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A Cursory Look at the Effects of Free Acid and Alkali on 12-Hydroxy Stearate Grease

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Abstract

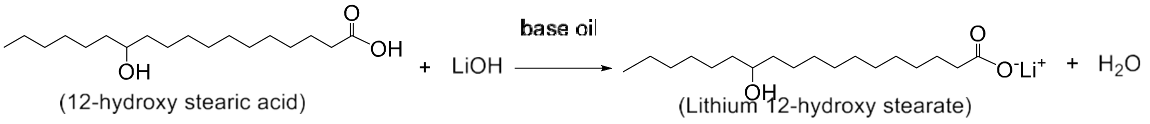
This paper reports on how free acidity and alkalinity affects the performance properties of 12-hydroxystearate grease. Specifically, a batch of acidic 12-hydroxystearate grease was prepared. A portion of the acidic grease was made alkaline by the addition of lithium hydroxide. The acidic and alkaline greases were treated with two additive packages containing extreme pressure, antiwear and corrosion inhibiting components. Standardized ASTM bench tests were then used to compare differences in additive response.

Introduction

The manufacturing process for soap-based greases typically involves the in-situ production of the soap thickener in the lubricant base stock. The process comprises thedissolution of either fatty acids or triglycerides commonly referred to as vegetable oil and fats in the base fluid. Metal hydroxides such as calcium hydroxide or lithium hydroxide are then added to react with the fatty acid or triglyceride to form insoluble metal salts that are commonly referred to as “soap”. This reaction is followed by a heating and cooling process that reforms the soap molecules into a mesh framework of fibers with an appearance similar to steel wool. This framework holds the base fluid within its pores and cavities to shape the grease [1-2].

Most of today’s soap-based greases are made using lithium 12-hydroxystearate as their primary thickener component. The main benefit of using lithium 12-hydroxystearate is high thickening efficiency. Another important advantage is the ability of lithium 12- hydroxystearate greases to maintain their consistency after an applied mechanical stress such as working, shearing or rolling [2].

As depicted in equation 1 and 2 below, the production of lithium 12-hydroxystearate grease involves the reaction of lithium hydroxide (LiOH) with either 12-hydroxy stearic acid (12-HSA) or hydrogenated castor oil (HCO) respectively:



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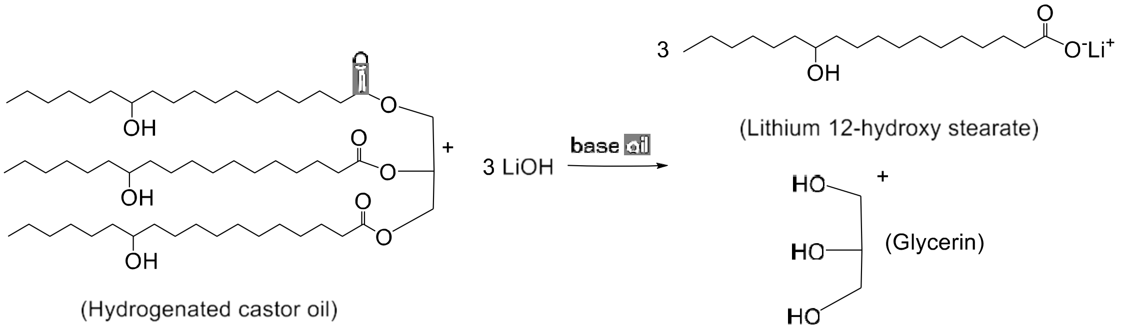


(2)

The preference in the industry is to produce lithium greases using a stoichiometric excess of LiOH [3-5]. This approach ensures complete conversion of the 12-HSA or HCO to the lithium soap that then leads to optimum thickening efficiency and mechanical stability.

The typical alkaline levels for lithium greases are in the range of 0.03 to 0.08 weight percent LiOH. Although these concentrations appear minimal, it is actually significant when the following factors are taken into account:

1. LiOH is a strong base that can react with many lubricant additives and alter their performance properties.
2. With a molecular weight of 23.95 grams/mole, LiOH has a molecular weight that is 10 to 25 times lower than most oil soluble lubricants additives. Thus on a molar basis, a LiOH content of 0.03 to 0.08 weight percent is equivalent to 0.5 to 2 weight percent of lubricant additive.

As a strong base, LiOH will react with weakly acidic additives in much the same manner as it does with 12-hydroxystearic acid to produce lithium soap thickener. Such additives include fatty acids, diacids, amine carboxylates, triazoles, mecapto-thiadiazoles and amine phosphates that are commonly used as corrosion inhibitors, friction modifiers and antiwear (AW) additives. These reactions will produce compounds with higher polarity and ionic character that will have limited oil solubility and stronger affinity to lithium soap fibers of grease. Thus, LiOH can in effect inhibit these additives from carrying out their function at the metal surfaces that they are intended to protect [6].

LiOH can also react with metal complexes such as zinc dithiophosphates (ZDDP) and antimony dithiocarbamates in metal exchange reactions. An example of this type of reaction was observed by Sivik and co-workers with LiOH and zinc dithiophosphate (ZDDP) [7]. In this study, phosphorus Nuclear Magnetic Resonance spectroscopy (^{31}P NMR) was used to analyze ZDDP in an acidic lithium 12-hydroxystearate grease containing no residual LiOH and alkaline lithium 12-

hydroxystearate grease containingresidual LiOH. The analyses showed that the ZDDP in the acidic grease did not undergo significant chemical changes. However, significant changes were detected in the alkaline grease. The changes involved a decrease in the level of neutral ZDDP, anincrease in the level of overbased ZDDP and the formation of lithium dithiophosphate. Sivik proposed that these changes took place via a metal exchange mechanism in which the zinc in neutral ZDDP exchanged with lithium in lithium hydroxide to form lithium dithiophosphate, zinc oxide and water. The resulting ZnO then reacted with neutral ZDDP to produce overbased ZDDP.

Besides chemical reactivity, LiOH can affect grease performance as a hygroscopic material. LiOH can adsorb water and contribute to the water content of greases. As perwork reported by Kaperick, trace amounts of water can have detrimental effect on the copper corrosion properties of lithium greases formulated with certain EP additives [8]. LiOH is also a water soluble electrolyte that can increase the ionic activity of water thatcomes in contact with lithium greases. The increase in the ionic activity of the water could increase the potential for rusting to occur at steel and grease interfaces [9].

The objective of this paper is to demonstrate the effects of residual fatty acid and LiOH on the properties of lithium greases using standard industry test methods and to provideevidence that both materials are factors that should be accounted for in the formulation and production of lithium greases.

Experimental

General Method**:** The approach for this study involved the production of a single acidicbase grease batch by in-situ reaction of hydrated lithium hydroxide ($LiOH \cdot H_2O$) with stoichiometric excess of 12-HSA. The alkaline base grease was then prepared by theaddition of $LiOH \cdot H_2O$ to a portion of that acidic base grease batch. The intent of this master batch approach was to guarantee the physical and chemical similarities of the acidic and alkaline base greases.

The acidic and alkaline base greases were then treated with two different additive packages described in **Table 1** to produce two pairs of formulated greases that werecompared using ASTM standard test methods listed in **Table 2**.

Table 1: Description of Additive Packages used to Formulate Greases

Name	General Composition	Grease treat rate
Pack 1	ZDDP-based package containing sulfur EP additive and corrosion inhibitors	4.00 m%
Pack 2	Ashless sulfur/phosphorus (S/P) additive package	3.8 m%

Table 2: Test Methods for the Comparison of Formulated Acidic and Alkaline Greases

ASTM Method	Property	Conditions
D2266	4-Ball wear, scar diameter	1200 rpm; 40 kg; 75 °C; 1h
D2596	4-Ball EP, weld point	1770 ± 60 rpm; 27 ± 8 °C; 10-s duration; 10 kgf load steps
D4048	Copper corrosion	100 °C, 24h
D1743	Bearing rust	Distilled water; 52 °C; 24h

Manufacturing Equipment**:** Base grease was produced in pilot plant unit that consists of a covered and jacketed 5-gallon kettle. The kettle is operated at atmospheric pressure and is vented through a port on the lid cover that is connected to a condensation tank. The kettle is also connected with two addition tanks for controlled delivery of base oil and aqueous LiOH slurry and a hopper with slideway for the charging of solids such as 12-HSA. Agitation is accomplished with single-motion, anchor-style agitator with scraper blades and fixed vertical baffle attached to the bottom of the lid cover. Heating and cooling is 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 kettleis also connected to a second pump used to circulate the contents of the kettle through the colloid mill, to provide additional agitation, and to discharge the final product. The operation of the entire unit is computer controlled.

Manufacturing Procedure: The acidic base grease was produced using raw material feeds listed in **Table 3**:

Table 3: Raw materials used to produce acidic base grease

Raw Material	**Weight, kg**	**Weight Percent**	**Moles**
600 SUS Group 1 base oil	8.980	75.11	---
2500 SUS Group 1 bright stock	2.059	17.22	---
12-HSA	0.897 (as RCO_2^-)	7.50 (as RCO_2^-)	3.00
0.124 kg $LiOH \cdot H_2O$ in 0.615 DI water	0.020 (as Li^+)	0.17 (as Li^+)	2.95
Final Grease Batch	11.956	100.00	---

The manufacturing procedure involved the following steps:

1. Kettle was charged with 4.12 kg of base oil (37.3 wt% of total base oil charge)including the entire amount of bright stock.
2. Agitator was started and the kettle temperature increased to 80 °C.
3. All of the 12-HSA was charged into the kettle and melted.
4. The entire LiOH slurry charge was delivered into the kettle.
5. Kettle temperature was set to 102 °C until water condensation ceased and stabletemperature was obtained.
6. Temperature was increased to 120 °C and held 25 minutes to continuedehydration.
7. Kettle temperature was increased to 206 °C at a rate of about 1°C/minute andheld at this temperature for 10 minutes.
8. Kettle was charged with 2.09 kg of base oil (18.9 wt% of total base oil charge) over 15 minutes while the kettle temperature was decreased to 150 °C at a controlled rate of about 1°C/minute.
9. During the temperature quench, grease circulation was started at a kettletemperature of 180 °C.
10. Kettle temperature was held at 150 °C for 1 hour while the grease was milledusing 0.008 inch gap setting.
11. Kettle temperature was decreased to 80 °C and kettle was charged with 2.8 kg ofbase oil (25.4 wt% of total base oil charge) and milled for another 30 minutes.
12. Final base oil charge (18.4 wt% of total base oil charge) was added and grease was discharged from the unit.

