and its simple blending (SbDTC + ZnDTC) was given as in the Table 1[8].

Table 1. EP performance in Lithium Complex Grease (ASTM D2509)			
Grease Composition:	Sb Content, %	Zn Content, %	Timken OK Load, lb.
Base + DTC Sb/Zn (*in situ*)	0.15	0.13	70
Base + SbDTC + ZnDTC (mixture at 1:1)	0.17	0.15	< 40

The Sb/ZnDTC by *in situ* synthesis outperforms the physical mixture of SbDTC and ZnDTC, moreover, it does not have the sulfurized olefin's drawbacks of pungent odor and lowering dropping point of lithium complex grease.

2 EXPERIMENTAL / MATERIALS AND METHODS

2.1 Base Oil, Greases and Additives

Base oil used in this study is 650SN Group I base oil. Base greases used include a lithium complex grease, a polyurea grease and a calcium sulfonate complex grease. All three base greases were obtained from real production batches by courtesy of two grease manufacturers.
The in situ liquid Sb/ZnDTC additive has antimony, zinc and sulfur content of 5.8%, 4.5%, and 18.5% respectively, and contains 20% petroleum base oil. In this paper, the additive is designated as Sb/ZnDTC. The interaction between Sb/ZnDTC and an organo-molybdenum additive is also investigated in this paper for an overall balance EP, AW and FR performances in greases. The Molybdenum additive evaluated is a solid molybdenum dibutyl dithiocarbamate, which contains the molybdenum of 28.0% and the sulfur of 24.5%. This Mo additive is designated as MoDTC. These two additives are commercially available.

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 performances in lubricating oil and greases. Experimental conditions were: 40 kgf load, 1200 rpm speed, 60 minutes, and 75°C. 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.

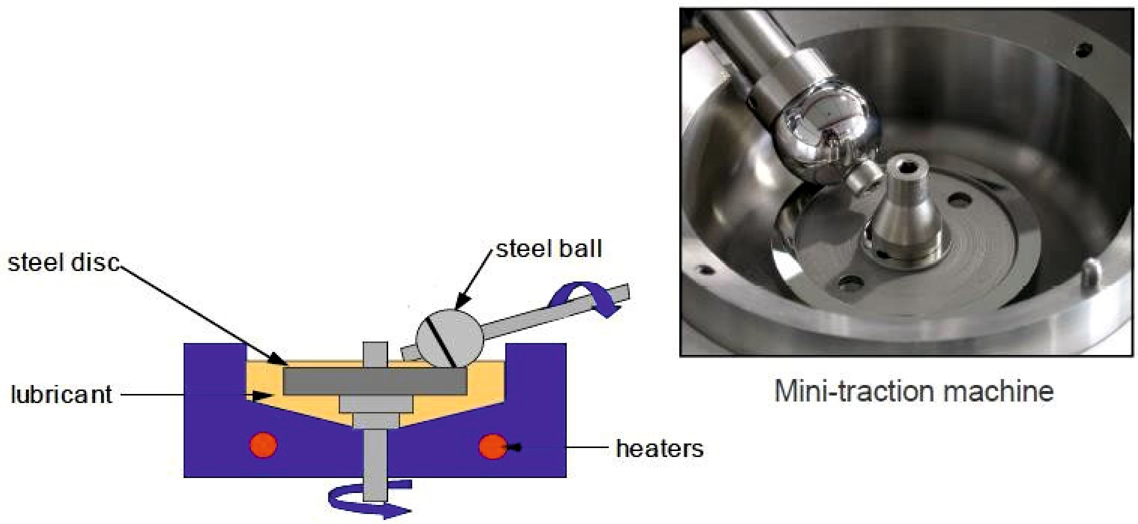
2.3 Four-Ball EP test

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 in boundary and mixed lubrication regime (Stribeck Curve) with "Ball on Disc" configuration. MTM consists of a rotating a 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, each Stribeck curves at 40^{0}C, 60^{0}C, 80^{0}C, 100^{0}C, 120^{0}C and 140^{0}C, 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 PDSC oxidation test

PDSC (Pressure Differential Scanning Calorimetry, ASTM D6186) was used to stimulate the oxidation in greases. A small quantity of oil is weighed into a sample pan and placed in a test cell. The cell is heated to a specified temperature and then pressurized with oxygen. The cell is held at a regulated temperature and pressure until an exothermic oxidation reaction occurs. The extrapolated onset time is measured and reported as the oxidation induction time (OIT) for the lubricating oil or grease at the specified test temperature. The test conditions: 3.5MPa pressure, 180, 200 and 210°C temperatures, 3.0 mg grease sample, and 100ml/min oxygen flow.

3 RESULTS AND DISCUSSION

3.1 Tribological performances in base oil

Sb/ZnDTC was added into Group I base oil, and the tribological performances were evaluated by four-ball friction and wear tests. The experimental results are given in Table 2.

Table 2. The EP, AW and FR Performances of Sb/ZnDTC in Group I Base Oil				
	Friction and Wear Test (40Kgf, 1200rpm, 75^{o}C, 60min.)		EP Test	
	Wear Scar,, mm	Average Friction Coefficient	LNSL, Kgf	Weld load, Kgf
650SN Base Oil	0.802 (30Kgf)*	0.100 (30Kgf)*	36	100
+ 2.0% Sb/ZnDTC	0.558	0.102	85	200
+ 3.0% Sb/ZnDTC	0.585	0.104	77	250
*Seizure occurred for the base oil under 40Kgf load, and the test for 60 min. failed, so just the wear scar and the friction coefficient under 30Kgf load for 60 min. was given for reference.				

It can be seen from Table 2 that, Sb/ZnDTC possesses excellent EP, good AW performances, but no obvious FR capacity in the base oil.

3.2 Tribological performances in greases

Sb/ZnDTC was added into lithium complex, polyurea and calcium sulfonate complex base greases, and the tribological performances were evaluated by four-ball friction and wear tests. The experimental results are given in Table 3.

Table 3. The EP, AW and FR Performances of Sb/ZnDTC in Greases				
	Friction and Wear Test (40Kgf, 1200rpm, 75^{o}C, 60min.)		EP Test	
	Wear Scar,, mm	Average Friction Coefficient	LNSL, Kgf	Weld load, Kgf
Lithium Complex Base Grease	0.588	0.099	82	250
+ 3.0% Sb/ZnDTC	0.508	0.092	114	315
Polyurea Base Grease	0.423	0.089	107	250
+ 3.0%Sb/ZnDTC	0.614	0.106	95	400
Calcium Sulfonate Complex Base Grease	0.375	0.098	100	315
+ 3.0% Sb/ZnDTC	0.478	0.089	100	620

It shows in Table 3 that, Sb/ZnDTC exhibits good four-ball EP performance, but no obvious FR capacity in the greases, and the AW properties can only be found in the lithium complex base grease. Thus, Sb/ZnDTC can only be treated as an EP additive in greases, and another kind of additive is needed in combination with it to achieve an overall balanced EP, AW and FR performances.

