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Multifunctional lubricant additives from fatty acid sulfide derivativessynthesized via thiol-ene “Click” addition

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ABSTRACT

Novel multifunctional bioadditives were synthesized from methyl oleate and methyl10-undecenoate via thiol-ene addition reactions. Thiol-ene addition of unsaturated fatty acid ester derivatives with different hetero atoms on the fatty acids was carried out under thermal conditions. The synthesized products were characterized by ^{1}H, ^{13}CNMR, and FT-IR spectral analysis. The tribological properties were evaluated using laboratory tribotests in a biolubricant base oil, which suggest that all the prepared compounds act as antiwear and extreme pressure additives. Antioxidant properties evaluated using differential scanning calorimetry reveal that all the additives improved the oxidation stability of base oil with heterocyclic based additives exhibiting better performance compared to commercial antioxidant. The synthesized sulfide derivatives have potential as multifunctional additives for biolubricant basestocks.

Keywords: Sulfide derivatives / Thiol-ene addition/Multifunctional/Antiwear /Oxidation stability/EP

INTRODUCTION

With growing concerns over sustainable development and environmental impact of petrochemical products, researchers are paying more attention to biobased materials.

The consumption of fossil resources increases the CO2 concentration in air, resulting in the risk of abnormal weather. This is why managing renewable resources is of importancefor the global environment. Biomass obtained from plants is a promising renewable resource because its major components are derived from CO2 and water throughphotosynthesis. Plant oils, providing linear carbon chains with carboxylic acid end-groupas well as double bonds in different positions and numbers with high purity, are very useful renewable raw materials. Vegetable oils and their derivatives (fatty alcohols, esters, andacids) have been extensively modified to generate biobased materials such as lubricants,polyurethanes, surfactants, additives and epoxy resins. The use of vegetable oils as platform chemicals for biolubricant and additive synthesis has numerous advantages, including inherent biodegradability and limited toxicity. The major drawbacks associated with vegetable oil-based base stocks include low thermo-oxidative stability, high pour point and cloud point, poor hydrolytic stability, and low biostability. Chemical modificationis one of the approaches being aggressively pursued to overcome this problem. The success of chemical modification in improving oxidative and tribological performance canbe greatly enhanced with the introduction of hetero atoms such as sulfur or nitrogen at the site of carbon–carbon double bonds on the hydrocarbon chains. Over the years, a number of reactions have been devised and applied to introduce chemical modificationsof the oils on these sites. Thiol-ene addition reactions are known for being one of the most efficient and simple modification and polymerization methods for alkenes. In this work, we report heat-mediated synthesis of sulfide derivatives from methyl esters of oleic acid, and 10-undecenoic acid, their characterization and their oxidation and tribological properties enhancement of a ecofriendly base oil.

EXPERIMENTAL

Methyl undecenoate or methyl oleate sulfide derivatives were prepared using thermally initiated radical reactions in the presence of AIBN peroxide initiator (Figure 1). Antioxidant activity of prepared additives was determined with differential scanning calorimeter (DSC) according to ASTM E 2009-08. DSC analyses were conducted on Q-100thermal analyzer from TA Instruments under oxygen atmosphere. The tribological performance of the synthesized compounds was conducted on a Stanhope SETA four-ball tester. The extreme pressure (EP) of base oil with and without additive was measured per IP 239 method under the following conditions: temperature, ambient; test duration, 60 s; rotatingspeed, 1475 rpm.

RESULTS&DISCUSSION

Compounds containing sulfur moiety are known to be antioxidant additives. Incorporation of sulfur moiety in fatty acid esters through thiol-ene reaction is supposed to provide antioxidant behavior. DSC was employed to understand the antioxidant behavior of the additives and commercial antioxidant BHT in base oil EJB. DSC provides the onset temperature (OT) and signal maximum (SM). They correspond to the temperatures when oxidation begins and maximum, respectively. Higher temperatures (OT or SM) are indications of higher oxidative stability of the tested compound [1]. The additive percentage in base oils was optimized using base oil doped with additive HETMS ranging 0.5–2% and their OT are 182.7, 195.9, 194.2°C, respectively. The maximum antioxidantactivity was observed at 1 wt% concentration, Hence, the antioxidant efficacy of synthesized sulfide derivatives and commercial antioxidant, BHT were evaluated at 1 wt%concentration in the base oil and the data is given in Table 1. Examination of the data inTable1 shows that sulfidation resulted in increased OT and SM of base oil with all the additives,

3.2 Tribological properties

The investigation of the efficacy of sulfide derivatives as antiwear additives was done byvarying their concentration in base oil. Figure 2 shows the variation of the wear scar diameter (WSD) of the lower steel balls with different additive concentrations. The resultsindicate that the additives displayed their antiwear efficacy even with small concentrations, in particular oleate derivatives which significantly reduced the WSD of thebase oil. The WSD decreased with increase of the additive concentration at 0.5%, implying that the antiwear property of the additive is dependent on its concentration in the

base stock. When the additive concentration was increased further the WSD was larger, indicating that additives demonstrated better antiwear property at a low concentration of 0.5%.This may be attributed to the formation of a more effective antiwear film by the additives through competing adsorption with base oil at a low concentration [2,3].
The efficacy of sulfide derivatives under extreme pressure conditions was also investigated in this study. The EP properties of the derivatives were evaluated at different concentrations varying from 0.25 to 2% in base oil is shown in Figure 3. It is observed that all the four additives are efficient in improving the EP properties of the base oil at the tested concentration. With increase in concentration weld load capacity improved up to 1 wt%. At 2%, the weld load capacity was more or less same for all the products indicating that 1% is the optimum concentration. All the four derivatives improved the base oil weld load capacity significantly improving from 160 to above 200 kg.