The base oil viscosity, thickener content and free acid content of the acidic base greasewere 143 cSt at 40 °C, 7.8 wt% of lithium 12-hydroxystearate and 0.1 wt% of unreacted12-HSA respectively.
The alkali grease was prepared by dispersing 1.5 weight percent $LiOH \cdot H_2O$ into the acidic base grease using a SpeedMixer^{TM} (from Flack Tek, Inc.). One part of this alkaline grease was then blended with nine parts of the acidic base grease using Hobartmixer and milling through a colloid mill.
All greases were degassed before testing. Degassing was done in shallow pans placed in a vacuum oven held at 29 inches Hg. For the base greases, the oven temperature was held at 60 °C and the greases were kept in the vacuum oven for 1 day. For the formulated greases, the oven temperature was held at 80 °C and the greases were keptin the vacuum oven for 30 minutes. Basic characteristics of the degassed acidic and alkaline base greases are summarized in **Table 4** below:

Table 4: Base grease characteristics

Property	Test Method	Acidic Base Grease	Alkaline Base Grease
Free 12-HSA	ASTM D128	0.1 wt%	---
Free LiOH	Calculated	---	0.08 wt%
Penetration, 60 Strokes	ASTM D1403	292 mm/10	293 mm/10
Dropping Point	ASTM D2265	201 °C	201 °C

Results and Discussion

Antiwear (AW) and extreme pressure (EP) performance data is summarized in Figures 1 and 2 respectively.

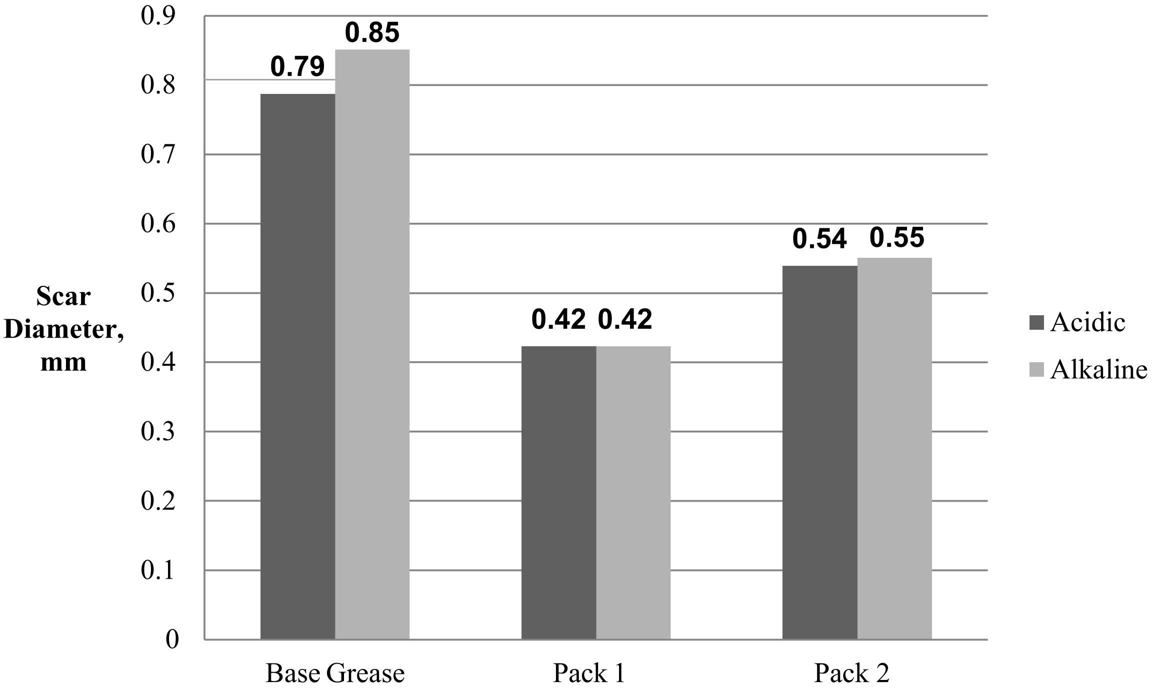


Figure 1: 4-Ball wear (ASTM D2266), 1200rpm, 40kg, 75 °C, 1h

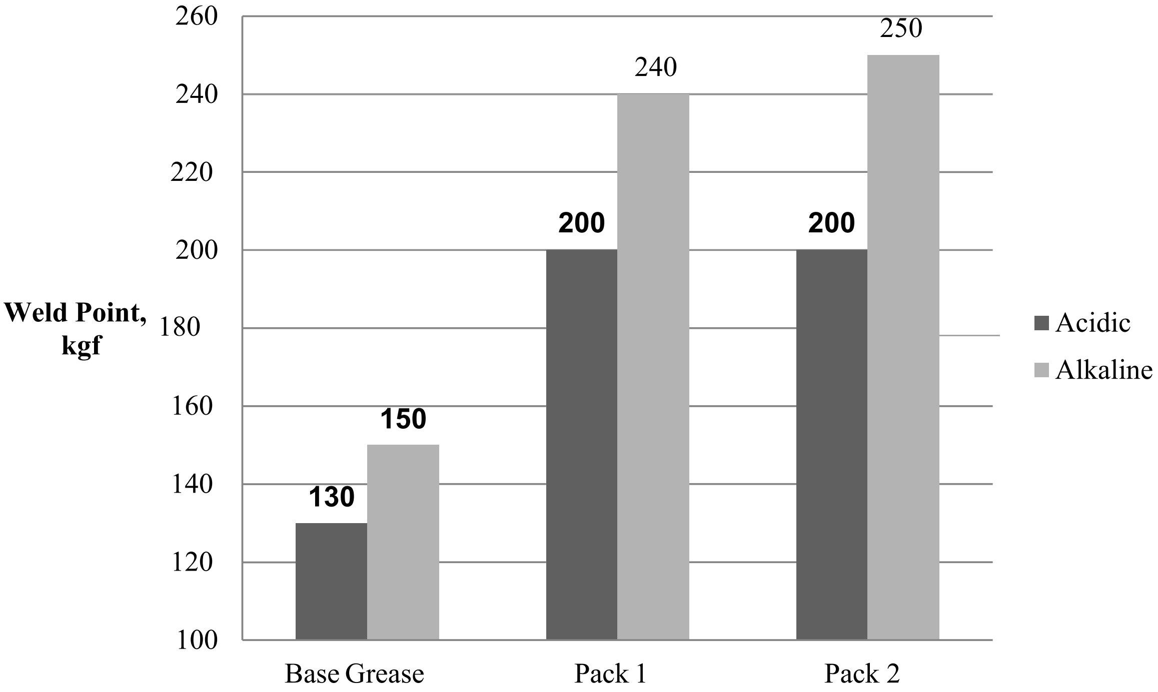


Figure 2: 4-Ball EP (ASTM D2596) using 10 kgf increment load steps

The data indicates that wear performance was not altered by the acid and alkaline content of the greases. On the other hand, the acidity and alkalinity of the greases significantly impacted EP performance. Specifically, the alkaline greases formulated with Pack 1 and Pack 2 gave weld points that were a load step higher than their acidic counterparts. These results suggest that the ability of sulfur EP (S-EP) additives to prevent welding was increased by LiOH and/or decreased by 12-HSA. It is widely accepted mechanism that S-EP additives prevent welding by the formation of shearable iron sulfide tribofilms at mating steel surfaces [10]. Thus, a plausible explanation for thehigher weld points produced by the alkaline greases is that LiOH promotes the formation of iron sulfide tribofilms by accelerating the breakdown of S-EP additives at mating steel surfaces. On the other hand, 12-HSA is fatty acid that is capable of adsorbing onto steel surfaces [11] and interfering with the formation of the iron sulfide tribofilms, thus providing a possible explanation for the lower weld points produced by the acidic greases.

Another factor that could explain the higher weld points produced by the alkaline greases is the interaction of phosphorus AW (P-AW) additives with LiOH. In the 4-ball EP test, both S-EP and P-AW additives are likely to be active at mating steel surfaces. However, the interaction of P-AW additives with LiOH and the soap thickener is expected to hinder the ability of the P-AW additives to diffuse to the mating surfaces [12]. The lack of surface competition with the P-AW additives indirectly increases the activity of S-EP additives and explains the higher EP performance produced seen by the alkaline greases. This explanation begs the question: why was wear performance not altered by the interaction of P-AW additives with LiOH? This could be explained by differences in test conditions. Specifically, the lower load of the 4-ball wear test decreases the activity of S-EP additives that then allow P-AW additives to function with reduce interference from the EP additives. The higher initial temperature of 4-ball wear test may also provide sufficient energy for the P-AW additives to overcome interactions that hinder their ability to reach mating surfaces. Additional work would be needed to further explore the validity of these proposed mechanisms.

As shown in **Figure 3**, alkaline greases formulated with Pack 1 and Pack 2 were both shown to be corrosive to copper:

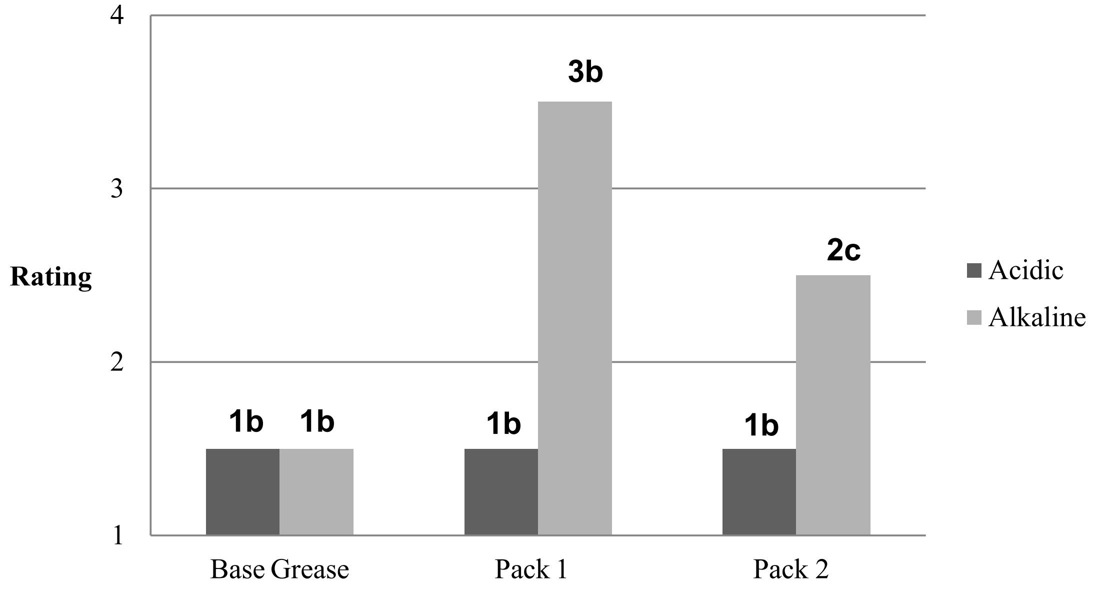


Figure 3: Copper Corrosion (ASTM D4048), 100 °C; 24h

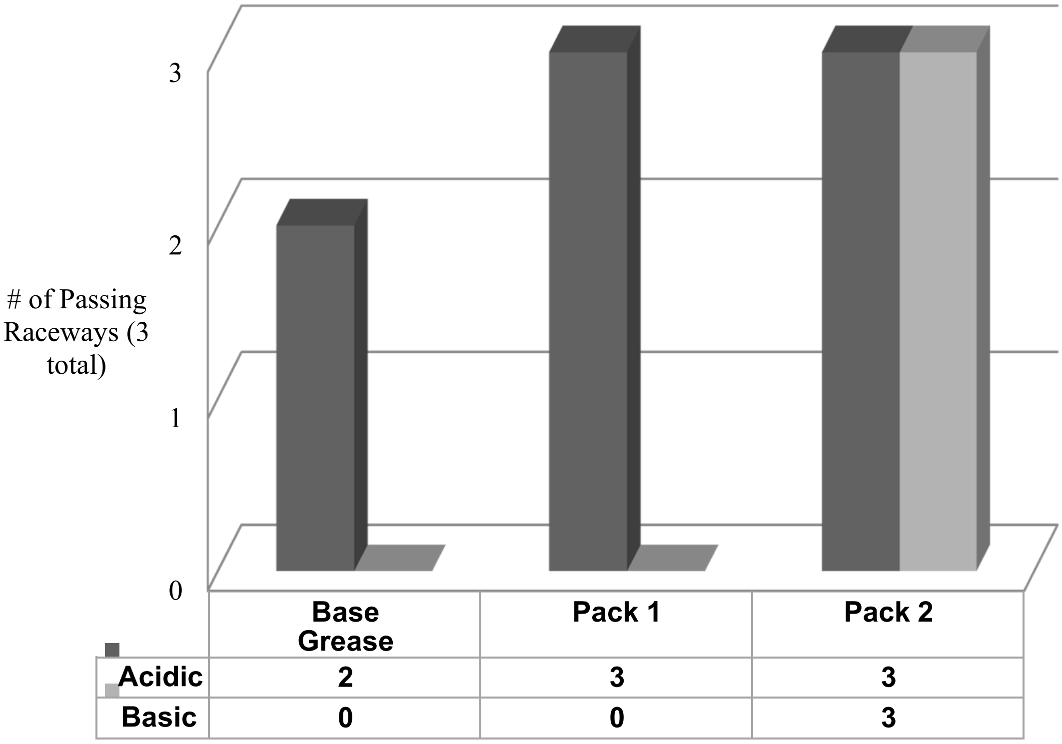
The 1b rating produced by the alkaline base grease indicates that the corrosivity of the formulated alkaline greases is due to the interaction of LiOH and additives in the packages. Considering the reactive nature of LiOH, it is possible that LiOH degrades the additives such as S-EP and P-AW additives to more corrosive species. Another plausible explanation is that LiOH converts the corrosion inhibitors to oil insoluble products that are more likely to adhere to soap thickener than to form protective barrierfilms on copper surfaces. It is also possible that this data is further support for one of the explanations of increased weld performance discussed above. Namely, if the interaction of the soap thickener with the P-AW additives does indeed allow more surface interaction by the S-EP chemistry, this phenomenon may also lead to the more aggressive attack of those same components towards copper as seen in these test results.

In regards to rusting, 12-HSA and LiOH are not expected to contribute to stainless steel corrosion. As previously mentioned in this paper, 12-HSA is a fatty acid that is capable of forming a protective barrier against corrosive species at steel surfaces [11]. With regard to alkaline species, stainless steels like 304 and 316 types are considered resistant to sodium hydroxide (NaOH) solutions at temperatures below 80 °C and up to the solubility limit of NaOH. Thus, the same is expected for LiOH [13].

As per the bearing rust test data summarized in **Figure 4,** the above assumptions held for 12-HSA but not LiOH. Specifically, both of the acidic greases passed the rust test with at least 2 of 3 raceways having no corrosion spot of 1.0 mm or larger in any direction. In the case of alkaline greases, the base grease and the grease formulated with Pack 1 failed the rust test with all three raceways having significant amounts of corrosion, which might be an indication that LiOH is actually corrosive to stainless steel.

To test the corrosivity of LiOH under ASTM D1743 test conditions, two modified tests were conducted using D1743 bearings treated with only base oil and exposed to eitherdistilled water or distilled water containing 0.09 weight percent LiOH. The results of thetwo tests did not support that LiOH was corrosive to the steel bearing in the absence ofthe soap thickener. Specifically, all three bearings exposed to distilled water had significant amounts of corrosion while the bearings exposed to water containing LiOH had two raceways with no visible corrosion spots and one raceway having only minor amount of corrosion. Thus, the corrosivity of the alkaline grease must be associated with the soap thickener or the combination of soap thickener and LiOH. This is not a surprise since both materials can contribute to the ionic activity of the test system and catalyze the redox reactions that are known to produce rust.

One possible explanation for the additional corrosivity may well be the negative interaction with corrosion inhibitors that are intended to prevent rusting. If these typically polar additives are either chemically (reaction to form another species) or physically (attraction to polar thickener) prevented from reaching the surface, they would be unable to carry out their intended function leading to excess corrosion underthese circumstances.



	Base Grease	Pack 1	Pack 2
■ Acidic	2	3	3
■ Basic	0	0	3

Figure 4: Bearing Rust (ASTM D1743), 52 °C; 48h

Conclusions

This initial study has demonstrated that free acid and alkali content of lithium soap grease can influence the performance characteristics in four-ball weld, copper corrosionand rust testing. While there was no clear evidence of effect on four-ball wear testing, itis possible that, under different conditions than those used in this study, wear performance might also be affected. Such an effect might also help support one or more of the mechanisms suggested above and should be part of future testing to furtherexplore the results seen in this study.

This work has provided evidence that free fatty acid or excess alkali content of fully formulated greases are factors that should be accounted for in the design and production of lithium soap grease.

References

[1] The Petroleum HPV Testing Group, "HIGH PRODUCTION VOLUME (HPV) CHEMICAL CHALLENCGE PROGRAM, Fatty Acids, Lithium & Calcium Salts used asLubricating Grease Thickeners, CATEGORY ANALYSIS AND HAZARDS CHARACTERIZATION", submitted to US EPA (www.petroleumhpv.org), February 9,2009, 5-6.

[2] "Challenging Conventional Wisdom: Is 12-hydroxystearic acid the best fatty acid for making high dropping point lithium grease?" *Lube 2014*, Issue No. 123, October 2014,18-20.

[3] Gilani, S. S. H. and Murray, D. W., *U. S. Patent 3,791,973*, Feb. 12. 1974.

[4] Ward, W. and Fish, G., "Development of Greases with Extended Grease and Bearing Life Using Pressure Differential Scanning Calorimetry and Wheel Bearing Life Testing" *NLGI Preprint*, NLGI 76th Annual Meeting, Tucson, AZ, June 13-16, 2009.

[5] Bertin, P. A.; and Bessette, P. A, "Biorefinery-Derived Long Chain Dibasic Complexing Agents for Lithium Thickened Lubricating Grease"", *NLGI Spokesman*,2015 79(5), 24-29.

[6] Canter, N. "Grease additives: Important contributors not be overlooked." *Tribology & Lubrication Technology*, December 2013, 28-29.

[7] Sivik, M. R. Zeitz, J. B., and Bayus D., "Interaction with Lithium 12-Hydroxystearate Grease, NLGI Preprint, NLGI 68th Annual Meeting, West Palm, FL, USA, October 28-31,2001.

[8] Kaperick, J.P. "Copper Corrosion in Grease - My Two Cents Worth", *NLGI Preprint*,NLGI 80th Annual Meeting, Palm Beach, FL, June 9-12, 2012.

[9] Kaperick, J.P., Aguilar, G. A., and Lennon, M. J. ""Rust Never Sleeps"- An Investigation of Corrosion in Grease Lubrication", *NLGI Preprint*, NLGI 82th AnnualMeeting, Coeur D'Alene, ID, June 9, 2015.

[10] Bovington, C. H., "Friction, wear and the role of additives" in *Lubricant Additives: Chemistry and Applications*, 2nd Edition, CRC Press, Rudnick, L. R. ed. (2009) 335.

[11] Buchweishaija, J., "Corrosion Inhibition of Carbon Steel by Amine-Fatty Acid in Acidic Solutions", Tanz. J. Sci., 29(1) 2003: 99-108.

[12] Aguilar, G. A., Kaperick, J.P., Lennon, M., and Pollard, G. "The Effect of Thickener on EP Additive Response", *NLGI Spokesman*, 2015 79(3), 12-21.

[13] "Corrosion Resistance of the Austenitic Chromium-Nickel Stainless Steels in Chemical Environments", THE INTERNATIONAL NICKEL COMPANY. INC., One New York Plaza, New York, N.Y. 10004, (1963) 15-16.

Enhancement of Performance Properties of Lithium Basegrease with addition of Polymer Blend

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Introduction:

Variety of polymer additives have been deployed in grease formulations to enhance its performance properties. Generally olefincopolymers (OCP) or ethylene-propylene diene type polymers are used . Introducing polymers into the grease can boost the properties of the grease such as mechanical stability, water resistance, adhesion, tackiness, high temperature stability, oil bleeding properties. The structure of the polymer including its molecular weight and MWD has a significant impact on grease properties. The soap moiety of a grease is a metallic salt of a long chain fatty acid (Li 12-hydroxy stearate). The soap thickener form interlocked fibers in the grease. It is true thatpolymers which can augment the additional three dimensional networks in grease demonstrate the best results in improving mechanical properties of the grease.

Background

There has been a continuous demand on increased performance properties of multipurpose grease with a cost-effective way . It has been a challenge for grease formulators to come out with an adequate solution. Lubricant rheology plays an important role in controlling energy losses in hydro dynamically lubricated contact surfaces, the situation becomes aggravated in presence of water ingress. The authors' laboratory has made an attempt to process a multipurpose Lithium base grease with the addition of polymer blend to improve the properties in the application of anti friction bearings operating under sub-zero to medium high temperatures in presence of water ingress.

The three dimensional network of polymers added to the grease is flexible, reversible, but with shorter chains between rigid blocks. As a result the total network could be described as bimodal or interpenetrated network consisting of a network of soap fibres and a network of polymers. With this background the authors' laboratory has made an attempt to use a blend of di block and tri block (styrene- rubber-styrene) copolymers in Li base grease with a view to enhanceits performance properties.