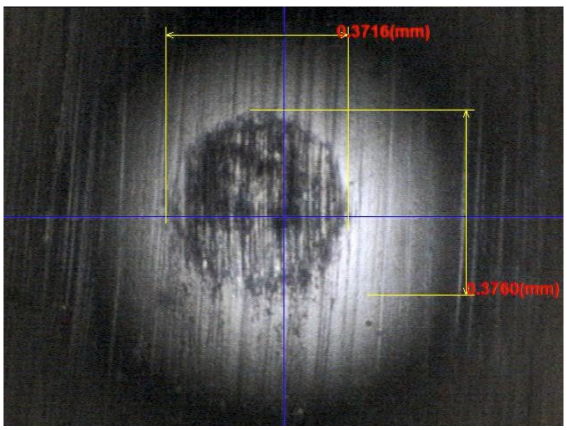
3.3 Tribological performances with organo-molybdenum additive in greases

As showed in Table 3, Sb/ZnDTC is not a good AW and FR additive for greases, so AW and FR additive is needed with it for the comprehensive performances. Molybdenum dibutyl dithiocarbamate (MoDTC) is well-known for its excellent FR and AW performances in greases [9]. Actually, the successful combination of SbDTC and MoDTC in lithium, lithium aluminum mixed greases for high Timken OK load, high four-ball wear load, low wear scar and low friction has already been reported [3].

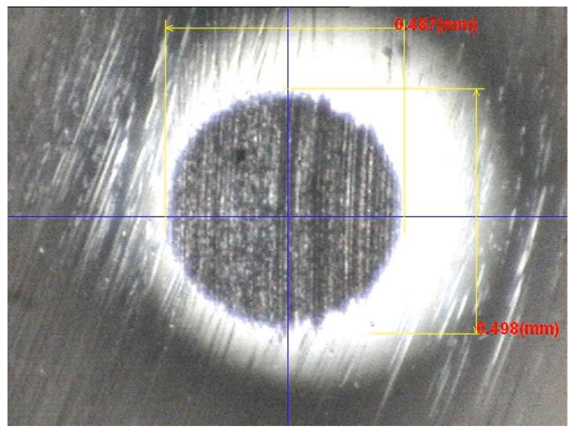
Sb/ZnDTC and MoDTC were added into the calcium sulfonate complex base grease, and the tribological performances were evaluated by four-ball friction and wear tests. The experimental results are given in Table 4.

Table 4. The EP, AW and FR Performances of Sb/ZnDTC with MoDTC in Calcium Sulfonate Complex Grease				
	Friction and Wear Test (40Kgf, 1200rpm, 75°C, 60min.)		EP Test	
	Wear Scar,, mm	Average Friction Coefficient	LNSL, Kgf	Weld load, Kgf
Calcium Sulfonate Complex Base Grease	0.375	0.098	100	315
+ 3.0% Sb/ZnDTC	0.478	0.089	100	620
+ 1.0% MoDTC	0.405	0.064	139	400
+ 3.0% Sb/ZnDTC + 1.0% MoDTC	0.375	0.068	139	620

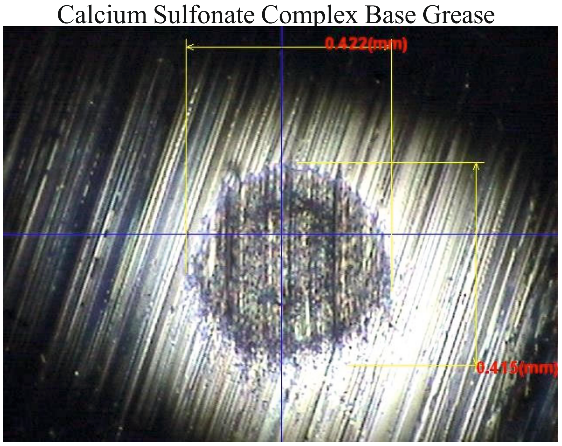
It is evident from Table 4 that, in the calcium sulfonate complex grease, the combination of Sn/ZnDTC with MoDTC can achieve excellent EP, AW and FR performances simultaneously. The wear scars and the friction coefficients of the greases with and without Sb/ZnDTC and/or MoDTC are shown in Figures 2 and 3.



Calcium Sulfonate Complex Base Grease



Base + 3.0%Sb/ZnDTC


Base + 1.0% MoDTC

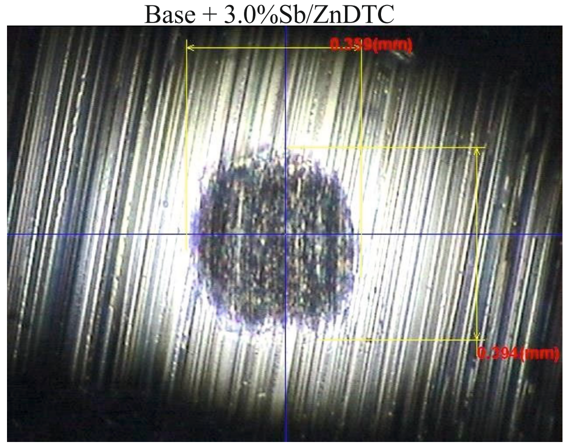

Base + 3.0%Sb/ZnDTC + 1.0% MoDTC

Figure 2. Four-ball wear scars by calcium sulfonate complex greases

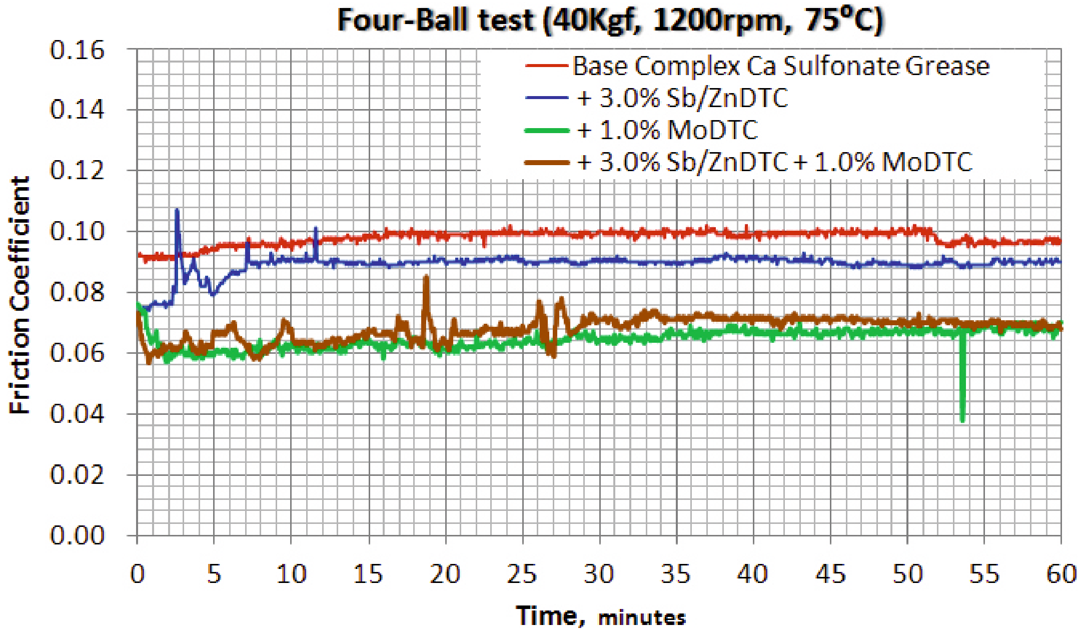


Figure 3. Friction coefficients of the calcium sulfonate complex greases by four-ball test

It can be seen that, in the calcium sulfonate complex grease, the combination of Sb/ZnDTC and MoDTC could achieve excellent FR and AW performances, while keeping the high EP properties (weld load, from 250Kgf to 620Kgf).

3.4 MTM Stribeck curve

3.0% Sb/ZnDTC was added into the calcium sulfonate complex base greases, and the frictional properties under slide/roll conditions were evaluated using Mini Traction Machine (MTM). The Stribeck curves at different temperature are shown in Figure 4.