This copolymers consist of a two-phase system — the polystyrene and elastomeric blocks are thermodynamically incompatible, the polystyrene blocks form hard domains within the elastomer matrix (flexible) and act as "physical crosslinks" between them. It is observed that the incorporation of the polymer blend particularly during the gelling stage of the process has a significant impact on improving the mechanical properties of the grease with much improved adhesion, tackiness and glossiness. The physico chemical properties have been studied and compared with the base grease.

Critical properties of the developed grease targeted for are appendedbelow.

- Improved mechanical stability
- Improved water resistance
- Improved cohesion and adhesivity
- Improved anti wear properties
- Improved oil separation even at low temperatures
- Improved tackiness
- Additionally improved transparency and glossiness

Experimental

The processing of the lithium base grease was conducted in a stainlesssteel pilot kettle fitted with stainless steel double motion paddle typestirrer with a batch size of 10 kg. The soap was made in around 40 % of the total oil volume. The saponification was carried out at around 90 to 95 deg C with a combination of HCO and 12 HSA for about 45 minutes .The temperature was increased to 115 to 125 deg C.

Intermittent water treatment was given to get free alkalinity as 0.2 %. Then the temperature was slowly raised to 190 to 195 deg C at a heating rate of 1 to 2 deg C per minute. The cooling was performed with the addition of residual portion of oil gradually, at a temperature of around 130 deg C polymer blend (previously dissolved in oil) was added slowly with continuous stirring at a low speed of about 20 rpm. At below 80 deg C the additives were added. Next day the grease wasmilled and de aerated with a help of vacuum pump at 1 torr.

Grease Composition

Base grease (A) : Lithium base

Base oil Viscosity : 165 cSt at 40 deg CVI of base

oil : 90

AW agent : 1.0 %

Mild EP agent : 0.5 %

Worked Penetration at 25 deg C = 256

Grease mixed with polymer blend (B)

Base grease (A) as above (including additives) : 94.8 %

Polymer blend : 5.2 %

Worked penetration at 25 deg C = 251

Polymer Blend used:

A mixture of two polymers - tri block and di block combinations

A-B-A triblock

A-B diblock

Molecular weight distribution : Mw / M n is near to 1

Physical nature of polymers : Undusted fluffy crumb having inherentclarity

Polymer blend is resistant to degradation by oxygen and ultravioletlight

Several experimental methods were employed to evaluate the greasesamples.

Results and discussion

Table 1

Parameters	Test Method	Grease A	Grease B
WP @60	**ASTM D 217**	**256**	**252**
WP @ 100,000		**284**	**267**
Difference		**24**	**15**

Table 1 shows that the Grease B is having much better shear stability

.It indicates that the additive, polymer blend at a 5.2 % treat level has a significant effect towards improving the shear stability of the grease.The grease can withstand better mechanical stresses compared to thebase grease. The cohesiveness of greases is qualitatively measured by cone penetration , so the data indicates that the polymer blended grease exhibits better cohesiveness. The Grease B provides good string-forming ability due to the interaction of the individual polymermolecules which helps the grease to stay in grade for longer time ensuring better life of the grease and equipment. Greater cohesiveness is required to keep the lubricant from being squeezed out from contacting surfaces.

Table 2

Parameter	Test Method	Grease A	Grease B
Roll stability,16 hrs, RT, %Change in penetration	**ASTM D 1831**	**13**	**5**
Same in presence of 5 % water		**21**	**7**

Table 2 clearly indicates that the Grease B exhibits better roll stability than its base grease even in presence of water. So the Grease B can withstand better rolling stress/ torque in presence of water also to render better service life in roller bearings. This is because soap thickener form tight interlocked fibers in the grease with the help of polymer blend network . The polymer soaked soap matrix gains bettermechanical stability because of stronger hydrogen induced cross links among themselves to yield a compact robust moiety disallowing water molecules to rupture these intimate linkages. Moreover the molecular weights of the blended polymers are in synchronise fashion so that it fits to the soap moiety without being affected by roll shearing.

Rheological properties of the Grease B remain more or lessunaffected under rolling forces.

Table 3

Parameters	Test Method	Grease A	Grease B
Water spray off, % sprayed off by mass, 39 deg C, 40 psi , 5 minutes	**ASTM D 4049**	**62**	**41**
Water wash out, % washedoff by mass, 80 deg C 1 h	**ASTM D 1264**	**4.1**	**1.2**

Many grease applications demand good water resistance in order to perform well for an extended period of time. The adherence of grease to the substrate is characterised by water spray-off or water wash outmeasurements. Table 3 shows that Grease B outperformed Grease A significantly towards water resistance / adhesion behaviour. Adhesion or tackiness is the attractive forces between dissimilar molecules and causes one material to stay in place on another. The data in the table clearly indicates that the Grease B will stick/ cling more tightly to thelubricating surfaces even in presence of water.

Table 4

Parameter	Test Method	Grease A	Grease B
Four ball weld load, Kg	**ASTM D 2596**	**200**	**250**
Four ball wear scar , dia inmm	**ASTM D 2266**	**0.81**	**0.52**

One of the most important attributes of grease is its anti wear properties. The grease should reduce the friction between the matingsurfaces and it should also be able to withstand the load under which the rolling elements are exposed. Otherwise there will be a catasphoric failure yielding excessive heat generation and bearing seizure. In both these behaviours Grease B performs better than the Grease A. The scar depth on the disc lubricated with the Grease B is much less compared to Grease A indicating the build-up of a resistanttribo film. This is due to the inert nature of the polymer blend which is having a low polarity index than the soap matrix, as a result the composite matrix renders better additive response by allowing easy migration of polar AW and EP additives to the metal surfaces.

Table 5

Parameter	Test Method	Grease A	Grease B
Oil separation, 100 deg C, 30 h	IS 1448 P : 89	1.77	1.5
Oil separation at 10 deg C, 30 h		Nil	0.42
Heat stability, 120 deg C , 2 h Then kept at RT	IS 1448 P:62	No break down, slight oilseparation, no fully reabsorbed within 24 h	No break down, slight oilseparation, fully reabsorbed within 8 h

a) The lubricating grease should be mechanically rigid but spongy enough to release optimum quantity of oil into the mechanical work zone to provide effective lubrication, channeling effect and equipment protection. But excessive oil separation can lead to starvation of the lubrication points when the grease has dried out.

b) The oil release behaviour of the grease can be significantly affected at low temperatures leading to inappropriate lubrication leading to excessive wear and equipment failure. This is particularly important at start-up, when speeds are too low to build up an elasto hydrodynamic lubrication film (EHL). Optimum oil bleed at low temperatures is beneficial from lubrication point of view at low temperatures.

c) When properly formulated and processed a well balanced grease can even reabsorb some of the migrated oil providing a reserve of lubricant to be released in the future when needed toprovide lubrication.

The above three important attributes towards the generation of oil film at medium as well as low temperatures (particularly in EHL regime) with reversible migration-reabsorbtion behaviour are well met by the Grease B. So Grease is very suitable to provide proper lubrication at low and medium high temperatures.

Transparency and Shine

The Grease B exhibits better transparency and shine in appearance. The factors responsible for this is not fullyunderstood. Though the following care has been exercised whileprocessing the greases to impart transparency and shine in finished grease.

1. Longer saponification time at moderate temperatures toavoid any grain formation
2. Avoided incorporation of excess water to stop opaqueness
3. Slow addition of oil during gelling process at a lower stirringspeed, to allow nucleation and growth in a regular homogeneous fashion
4. Effective milling to impart clarity
5. De aeration for better transparency
6. Incorporation of high clarity and high refractive index (1.5)polymer blend

Definitely the polymer blend plays an important role in bringing up thebetter transparency and shine in the grease. The chain flexability , molecular geometry and polymer backbone orientation are responsible for imparting extra transparency as well as shine in the whole network. The exact reason for this is under study.

Conclusion:

The study indicates that the developed polymer blend grease exhibitsbetter performance with regard to mechanical and roll stability, ant wear and extreme pressure properties, water spray off and wash out characteristics, cohesiveness and adhesivity and oil bleed behaviours at medium and low temperatures compared to the conventional Lithium base grease under otherwise identical conditions. So it will serve better way in equipment with greater reliability. Additional benefits achieved that the grease appears to be more transparent and glossy.

References

1. Energy efficiency and lubrication mechanisms of polymer thickened greases , Johan Leckner, 27th ELGI Annual GeneralMeeting, April 2015
2. The enhancement of grease structure through the use of functionalized polymer systems, Scharf C.R and George H.F.NLGI Spokesman 1996, 59 (II), 4-16
3. Tackifiers for high temperature lubricants, Levin , Victor NLGISpokesman 2004 , 68 (4), 25-32
4. High refractive index polymer: fundamental and practical applications , J. Mater. Chem 19 (47) : 8907, Jin-gang Liu andMitsuru Ueda (2009)
5. The adhesiveness of grease, Daniel M Vergo , NLGISpokesman, 81st Annual general Meeting , 2014
6. Benefits of polymer additives in grease, Larson, B.K. andVictor Levin , NLGI conference , 2009
7. British Polymer Journal, J. M. Mark , 17,2 (1985)

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Study of bio –polymers as additives in greases to improve key performance properties

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Abstract

Effective protection of gears against external media such as abrasive dust and water is a challenging task. Gear lubricants should be designed for high load-bearing capacity, withstanding extremes of temperature and providing adequate lubrication when the drive is subjected to shock load. They should also protect the gears from wear, corrosion and water by adhering well to the gear teeth. Sufficient lubrication of the gears in all phases of operation is critical to the smooth functioning and long service life of the equipment. Grease is the most effective lubricant for gears which operate at varying speed and temperature. In this study, additives such as biopolymer which improve anti-wear properties, increase the water-resistance, enhance the boundary lubrication, improve stability at higher temperature and boost the adherence to gear surfaces were added to NLGI 2 grease. Inclusion of biopolymer at 3% and 5% concentrations reduced wear by 20-28%, enhanced the corrosion resistance and significantly reduced oil separation at high temperature.