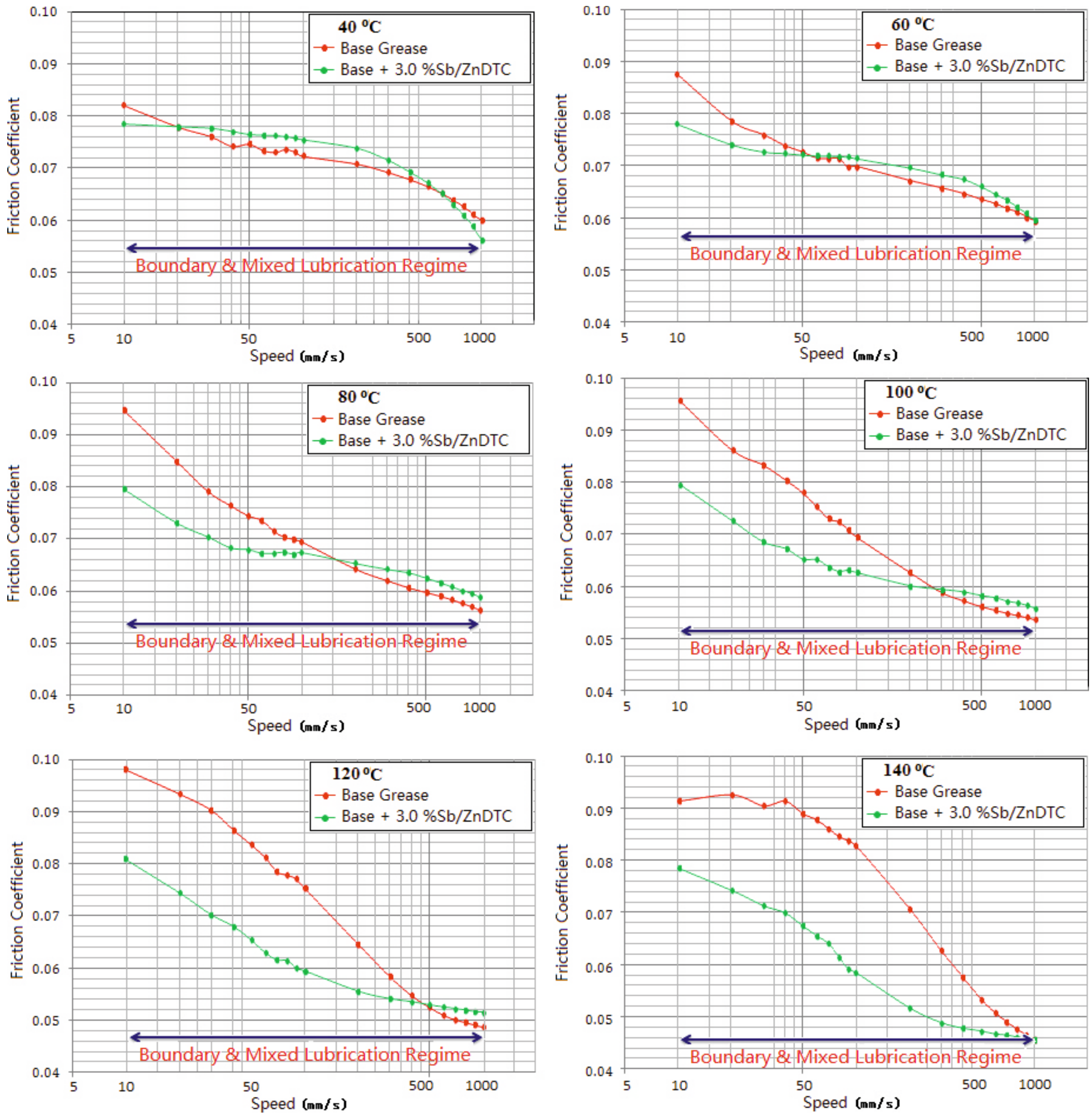


Figure 4. MTM Stribeck curve of the calcium sulfonate complex grease with and without Sb/ZnDTC at different temperature

From Figure 4, it could be found that, with the increase of the temperature, the friction-reducing efficiency by Sb/ZnDTC becomes higher and higher under boundary (10-100mm/s) and mixed (100-1000mm/s) lubrication regimes. Especially at middle and high temperatures (⩾100ºC), Sb/ZnDTC can reduce the grease's friction coefficient under almost whole boundary and mixed lubrication regime (10-1000mm/s).

3.5 Anti-oxidation performance

PDSC was employed to evaluate the antioxidation performance of Sb/ZnDTC in lithium complex, polyurea and calcium sulfonate complex base greases. The oxidation induction times at different temperature are given in Table 5.

Table 5. The Antioxidation Performances of Sn/ZnDTC in Greases			
	PDSC Test, Oxidation Induction Time, min.		
	180ºC	200ºC	210ºC
Lithium Complex Base Grease	82.7	23.9	9.3
+ 3.0% Sb/ZnDTC	190.2	46.4	22.5
Polyurea Base Grease	54.8	15.9	5.9
+ 3.0%Sb/ZnDTC	251.0	75.6	22.3
Calcium Sulfonate Complex Base Grease	9.8	/	/
+ 3.0% Sb/ZnDTC	86.0	/	/

It is evident from Table 5 that, Sb/ZnDTC possesses excellent antioxidation performance in all these three greases, which increases the oxidation induction times significantly. Due to the chemical characteristics as dithiocarbamate derivative, Sb/ZnDTC serves as a hydroperoxide decomposer. The PDSC oxidation diagrams of the polyurea greases with and without Sb/ZnDTC are illustrated in Figure 5. It shows in Figure 5 that, Sb/ZnDTC could increase the OIT of the base polyures grease more than 3.5 times, which demonstrates Sb/ZnDTC's outstanding antioxidation capacity in grease.

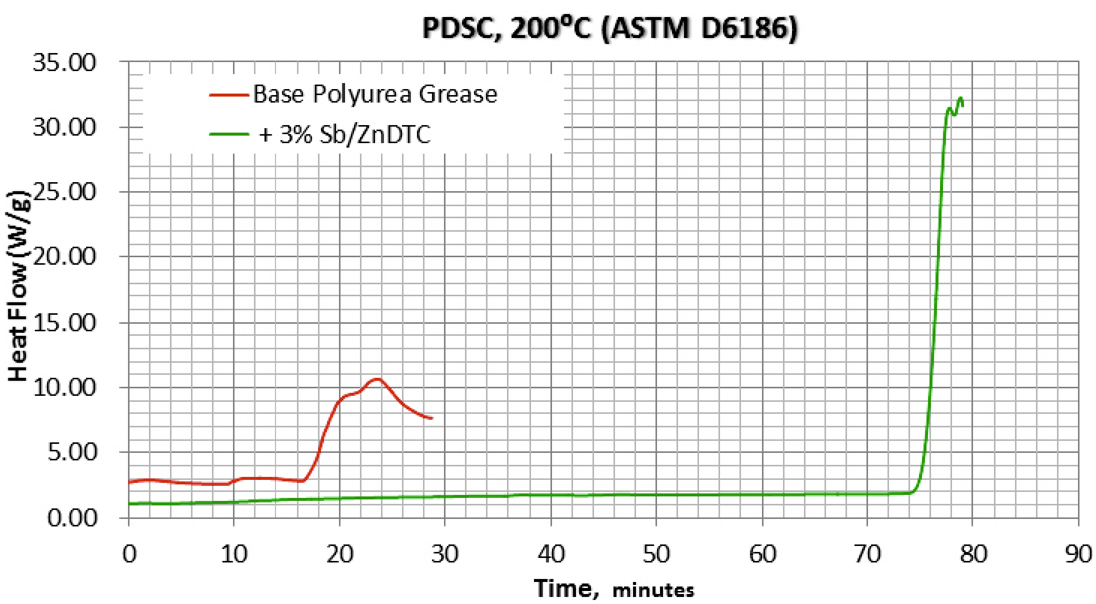


Figure 5. The antioxidation performance of Sb/ZnDTC in polyuria grease

4 CONCLUSIONS

(1) The di-metal salt of dithiocarbamate (Sb/ZnDTC) by *in situ* synthesis possesses excellent EP, good AW, but no FR performances in base oil;
(2) Sb/ZnDTC exhibits good EP performances in lithium complex, polyurea and calcium sulfonate complex greases.
(3) The combination of Sb/ZnDTC and molybdenum dialkyl dithiocarbamate (MoDTC) as AW and FR additive, could give a balanced overall performances in grease with high EP and excellent FR/AW characteristics.
(4) The MTM (Mini Traction Machine) Stribeck curves indicates, Sb/ZnDTC could effectively reduce

the friction coefficients under boundary and mixed lubrications in calcium sulfonate complex grease, especially at high temperature.

(5) The PDSC (Pressure Differential Scanning Calorimetry) oxidation test proves that Sb/ZnDTC is an excellent antioxidant in greases as hydroperoxide decomposer.

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Development of Extreme Pressure Greases based on a novel ecofriendly Extreme Pressure Additive.

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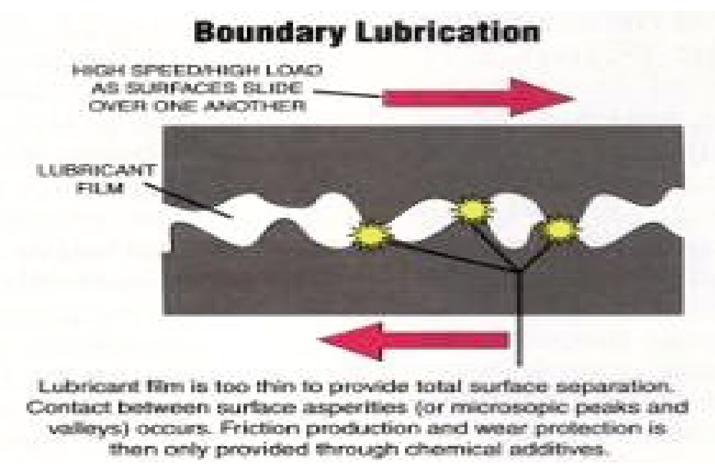
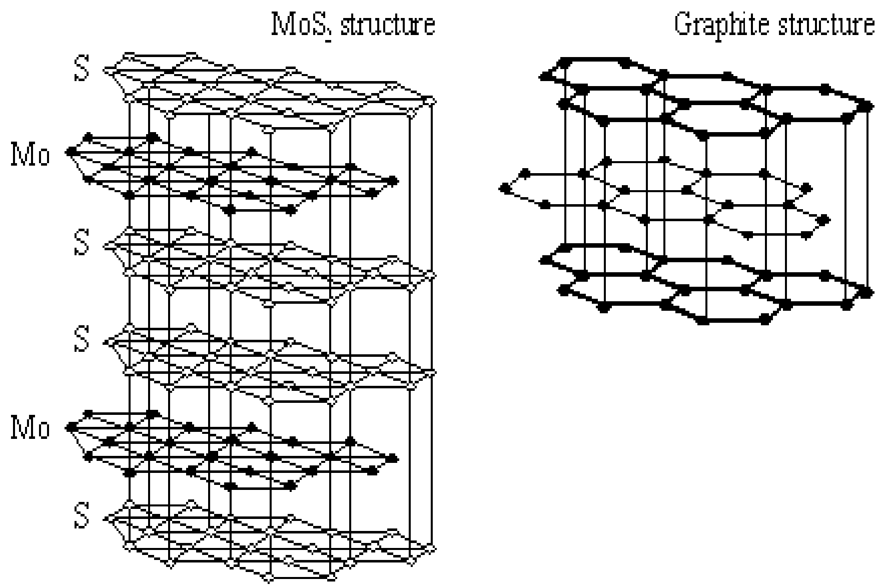
Introduction:

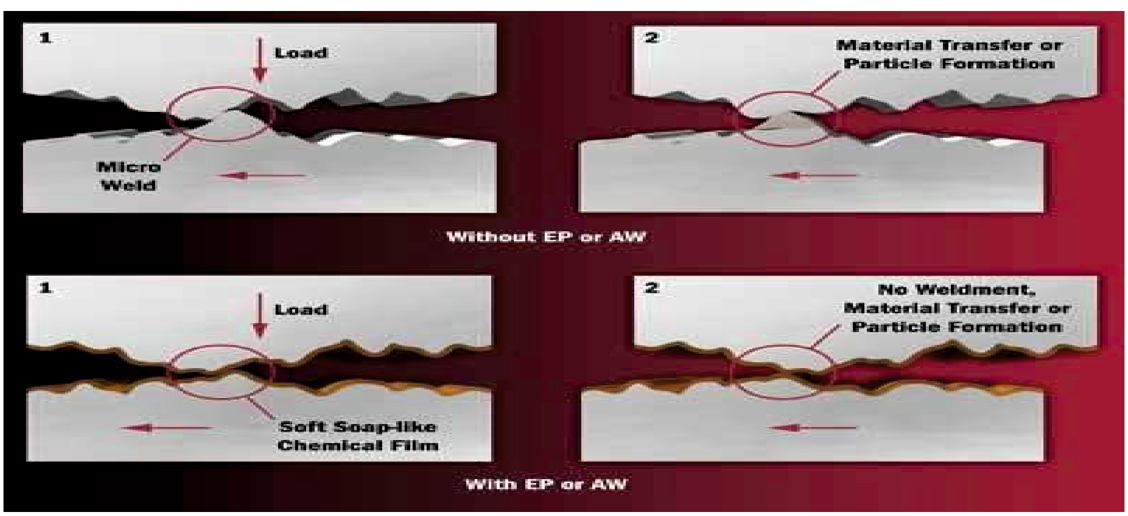
Greases used in many of the industrial and off highway machinery are expected to perform in most demanding situations. The machineries are working under very highand shock load conditions, high temperature and water prone environments. In order to protect the machine elements and moving parts, a grease is expected to sustain and perform by offering the required extreme pressure and anti wear characteristics. Generally such high performance products are formulated with special additives, solid lubricants etc.

Extreme Pressure & anti wear properties are obtained in grease formulations by the useof Chemical additives such as Sulphurised Fats & Fatty acids, Sulphurised Isobutylenes, Metal Dithiophosphates, Metal Dithiocarbamates, Amine Phosphates, Polysulphide compounds and many Solid lubricant powders like Graphite, Molybdenum disulphide and Polytetrafluroethylene(PTFE), Boron nitride etc.

These additives and solid lubricants are used alone or in combination with one another to effectively achieve the required extreme pressure & anti wear properties for the greases. The chemical additives mainly act by modifying the contacting surfaces with a film of reactive products generated at high working pressure and temperatures during elasto- hydrodynamic & boundary conditions. On the other hand the solid lubricants like graphite and Molybdenum disulphide have hexagonal crystal structure and have lubricity mechanism that largely relies on the formation of very strong and flexible layers that slide over one another under stress. The effectiveness of these solid lubricants is greatly influenced by their purity, particle size and surface area.







There is a tremendous pressure on the grease formulators to develop cost effective andhigh performing products to meet the ever increasing demand from the end users. The use of traditional and high performance additives, while offering the required performance characteristics, may increase the cost of products. Many solid lubricants like MoS2, Boron nitride are cost prohibitive and have availability issues.