Keywords: grease, biopolymer, anti-wear, oil separation, anti-corrosion

1. Introduction

In general, grease is a solid to semi fluid product, is a dispersion of a thickening agent in a liquid lubricant. Greases are manufactured by combining three essential components, base oil, thickener, and performance additives. Base oil comprises the largest component of grease, representing 80 % by weight. The choice of base fluid may be mineral oil, synthetic oil, or any fluid that provides lubricating properties. Base oil portion of grease performs the actual lubrication except in very slow or oscillating applications. The thickener may be any material that, in combination with the base oil, will produce the solid to semi-fluid structure. . Principal thickeners used in greases include lithium, aluminum, calcium soaps; clay; polyurea; either alone or in combination. Lithium soap is the most common thickener in use today. As in lubricating oil additives, additives in grease impart special properties. Additives and modifiers commonly used in lubricating greases are oxidation or rust inhibitors, polymers, extreme pressure (EP) additives, anti-wear agents, lubricity or friction-reducing agents. [1]

Greases provide a physical seal preventing ingress of contaminants, resist the washing action of water, and can stay in place in an application even in vertically mounted positions. Greases are uniquely suited for use in applications where relubrication is infrequent or economically unjustifiable, due to the physical configuration of the mechanism, type of motion, type of sealing or the need for the lubricant to perform all or part of any sealing function in the prevention of lubricant loss. As a result, greases are used in approximately 80% of rolling elements bearings.

The lubricating grease serves as a reservoir for lubricating oil .Oil release from lubricating greases is induced by mechanical forces and temperature. Other reasons for oil separations are Volatility of base oils in high temperature environments, thermal run-away, mechanical wring-out, hydrostatic extrusion and vibration and centrifugal forces. Insufficient oil release or excessive loss of oil from lubricating grease causes lubricant starvation and may leadto bearing failure. Oil bleeding rate directly affects the useful service life and performance of the grease in turn bearing life. Thus, it is apparent that oil bleed characteristics of lubricating grease have a role in performance assessment of lubricating greases. Higher oil separation in grease samples lowers the grease performance in terms of providing long term lubrication.

There are different tests that are used to measure grease's bleeding tendency and oil separation characteristics. These tests can be categorized into two groups: static and dynamic bleed tests. The most common tests used to evaluate oil separation and bleeding are ASTM D- 1742 for Oil Separation from Lubricating Grease during Storage for predicting the tendency of grease to separate oil during storage when stored at room temperature. ASTM D-6184 Test Method for Oil Separation from Lubricating Grease (Conical Sieve Method), for checking the tendency of the oil separation in lubricating grease at elevated temperatures. The U.S. Steel Pressure Oil Separation Test is used to measure the oil separating and caking characteristics of grease under conditions of high pressures and small clearances in a centralized grease pumping system. The ASTM D-4425 Oil Separation from Grease by Centrifuge –method evaluates the oil separation tendency of grease when subjected to high centrifugal forces. Oil bleed tendency at high temperatures and methods of improvement have not been studied extensively.

Commercially used additives for enhancing oil separations are poly isobutylene (PIB), ethylene-propylene copolymers (OCP), styrene-hydrogenated butadiene (SBR), styrene- hydrogenated isoprene (SI), radial hydrogenated poly isoprene (Star), acid functionalized polymers (FP), poly methacrylate (PMA), styrene ester copolymers (SE), and styrene ethylene butylene copolymers (SEBCP). [2]

The present work is focused on the study of the oil bleed tendency of NLGI grade 2 EP greases by incorporating biopolymer based additives into the thickener system. The expected benefits of biopolymer additive to enhance grease performance in terms of oil separation, anti- wear properties, corrosion inhibition and Viscosity boost up.

Biopolymer is an elektrionized vegetable ester based lubricity component which acts as a friction modifier, anti-wear agent and anti-corrosion agent in greases as well as in metal working lubricants. [3] In an elektrionization process, feed stocks undergo electroionizing treatment which leads to an increase in viscosity, polarity and viscosity index. Increasing the polar functionality of the triglyceride molecules of vegetable oil has a positive impact on wear protection, probably due to the stronger adsorption to the metal surface and the stabilization of the adsorbed by later interlinking. It is particularly suitable in synergy with common EP and anti-wear additives to bring an additional and earlier low friction protective film as well as to improve oil separation characteristics.

Typical properties of biopolymer used in the current study are presented in Table 1.

Table 1: properties of biopolymer additive

Property	ASTM	Unit	Value
Viscosity at 40 °C	D445	mm^2/s	2200
Density at 15 °C	D1298	g/cm^3	0.91
Viscosity Index	D2270	-	260
Saponification number	D94	mgKOH/g	92
Pour Point	D97	°C	-3
Flash Point	D93	°C	270

Featuring a unique combination of viscosity and polarity, ionized biopolymer generate sufficiently thick and resilient protective film by adsorption to rubbing surfaces reducing friction coefficient in metal working lubricant (The typical results obtained by the author's earlier study on coefficient of friction improvement using biopolymer additive in metal working lubricant are presented in Fig.1) The performance benefits in metal working and other lubricants have been further extended in current studies on grease.

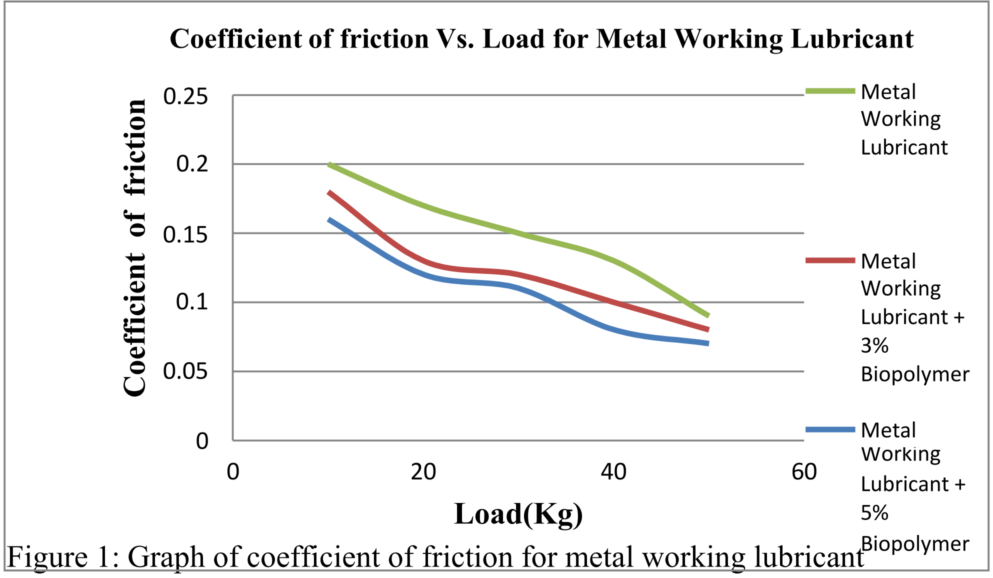


Figure 1: Graph of coefficient of friction for metal working lubricant

2. Experiments

Addition of Biopolymer additive to NLGI grade 2 EP greases

An NLGI 2 grade, mineral oil-based EP greases with lithium type thickener was used as the starting material. The Biopolymer was blended with grease using Mechanical Grease Worker. 200 strokes were given with mechanical grease worker for uniform mixing. 3% and 5% biopolymer was incorporated in thickener system of EP2 greases and its key properties were measured and evaluated.

SAMPLE 1 is EP LITHIUM GREASE is multi-purpose extreme pressure grease made from lithium complex soap stock which imparts well high and low temperature characteristics and chemical stability. 3 % bio-polymer and 5 % bio-polymer is incorporated in thickener system of EP 2 greases to see the change in performance in terms of oil-separation at 100°C and oil separation at 40°C. Wear Scar characteristics was analyzed. All key properties of sample 1 grease were compared with, grease having biopolymer additive.

SAMPLE 2 is a premium, heavy duty, extreme pressure multi-purpose lithium complex grease. Sample 2 is one –year old sample of grease which was kept aside for studying its high oil separation characteristics and to study the improvements with biopolymer addition.3 % biopolymer and 5 % biopolymer is added in thickener system to see the change in performance in terms of oil-separation at 100°C and oil separation at 40°C. Wear Scar characteristics was anayzed. All key properties of sample 2 grease were compared with, grease having biopolymer additive.

2.1 Experimental tests and results

2.1.1 Oil Separation ASTM D-6184 (Cone Sieve Method) (Heat Stability)

When lubricating grease separates oil, the residual material may change in consistency, which can affect the ability of the product to function as designed. Oil separation of EP 2 greases (Sample 1 and Sample 2) was determined using ASTM D -6184 method.

2.1.2 Oil Separation ASTM D-1742 (Storage Stability)

When lubricating grease separates oil, the remaining composition changes its consistency. This can affect the ability of the product to function as designed. It has been found that the results of this test correlate directly with the oil separation that occurs in grease during storage. Oil separation of EP 2 greases (Sample 1 and Sample 2) was determined using ASTM D -1742 method.

Oil separation test results for sample 1 and sample 2 are presented in Table 2 & Table 3.

Table 2: Oil separation values of blank EP2 greases (Sample 1) (Heat and storage stability*)*

Sr. No.	**SAMPLE**	**Oil separation- Storage ASTM D 1742 (% of oil separated)**	**Heat stability test ASTM D -6184 (% of oil separated)**
1	Sample 1	3.38	5.03
2	Sample 1 + 3% Biopolymer	2.85	4.85
3	Sample 1 + 5% Biopolymer	2.35	3.75

Table 3: Oil separation values of blank EP2 greases (Sample 2) (Heat and storage stability)

Sr. No.	**SAMPLE**	**Oil separation- StorageASTM D 1742 (% of oil separated)**	**Heat stability test ASTM D -6184 (% of oil separated)**
1	Sample 2	6.31	5.54
2	Sample 2 + 3% Biopolymer	4.53	4.98
3	Sample 2 + 5% Biopolymer	3.35	3.82

2.1.3 Wear preventive characteristics ASTM D 2266 (Wear scar measurement)

The anti-wear property of the greases was measured by comparing wear scar diameters for the original grease and the grease with added polymer. Wear scar measurements were conducted in duplicate on a Four Ball Wear Test Machine conforming to ASTM D 2266 (Standard Test Method for Wear Preventive Characteristics of Lubricating Grease (Four Ball Method)) and the average value was taken. Wear scar diameter measurement results of sample 1 and sample 2 are presented in Table 4 and Table 5 and graphically represented in Fig. 2

Table 4: Wear Scar Diameter measurement (Sample 1)

PRODUCT	Wear Scar Diameter (mm)	% Reduction in wear scar diameter
Sample 1	0.63	-
Sample 1 + 3% Biopolymer	0.49	22.22
Sample 1 + 5% Biopolymer	0.45	28.57

Table 5 : Wear Scar Diameter measurement (Sample 2)

PRODUCT	Wear Scar Diameter (mm)	% Reduction in wear scar diameter
Sample 2	0.64	-
Sample 2 + 3% Biopolymer	0.51	20.3
Sample 2 + 5 % Biopolymer	0.47	26.5