Most of these additives and solid lubricants (except probably the Graphite) are environmentally very sensitive. The current and future requirements calls for managing the maintenance cost of the machinery and the disposal cost of used lubricants within the acceptable and sustainable levels. This has led to grease formulators to look for alternative, cost effective, better or equally performing and environmentally safe/ benign chemicals or compounds for use as extreme pressure and anti wear agents.

In this context our Company's Applications Research Laboratory has undertaken a study for the development of Lithium Soap and Sulphonate Complex thickener based extreme pressure greases with required EP and antiwear characteristics using a chemical compound **(designated as N-CC**) which can reduce the ultimate cost of the lubricant (grease), while the used product's disposal cost is minimized.
The greases developed using this novel compound were evaluated for various properties and the results are presented.
The study presented in this paper relates to the evaluation of effectiveness of such a chemical compound to offer the required extreme pressure and anti wear properties. At the same time the effect (synergistic or antagonistic) of such additive on the other important properties of the grease is also evaluated.

Experimental methods:

A. Sample preparation:

Samples of base greases were prepared for the following thickener systems using mineral base oil of ISO VG 220 viscosity using the conventional methods known for the manufacture of greases.

Lithium soap
Lithium Complex soap,
Lithium-Calcium soap and
Sulphonate Complex thickeners

The above base greases were used for formulating extreme pressure & anti wear greases using the chemical compound under investigation **(at the treat rate of 3%)** withother required additives for providing anti oxidant, anti rust protection in NLGI 2 consistency.
The above formulated greases & the greases formulated with conventional additives {**Sulphurised isobutylene (2%) & MoS2 (3%)**} were evaluated for tribological characteristics and compared.

B. Evaluation of formulations:

In order to evaluate the tribological properties like wear, friction and load carrying abilitythe following experimental procedures were used.

Wear preventive characteristics of greases using four ball wear test:

A well known test to characterize the ability of the lubricant to prevent wear is to determine the wear scar diameter using a four ball test machine. In this method one steel ball is rotated against three stationary balls kept immersed in the sample under study. We have conducted this test on all the grease samples using the followingconditions.

1. Speed = 1500 RPM
2. Load= 400N
3. Temperature= 75 Deg C
4. Time= 1 hr

At the end of the 1 hr test, diameter of the scar produced on all the three balls is measured. The average scar diameter obtained is a measure of wear preventive property of the grease.

Friction reduction characteristics of greases using SRV Friction & Wear Tester:

One of the most common tests used to study the friction reduction characteristics of lubricants is to evaluate the Coefficient of Friction in a SRV machine. In this test the ability of a lubricant to reduce friction between two contacting surfaces,(example a ball on disc) when the lubricant is held in between the specimens, is measured by determining the Coefficient of Friction under a set of conditions (load, oscillation, frequency and temperature).This test is conducted for 2 hrs and the minimum and maximum coefficient of friction data obtained is used to characterize friction reduction and thereby wear prevention capacity. The following test conditions were used while determining the coefficient of friction of individual samples.

1. Specimen: Steel ball on steel disc
2. Load: 200N
3. Frequency: 50 Hz
4. Amplitude: 1.00 mm
5. Temperature: 50 Deg C
6. Duration: 2 hrs

Extreme Pressure property by four ball weld load test:

One of the most widely used and accepted tests to characterize the extreme pressure or load carrying capacity of high performance industrial greases is to evaluate the four ball weld load. In the present study we have used this test to evaluate the four ball weld load of all the greases. In this test one stainless steel ball kept in a spindle attached to a motor is rotated against three stationary balls kept immersed in the lubricant in a ball potassembly. Load is applied on the three balls from below. Test is conducted as per IP239 method.(Speed = 1450 rpm; Time= 60s) As the applied load is increased, at a particular load the four balls weld together when the lubricant loses its load carrying capacity. This load is declared as the weld load for the particular lubricant. The values obtained for all the greases are used to differentiate the extreme pressure property of the greases taken for the study.

The formulated greases with the chemical compound under investigation were also evaluated for oxidation resistance, corrosion resistance properties using the well known techniques like bomb oxidation stability test(ASTM D 942) and Emcor anti corrosion test (IP 220) respectively to understand the synergistic or antagonistic effects of the selected additive under investigation.

Results and discussions:

Characteristics of the formulated Greases:

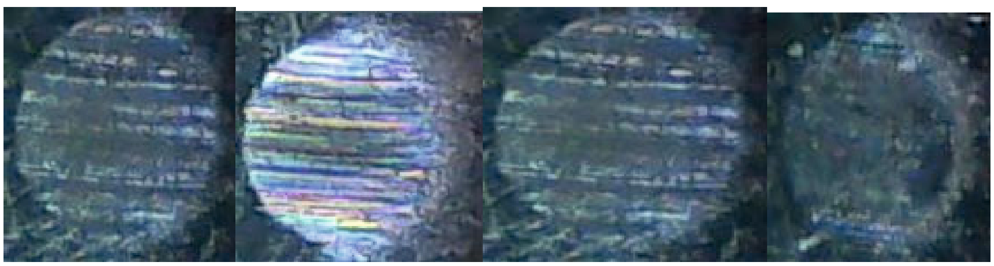
The following are the important characteristics of the greases formulated with thechemical compound (**N-CC**) under investigation.

Property	**Li Grease with N-CC**	**Li CPx Grease with N-CC**	**Li-Ca grease withN-CC**	**Sul Cpx Grease with N- CC**	**Test method (ASTM/IP)**
Worked Penetration(60X)	278	282	280	295	D 217
Worked Penetration(10^5 X)	306	312	306	325	217
Drop Point, Deg C	198 (ASTM D 566)	285 (ASTM D 2265)	194 (ASTM D 566)	330 (ASTM D 2265)	
Four Ball weld load, kg	400	355	400	355	IP 239
Wear Scar dia, mm	0.52	0.535	0.55	0.51	D 2266
COF by SRV Min/ Max & Avrg	0.119/0.178 (0.149)	0.102/0.116 (0.109)	0.114/0.168 (0.141)	0.103/0.117 (0.110)	¤
Emcor anti rust test, Rating	0,0	0.0	0,0	0,0	IP 220
Oxidation stability, pressure drop, PSI	6	6	7	7	D 942
Last non-seizure load, kg	63	80	63	63	D 2596

¤ Test Condition for SRV: 200 N/ 80 Deg C/50 Hz/2.00 hrs/Amp:1

The new additive (Chemical Compound) has no adverse effect on the basic properties of the developed greases like worked penetration, prolonged worked penetration, dropping point, oxidation stability, Emcor anti rust test and Last non-seizure load. This is described in the above table in all the types of greases selected for investigation.