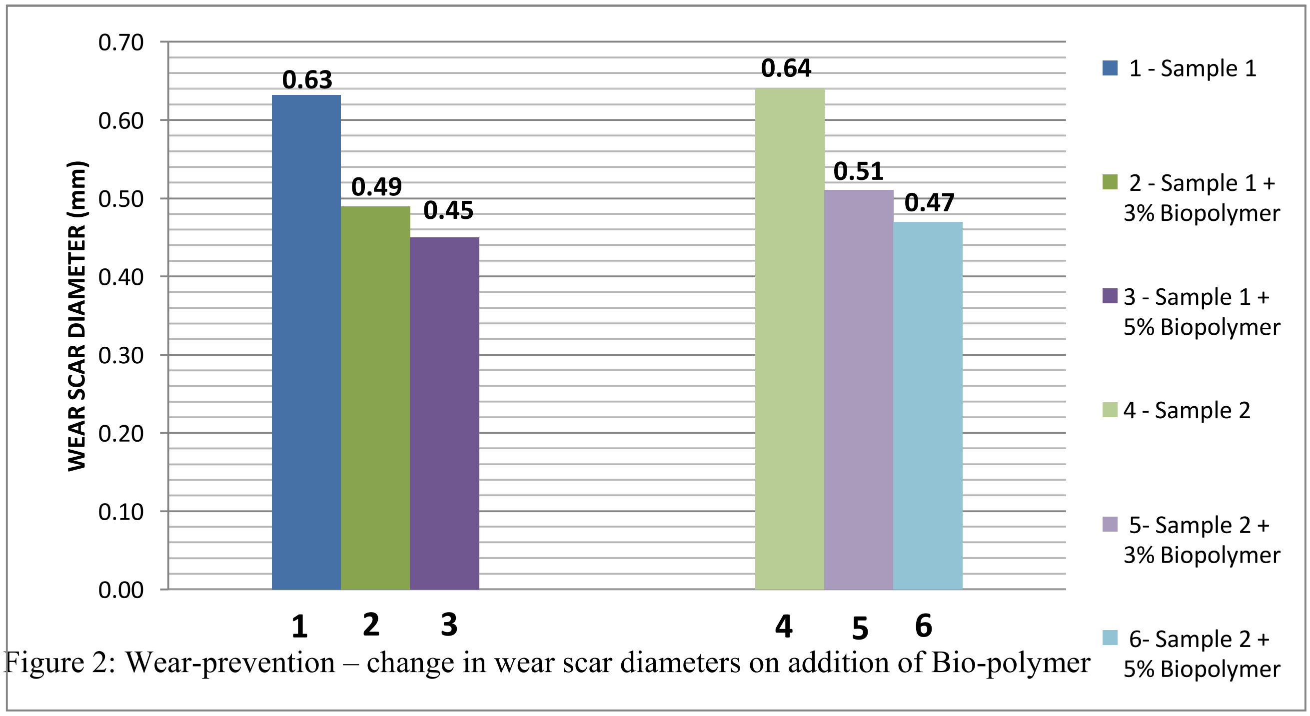


Figure 2: Wear-prevention – change in wear scar diameters on addition of Bio-polymer

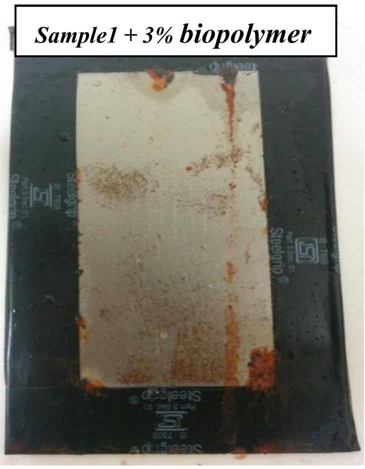
2.1.4 Anti-Corrosion Characteristics (ASTM B117) (5% SALT SPRAY TEST)

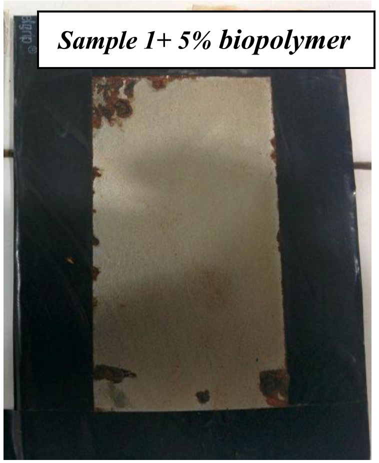
The **salt spray test** is a standardized and popular corrosion test method, used to check corrosion resistance of materials and surface coatings. Salt spray test performed for grease samples with and without addition of biopolymer. Standard ASTM B117 Method was followed for the same. Q panels were used which were coated with paint at one surface. Q panels were taped along the 4 edges and area was confined for grease application and grease samples were applied by Hegman gauge for film uniformity.

Salt Spray Test results

SALT SPRAY TEST: 5% Sodium chloride solution, ASTM B117, after 500 Hours


Sample 1


Sample1 + 3% biopolymer


Sample 1+ 5% biopolymer


Sample 2


Sample 2 + 3% biopolymer


Sample 2+ 5% biopolymer

3. Conclusion

3.1 Biopolymer was added in NLGI grade 2 extreme pressure greases and several key properties were compared with original extreme pressure grease samples.

3.2 Oil separation properties of EP greases with biopolymer at high temperature (ASTM D 6184) improved by 25-30% and brought its values within BIS limits. Oil separation properties of EP greases with biopolymer at storage temperature (ASTM D 1742) improved by 20 -25 % and oil separation values are within BIS limits.

3.3 Addition of biopolymer enhanced lubricating properties of grease and reduces wear scar diameter by 22-28% by addition of biopolymer & brought its value within BIS limit. Further studies on coefficient of friction enhancement in grease formulations are on progress

3.4 Improvement in anti-rust properties was seen with addition of biopolymer in extreme pressure NLGI grade 2 greases.

3.5 Biopolymer based grease is more environmental friendly than commercial polymer added greases.

References

1. A. A. Gordon : ‘ paper on lubricating greases’ http://ijari.org/CurrentIssue/ICARI2014/ICARI-ME-14-02-107.pdf
2. B. K. Larson and V. Levin: ‘Benefits of polymer additives in grease’, www.nlgi-india.org/images/PDF/David%20Devore.pdf
3. Michel Roegiers; Hongli Zhang ; Boris Zhmud : ‘Elektrionized^{TM} Vegetable Oils as Lubricity Components in Metalworking Lubricants’
4. P. Bessette : ‘Grease Additives: Important contributors not to be overlooked’, Dr. NeilCanter, ed., www.stle.org/assets/document/**Grease**_Additives.pdf
5. Meijer, D.; Lankamp, H. Polymer Thickened Lubricants for High Temperatures. U.S. Patent 5846918, 1998. http://www.mdpi.com/2075-4442/2/4/237/htm
6. Global Lubricants Market Analysis and Segment Forecast – Grand View Market Research, www.grandviewresearch.com/industry-analysis/**lubricants-market**

7. Delgado, M.A.; Valencia, C.; Sanchez, M.C.; Franco, J.M.; Gallegos, C: ‘Influence of soap concentration and oil viscosity on the rheology and microstructure of lubricating greases.’ https://www.google.co.in/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0ahUKEwjhysujmKTKAhXDUY4KHVlIDtEQFggbMAA&url=http%3A%2F%2Fpubs.acs.org%2Fdoi%2Fabs%2F10.1021%2Fie050826f&usg=AFQjCNHVv0KgViyp8DVY_F4Gn7epjbiNJA&bvm=bv.111396085,d.c2E

Characteristics of Polyurea Greases prepared with Synthetic Base Stocks OSP and PAO

Vijay Deshmukh & N. S. Ramanathan

Abstract:

NLGI production survey 2014 indicates that consumption of polyurea greases is going up in last few years. The high temperature capability, its structural reversibility and excellent oxidation stability make polyurea greases the most suitable greases for long life or "packed to life" applications.

The operating temperature range of polyurea greases can be further widened by use of synthetic base oils such as Oil Soluble Polyglycol (OSP) and Poly Alpha Olefin (PAO).

Authors have prepared synthetic polyurea greases using OSP and PAO as base stocks. The greases have been evaluated fully including their low temperature and high temperature properties. The test data obtained has been discussed.

Introduction:

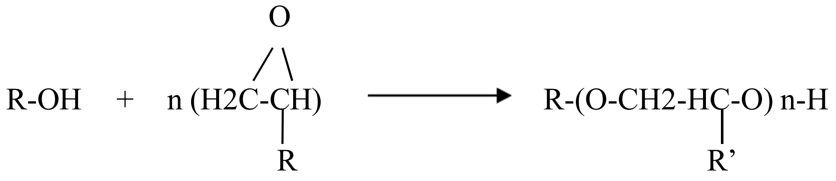
Over the last few years, Poly urea greases have attained importance as good high temperature greases. They are being increasingly used in steel plants for high temperature applications such electric arc furnace, caster bearings, roller table bearings, furnace door bearings & other industrial applications. Polyurea greases are especially suitable for "pack to life" applications. These greases have high dropping points, excellent oxidation stability and good shear reversibility i.e. the ability of the grease to soften under working and to regain its consistency upon removal of the stress. This property plays an important role in its long life performance. Lot of patents and literature has been published on preparation, properties and application of polyurea greases. (1-5)

Conventional polyurea greases were having disadvantages such as poor shear stability, poor rust protection, poor compatibility with other types of greases and poor additive response. However, polyurea grease technology has been improved and superior polyurea greases have been developed in terms of their mechanical stability, EP properties, water resistance, rust protection & compatibility.(6)

Recent NLGI Grease Production Survey 2014 indicates that polyurea greases constitute around 5% of the total grease produced in the world. The major consumption of polyurea greases is in Japan where almost 25% of the total grease consumed is polyurea grease.

Although majority of the polyurea greases consumed are based on mineral oil, not much work has been done on synthetic polyurea greases. The working temperature range of polyurea greases can be further widened by use of synthetic oils such as Oil Soluble Polyglycols (OSP) & Poly Alpha Olefins (PAO).The use of these base oils can further improve the oxidation stability and extend the life of polyurea greases.