WEAR SCAR DIA			
Lithium EP	**Li Compx EP**	**Li-Ca EP**	**Supl Compx EP**
0.520 mm	**0.535 mm**	**0.55 mm**	**0.51 mm**

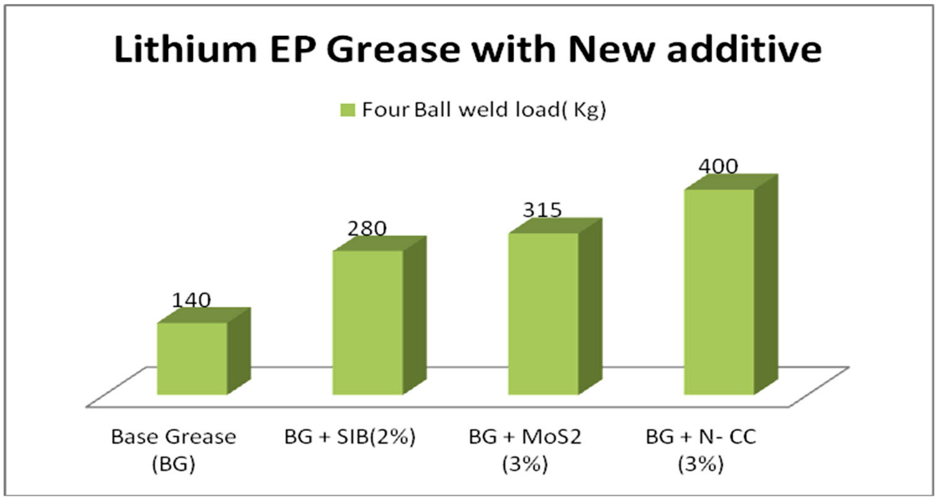


EMCOR RUST TEST				
	Lithium EP	**Li Compx EP**	**Li-Ca EP**	**Sulph Compx EP**
Ratings	**0,0**	**0,0**	**0,0**	**0,0**

<u>Lithium EP Grease:</u>

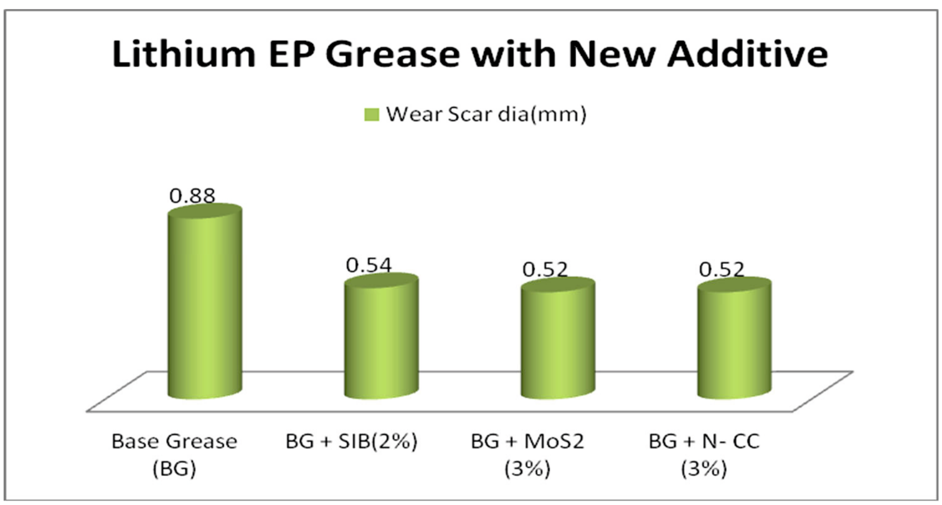
1. <u>Extreme Pressure Property:</u>

The extreme pressure property of the developed grease when tested as per IP 239 method has shown comparatively higher weld load as against the greases made with both SIB & MoS_2 individually. The weld load of 400 Kg as obtained by IP 239 method is good enough to perform as an EP grease in most of the industrial applications.



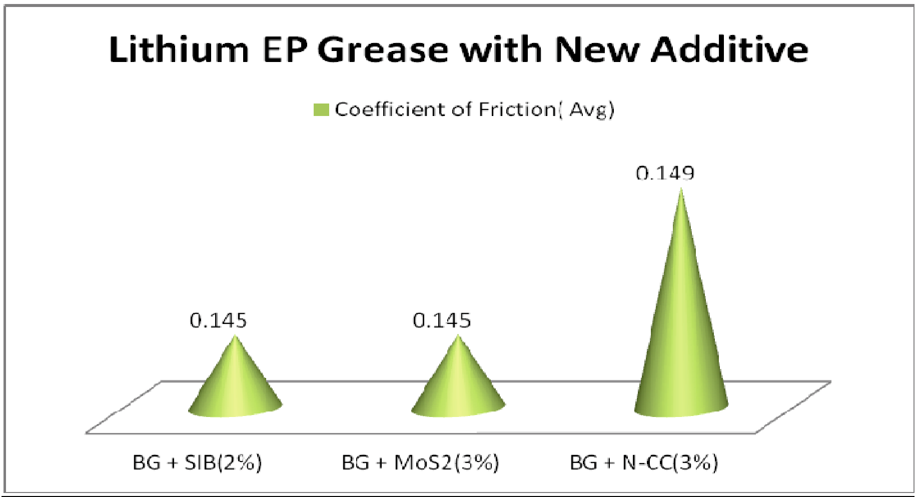
2. Anti wear Property:

The comparative test results obtained for the wear scar dia when done as per ASTM D 2266 method indicate almost similar value for both greases based on MoS2, SIB and the new grease. The EP, antiwear grease based on the new additive is as good as those based on the conventional additives and substantial wear reduction is obtained compared with base grease.



3. Coefficient of friction:

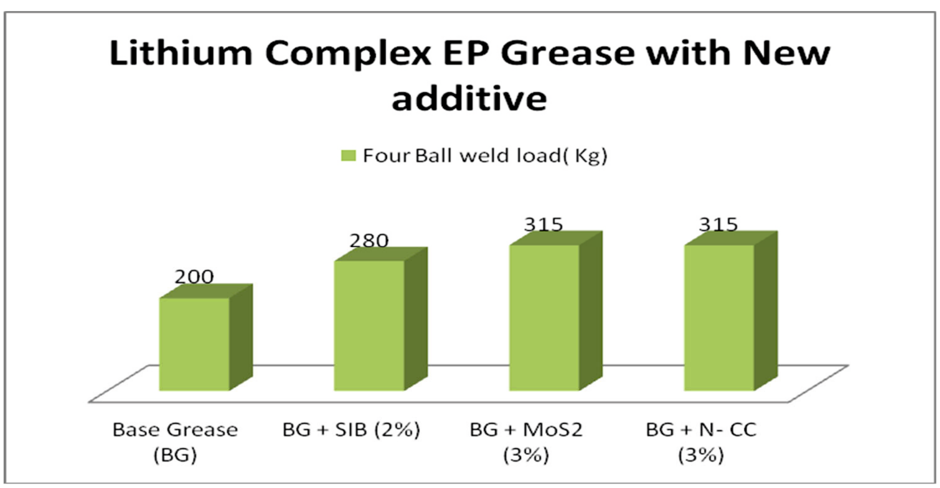
When the COF is measured using SRV friction & Wear Test machine the values obtained for conventional additive based greases & the new additive are more or less similar with marginally better result for grease based on SIB & MoS2



Lithium Complex EP Grease:

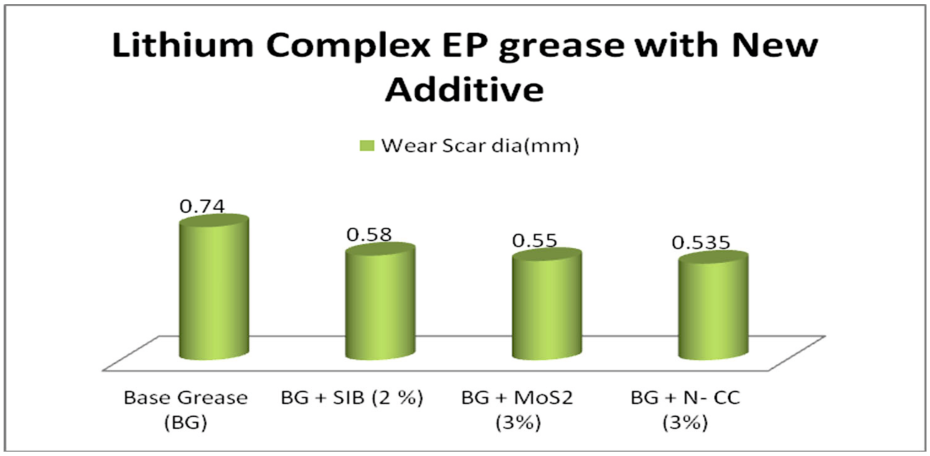
1. Extreme Pressure Property:

The extreme pressure property of the developed grease when tested as per IP 239 method has shown higher weld load as against the base grease and the one made withconventional SIB additive system, while the results obtained for grease made with MoS2 solid lubricant and the one made with additive under investigation is similar. This indicates that the performance of this additive system in Lithium Complex grease is better or comparable with other additive systems. However its effectiveness is slightly less pronounced when compared to Lithium Base grease.