The recent developments in PAG technology has led to development of Oil Soluble Polyglycols (OSP). By increasing the ratio of carbon to oxygen in PAG, the oil solubility of PAG can be increased and fully oil soluble PAGs can be prepared.



$$\text{R-OH} + n\,(\overset{O}{\overbrace{\text{H}_2\text{C-}\underset{R}{\text{CH}}}}) \longrightarrow \text{R-(O-CH}_2\text{-H}\underset{R'}{\text{C}}\text{-O)}\,n\text{-H}$$

Alcohol Alkylene Oxide Polyalkylene Glycol

R, R’= H, CH3, alkyl, aryl groups

Conventional PAGs are derived from ethylene oxide (EO) and propylene oxide (PO) where as OSP are mainly derived from butylene oxide (BO) OSPs have high viscosity Index (VI), low pour point, better frictional properties and excellent solvency power. (7) OSP offer very thick films over a temperature range (8). Greases prepared with OSP have shown significantly longer high temperature bearing performance versus their conventional hydrocarbon counterparts. (9) Another important property of OSP is their excellent deposit control characteristics. This means small amount of OSP added to the lubricant will minimize the generation of insoluble. (10) OSP are available in various ISO VG grades which give grease formulator wider choice to select the most suitable VG grade OSP for selected applications. OSP are also compatible with hydrocarbon oils & poly alpha olefins. So they can be used in combination with petroleum oils or PAOs. PAGs are unique amongst the synthetic lubricants in the degree to which their chemical and physical properties can be modified by change in molecular weight, end groups and monomer selection. (11)

Another important property of OSP is their seal swell characteristics. Usually, esters are used to negate the seal shrinkage characteristics of PAO specially NBR seals. OSP can also be used as seal swelling additives in certain applications.

OSP are HX1 base fluids and additives and can be used in food lubricants. With proper selection of additives, OSP base polyurea greases can be excellent low temperature and high temperature food grade greases.

The polarity of OSP enables them to reach metal surface and significantly reduce the coefficient of friction. Being polar, they are also used to increase the solvency of PAOs.

The various grades of OSP and their properties are given in Table 1.

Table 1 TYPICAL PHYSICAL PROPERTIES OF OSP*

Grade	Viscosity @40° C, cSt	Viscosity @100 °C, cSt	VI	Pour Point, °C	Flash Point, COC,°C
OSP -32	32	6.5	146	< -43	242
OSP-46	46	8.5	164	<-43	240
OSP-68	68	12	171	<-40	258
OSP-150	150	23	186	-37	258
OSP-220	220	32	196	-34	258

*courtesy Dow Chemical Company.

Poly Alpha Olefins (PAO) are Group 4 base oils. These are synthetic base stocks and are manufactured by catalytic oligomerization of linear alpha olefins. These are classified based on their viscosities at 100 °C. One has to blend these grades to get desired ISO VG grade base oils. Their physical properties are given in Table 2.

Table 2 TYPICAL PHYSICAL PROPERTIES OF PAO

Grade	Viscosity @40° C, cSt	Viscosity @100 °C, cSt	VI	Pour Point, °C	Flash Point, COC,°C
PAO 6	31	5.8	138	-57	246
PAO 8	48	8.0	139	-48	260
PAO 10	66	10.0	137	-48	266
PAO 40	396	39.0	147	-36	281
PAO 100	1240	100.0	170	-30	283

The authors have used two synthetic oils OSP and PAO to prepare polyurea greases and their characteristics have been evaluated.

Experimental:

Polyurea Grease-OSP was prepared in the laboratory in-situ using isocyanides, diamine and primary amine as raw materials and the base oil used was Oil Soluble Polyglycol (OSP).
Similarly, Polyurea Grease-PAO was prepared in situ using the same raw materials i.e. isocyanides, diamine and primary amine and PAO as base oil.
Both the greases were additized with the same EP, antiwear, corrosion inhibitor and metal deactivator additives in same percentages. Both the greases were evaluated and their test data given in Table 3 and Table 4 resp.

Further, shear reversibility characteristics of Polyurea greases prepared with OSP & PAO was evaluated by subjecting these greases to 10,000 double strokes in grease worker. Then their penetration was checked over a period of 2 hrs. The graphs 1 & 2 show their shear reversibility characteristics.

Results and discussions:

Polyurea greases were prepared with low viscosity base oils OSP and PAO to check their low temperature capability. Both the greases gave very low torque at minus 50 degree Celsius. OSP/PAO base oils can be used in combination with mineral oil to get the desired low temperature capability.

Both the greases have good low temperature properties. In addition, EP and AW properties are also good. As expected, the oxidation stability of these greases is also excellent.

The shear reversibility of both the greases was tested and both the greases are found to be shear reversible. This property helps in “packed to life” applications.

The extent of shear reversibility will vary depending upon the initial consistency, degree of stress, composition of grease etc.

Although polyurea grease is being extensively used for industrial applications, proper selection of base oil viscosity and additive package can give polyurea grease meeting GC-LB specification for automotive applications.

Authors plan to develop polyurea greases with OSP and PAO meeting GC-LB specification for automotive applications.

Summary- Very good polyurea greases can be prepared with OSP and PAO base oils for low temperature applications. The greases can be suitably additized to get good EP, antiwear and anti rust properties

Acknowledgement:

Authors wish to thank the management of Standard Greases & Specialities Pvt. Ltd. for granting permission to present the above work in NLGI-India Chapter Meeting 2016.Also thanks to laboratory personnel for their help in carrying out the tests.

Table 3 Properties of Poly urea Grease-OSP

Characteristics	Test Method, ASTM	Test data
Appearance	Visual	Smooth, homogeneous
Color	Visual	Off white
Penetration, w/p (x60)	D-217	300
Dropping Point, °C	D-2265	276
Copper corrosion, rating	D-4048	1b
Heat Stability,100°C,24 Hrs.% wt	D-6184	4.0
Four Ball Weld Load, Kg.	D-2596	200
Four Ball Wear, mm	D-2266	0.49
Water wash out test, % wt	D-1264	2.9
Low Temperature Torque @ - 50°C	IP-186	
Starting Torque, mNm		518.27
Running Torque, mNm		138.56
Oxidation stability Test,100 hrs. Pressure drop, psi	D-942	3
Rust test	D-1743	Pass

Table 4 : Properties of Poly Urea Grease-PAO

Property	Test Method, ASTM	Test data
Appearance	Visual	Smooth, homogeneous
Color	Visual	White
Penetration, w/p (x60)	D-217	300
Dropping Point, °C	D-2265	275
Copper corrosion, rating	D-4048	2b
Heat Stability,100°C,24 Hrs.% wt	D-6184	1.5
Four Ball Weld Load, Kg.	D-2596	200
Four Ball Wear, mm	D-2266	0.54
Water wash out test, % wt	D-1264	2.2
Low Temperature Torque @ -50°C Starting Torque, mNm Running Torque, mNm	IP-186	347.0 86.0
Oxidation Stability, pressure drop, psi	D-942	1.0
Rust test	D-1743	Pass

FIG.1 SHEAR REVERSIBILITY POLYUREA GREASE WITH PAO

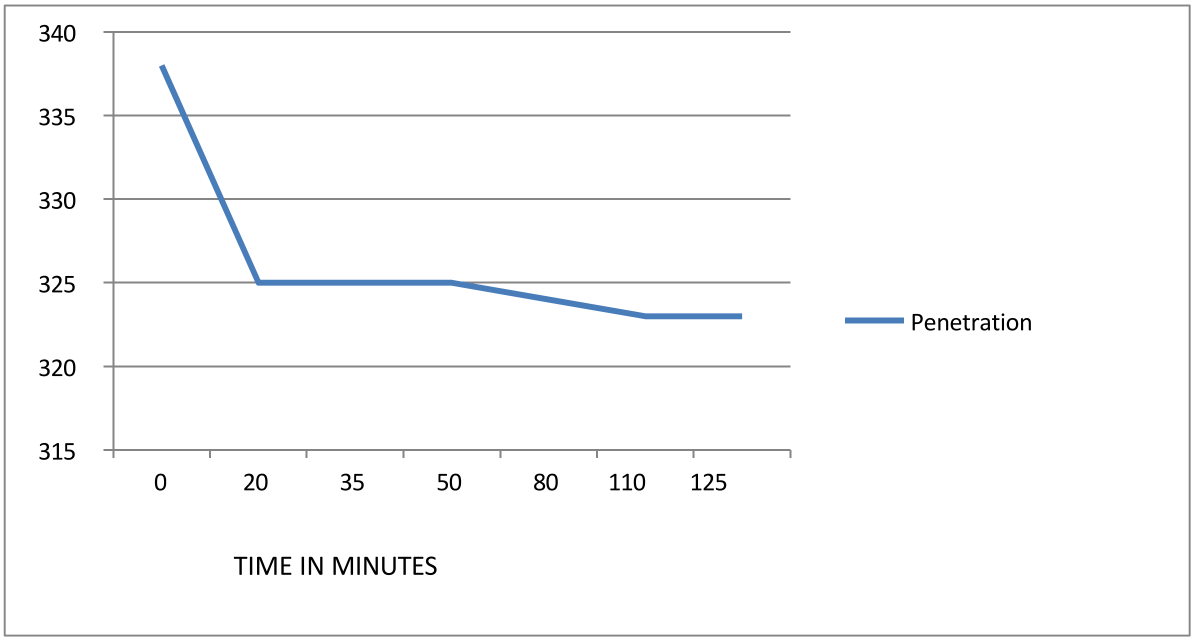
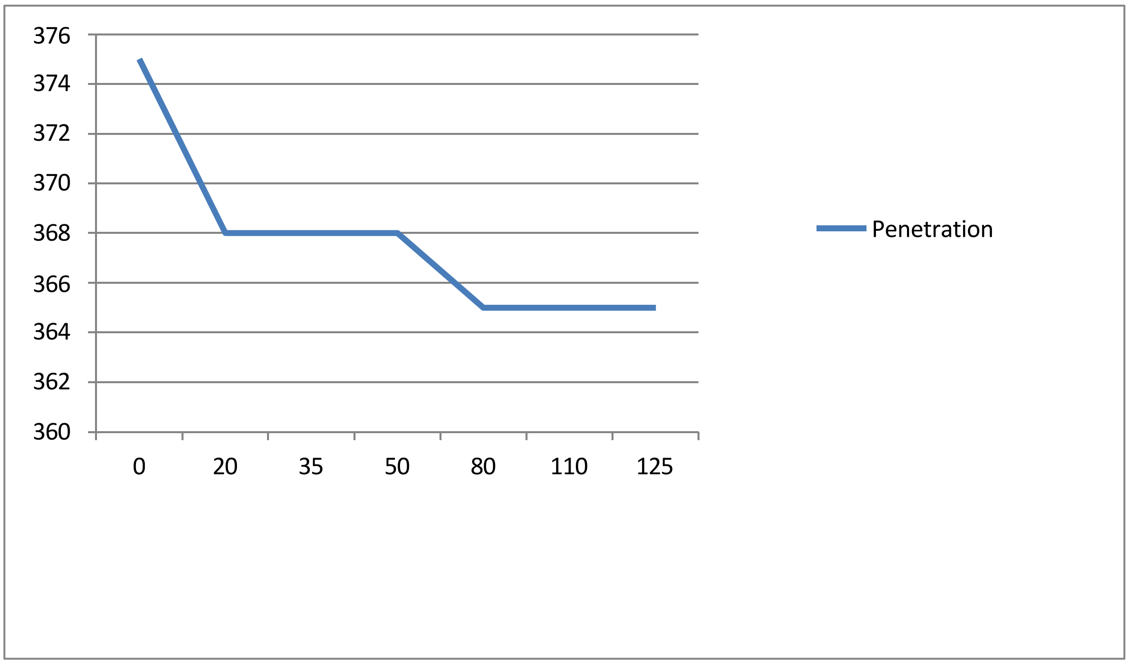
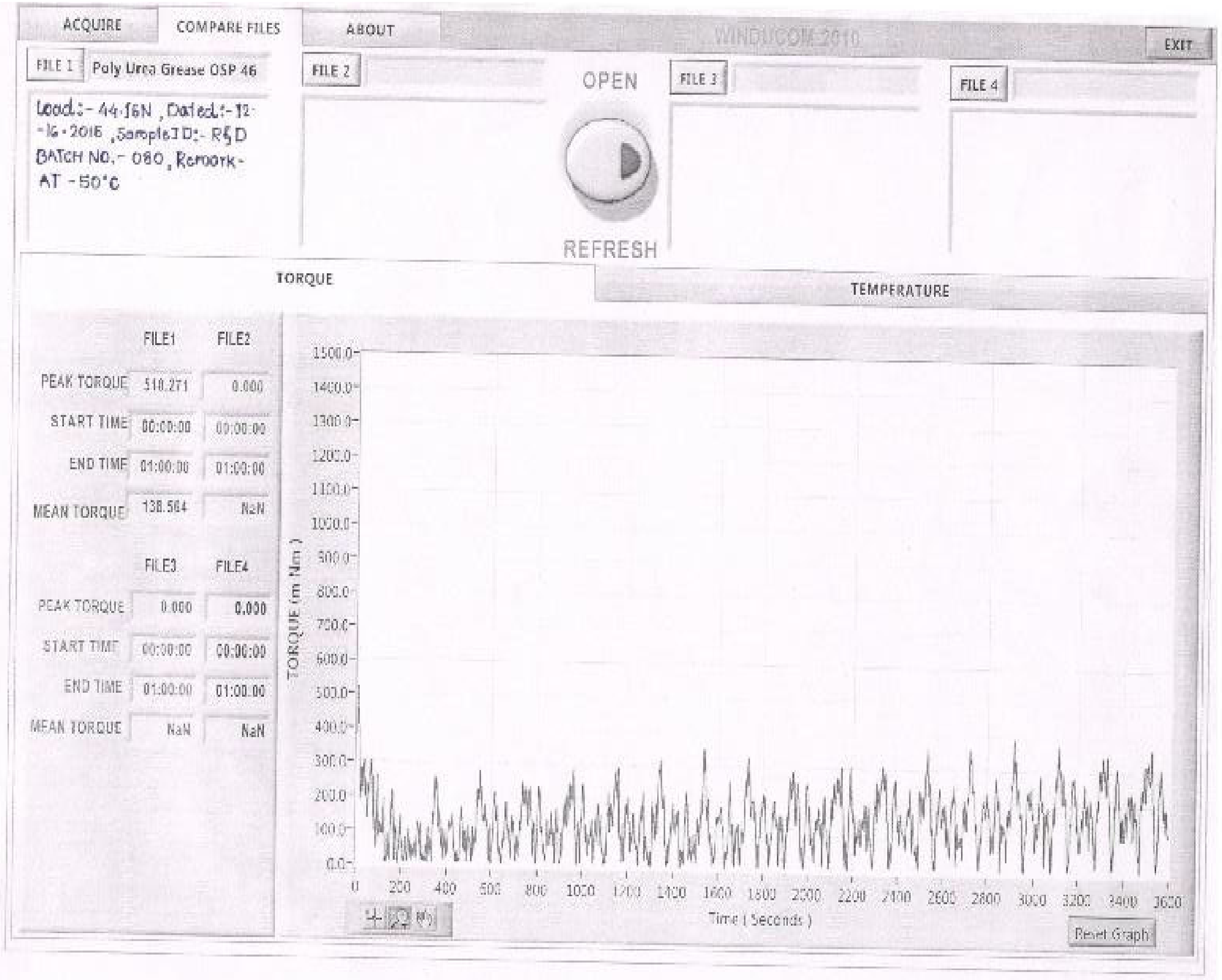


FIG.2 SHEAR REVERSIBILITY POLYUREA GREASE WITH OSP



SHEAR REVERSIBILITY OF POLYUREA-OSP GREASE



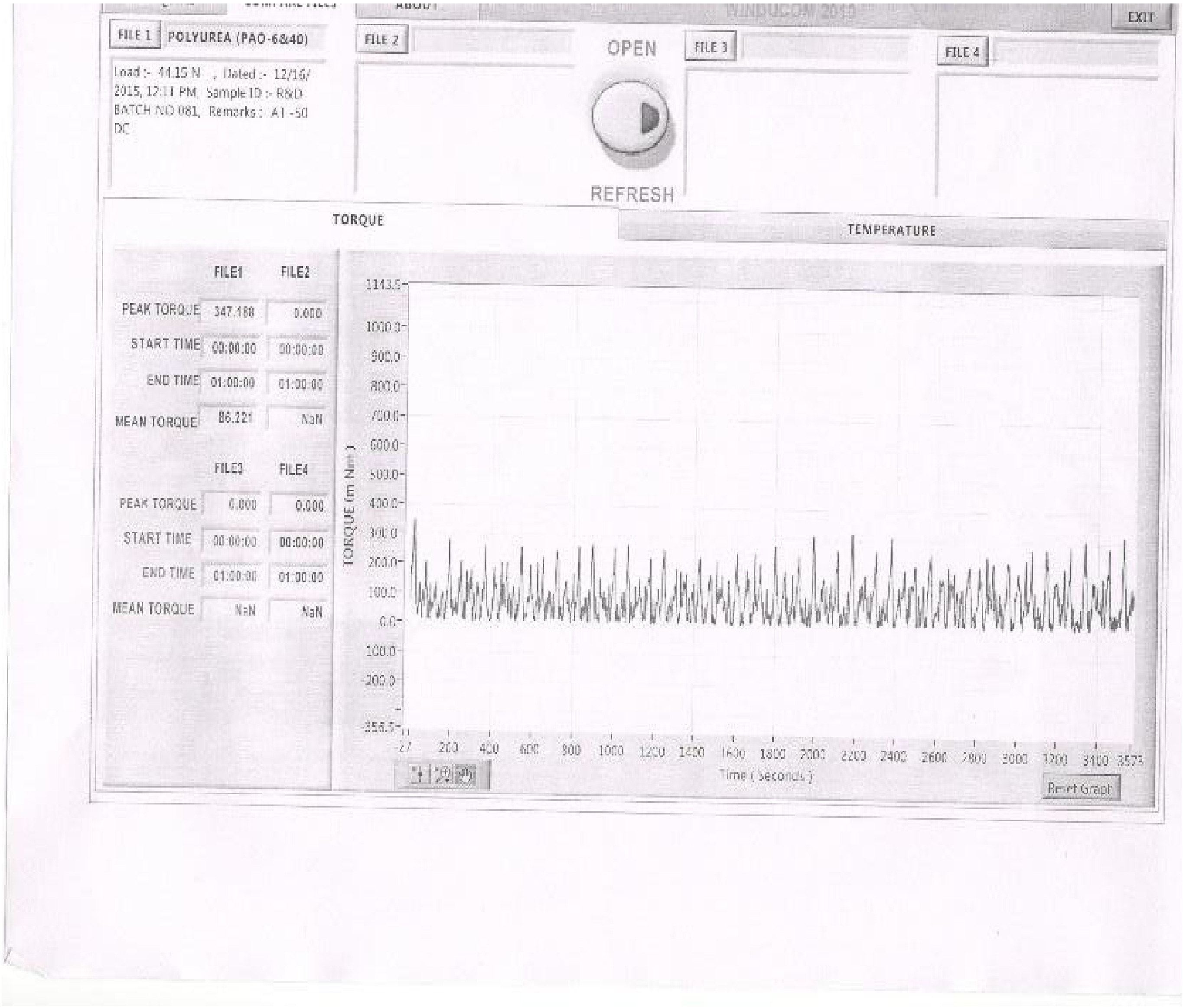
FILE 1 Poly Urea Grease OSP 46

Load:- 44.16N , Dated:- 12-
-16-2016 , SampleID:- R&D
BATCH NO.- 080 , Remark-
AT -50°C

	FILE1	FILE2
PEAK TORQUE	510.271	0.000
START TIME	00:00:00	00:00:00
END TIME	01:00:00	01:00:00
MEAN TORQUE	138.564	NaN

	FILE3	FILE4
PEAK TORQUE	0.000	0.000
START TIME	00:00:00	00:00:00
END TIME	01:00:00	01:00.00
MEAN TORQUE	NaN	NaN

LOW TEMPERATURE TORQUE- POLYUREA GREASE WITH OSP



FILE 1 POLYUREA (PAO-6&40)

Load :- 44.15 N , Dated :- 12/16/2015, 12:11 PM, Sample ID :- R&D BATCH NO 081, Remarks : A1 -50 DC

	FILE1	FILE2
PEAK TORQUE	347.180	0.000
START TIME	00:00:00	00:00:00
END TIME	01:00:00	01:00:00
MEAN TORQUE	86.221	NaN

	FILE3	FILE4
PEAK TORQUE	0.000	0.000
START TIME	00:00:00	00:00:00
END TIME	01:00:00	01:00:00
MEAN TORQUE	NaN	NaN

LOW TEMPERATURE TORQUE-POLYUREA GREASE WITH PAO

References:

1. US Patent 5,145,591
2. US patent 5,523,009
3. US Patent 5,554,586
4. US Patent 5,314,982
5. US Patent 4,111,822
6. “Robust Polyurea Grease for wide range of Industrial Applications” by Anup Kumar et al.
7. “Characteristics of OSP- based Lithium Complex Grease” by G. Khemchandani presented at 80th NLGI Annual Meeting June 2013.
8. “Poly Alkylene Glycols- How different Polymer Architectures Influence Tribology Performance “ by Martin Greaves, presented at STLE Meeting 2015.
9. “Synthetic Greases Poised for Growth”by John Lorimor, Compoundings, Aug.2013,Vol,63,No.8.
10. “New Type of Polyalkylene Glycols” by Dr. Neil Canter, Tribology and LubricationTechnology,Oct.2010.
11. “Innovations in Polyalkylene Glycol based Lubricants” by Richard Butler & G. Khemchandani presented at STLE National Meeting 2011.