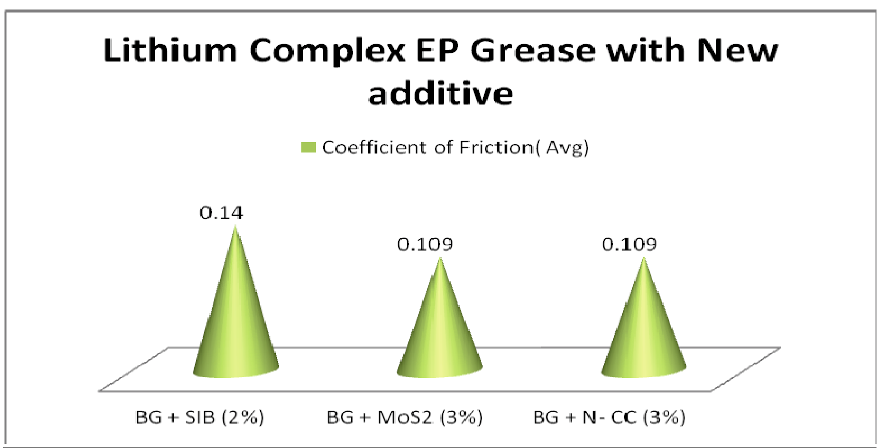
2. Anti wear Property:

In Lithium Complex grease the effectiveness of AW property for the new additive is more or less comparable to that based on other additive systems while the new additivehas substantially reduced the wear compared to base Lithium Complex Grease.



3. Coefficient of friction:

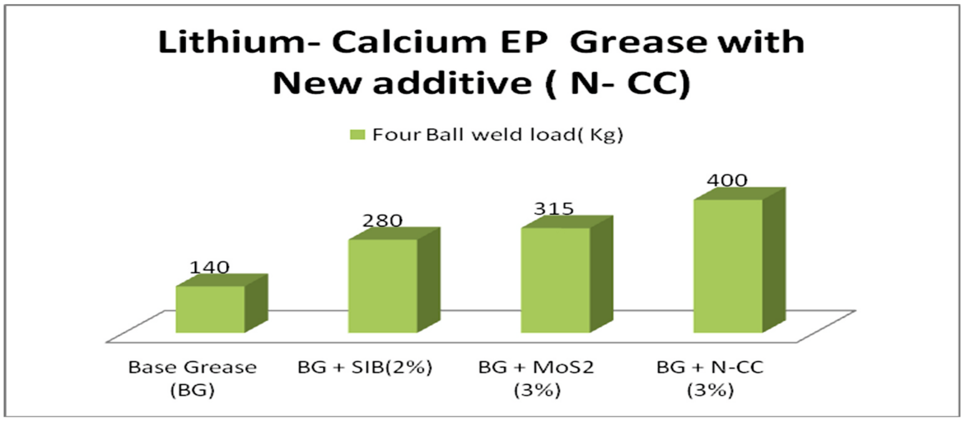
The frictional coefficient as obtained in SRV test machine indicates a better friction reduction characteristics with new additive system as compared to the result obtainedfor SIB based grease and comparable with MoS2 based grease.



Lithium - Calcium EP Grease:

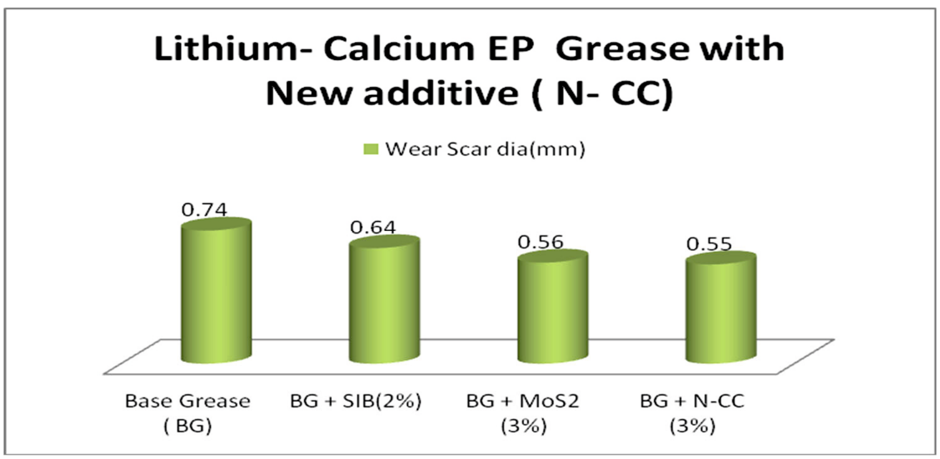
1. Extreme Pressure Property:

The extreme pressure property of the developed grease when tested as per IP 239 method has shown comparatively higher weld load as against the greases made with both SIB & MoS2 individually. The weld load of 400 Kg as obtained by IP 239 method is good enough to perform as an EP grease in most of the industrial applications. It is also inferred that the weld load performance of the grease with new additive in Li –Ca thickener system is as good as that in Li soap thickener system.



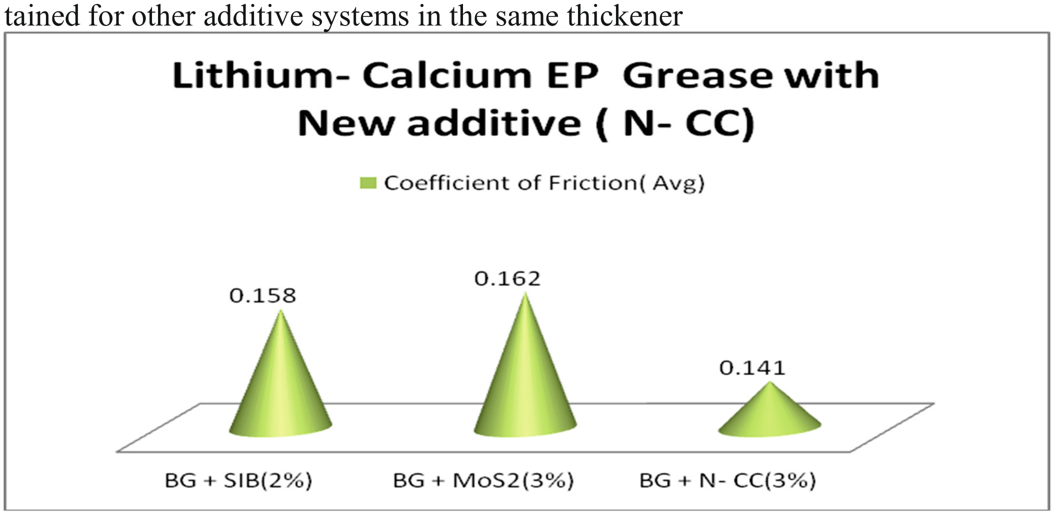
2. Anti wear Property:

The anti wear property of the greases based on both MoS2 & New additive are similar and better than that for the grease based on SIB.
However the new additive has substantially reduced the wear when compared to base grease.



3. Coefficient of friction:

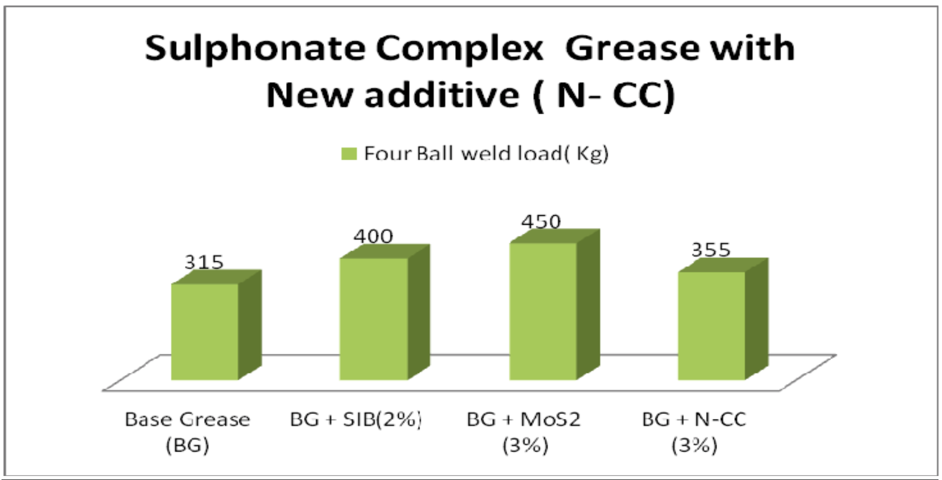
When the Coefficient Of Friction is measured using SRV friction & Wear Test machine, the values obtained for new additive in Li-Ca thickener grease is much better compared to those obtained for other additive systems in the same thickener



Sulphonate Complex Grease:

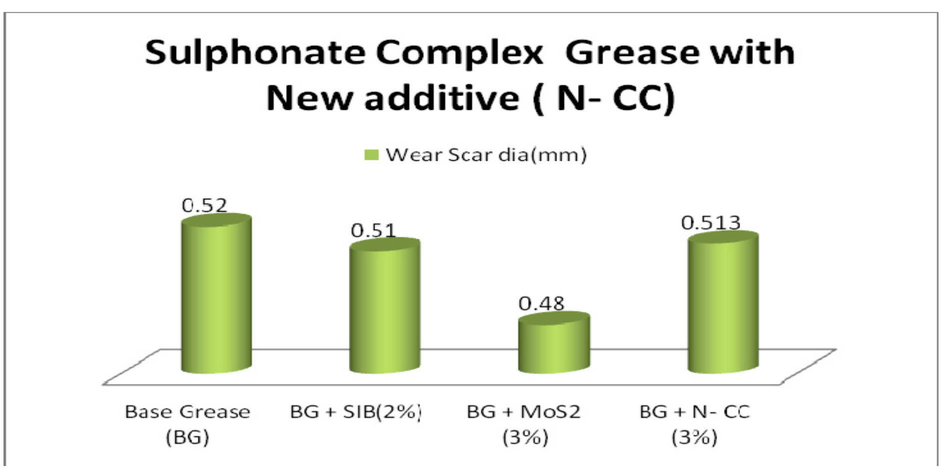
1. **Extreme Pressure Property:**

The Sulphonate Complex Grease as such inherently possess good EP and anti wear property associated with it due to Calcite formation. We have evaluated the effectiveness of the new chemical compound for further enhancing the weld load characteristics. It has been observed that the new additive could only marginally increase the weld load. However the conventional additive systems like MoS2 and SIB could give greases with higher weld load values indicating that the new additive may not be the choice for increasing the performance of Sulphonate Complex Greases in terms of weld load characteristics.



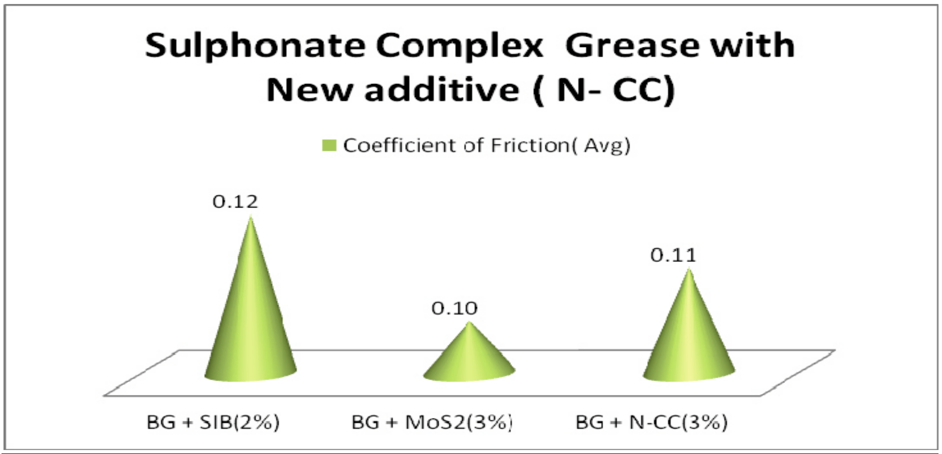
2. **Anti wear Property:**

The new additive system does not offer any substantial improvement over base Sulphonate grease in wear reduction while the addition of MoS2 could offer a slightlybetter wear reduction.



3. Coefficient of friction:

The frictional coefficient as obtained in SRV test machine indicates not much improvement by using the new additive in Sulphonate complex thickener. However there is no negative effect by this chemical compound.



Cost Comparision:

In the foregoing examples of our investigation of the new chemical compound in various types of greases, it is observed that this new additive is either as effective or better than the currently used liquid and solid additives. While comparing the net additive treat cost of existing and new additives in the following usage levels, the effective cost of the grease can be brought down.

Additive	SIB	MoS2	N-CC
Treat rate, %	2	3	3
Nett Additive treat cost	Higher	Highest	Lowest

Eco friendly aspect of the new additive:

The designated additive N-CC is a chemical compound which sans heavy metals like Lead, Antimony and free from Chlorine. It is a by product obtained from a natural resource having considerable potential to be a ecosafe alternative for the presently available additives and chemicals.

Conclusions:

1. A new Chemical Compound as an extreme pressure additive in formulating EP antiwear grease in various types of greases is provided in this study.

2. The formulated greases in various types of thickeners have shown acceptable characteristics, and there is no antagonistic effect on the performances of other additives like antioxidant, anti corrosion etc.

3. The performance of the greases formulated with this new additive is evaluated through well known test for extreme pressure, antiwear and friction reduction properties like Four ball weld load, Wear Scar Dia measurement by Four Ball Test machine and Coefficient Of Friction measurement by SRV Test Rig.

4. The effectiveness of this additive in improving the EP and AW characteristics in Lithium, Lithium Complex & Lithium – Calcium thickener based greases is well demonstrated.

5. This additive is more effective in both Lithium and Lithium- Calcium thickener greases, equally effective in Lithium Complex thickener based greases when compared to the conventional additives like Sulphurised isobutylene (SIB) and MoS2.

6. In Sulphonate Complex thickener based grease the effect of this additive in improving the EP and AW properties is not well pronounced, while the other additives makes a better choice. However this new additive did not have any negative effect on these properties in Sulphonate Complex thickener greases.

7. Considering the lowest nett additive treat cost, this additive qualifies as a promising substitute for the currently available additive systems.
8. In the Environment friendly score the new additive has potential to be a Eco safechoice.

9. Further studies are on for the full commercial exploitation of the new chemicalcompound in grease formulations.

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