CONCLUSIONS

New multifunctional additives were synthesized via thiol-ene click reaction under thermal conditions. These molecules were designed by keeping the view that the induction of sulphur into the fatty acids via free radical addition will not only provide tribiological but also antioxidant properties. The synthesized sulfide derivatives were found to have excellent antioxidant, extreme pressure and antiwear properties for the bio base oil.

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Table 1: Antioxidant activities of sulfide derivatives on base oil at 1% concentration.

Antioxidant	**Oxidative Onset Temperature** (°C)	**Signal Maximum (°C)**
Without	165.4	198.4
HESTMS	196.3	228.7
HESTMU	193.5	224.5
AESTMS	195.3	231.0
AESTMU	193.7	228.7
BHT	193.0	230.1

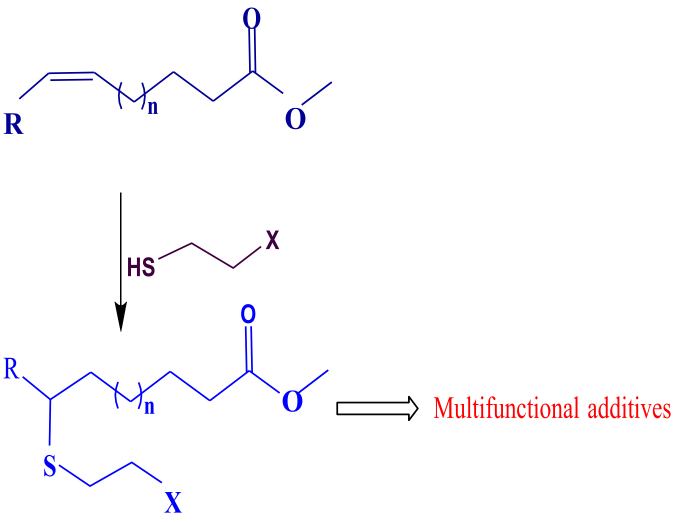

Figure 1. Synthesis of sulfide derivatives

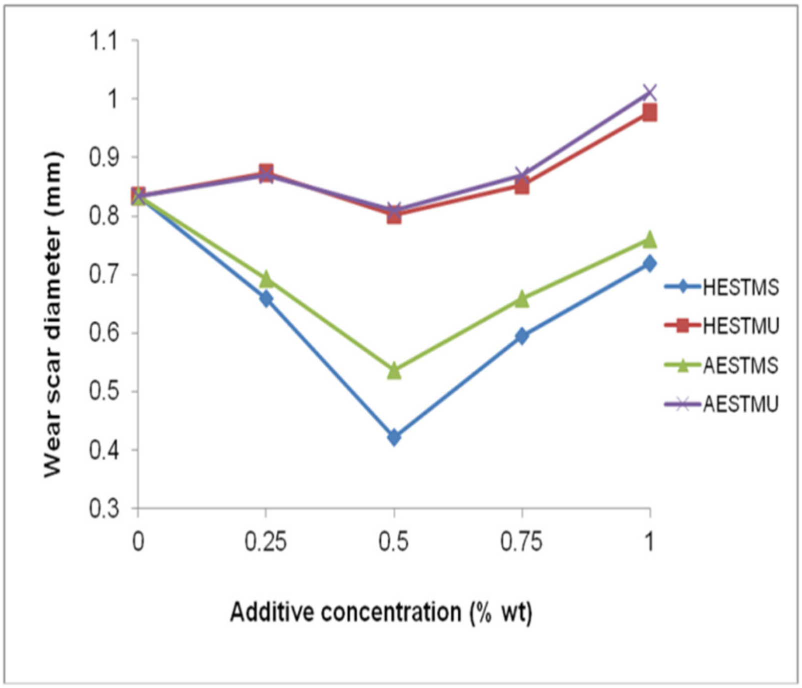

Figure 2: Wear scar diameter of thiol-ene derivatives at different concentrations in baseoil

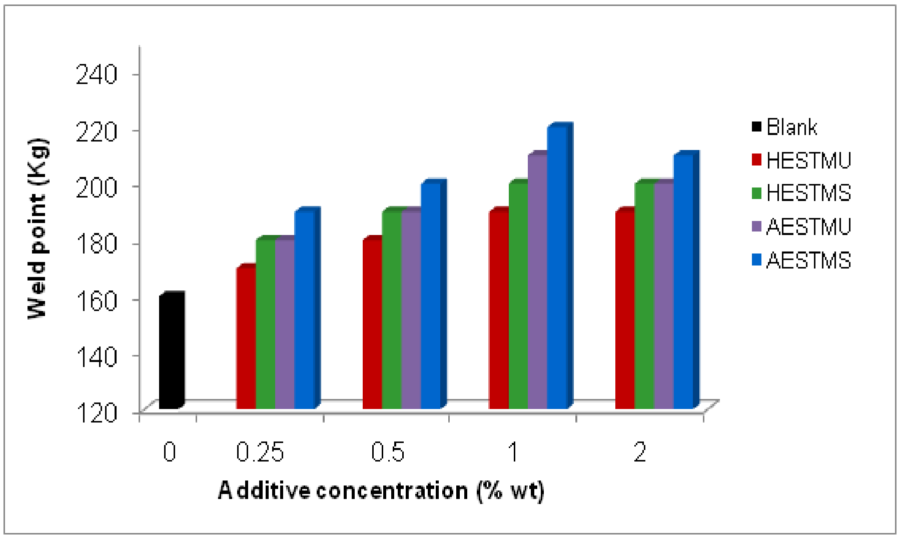

Figure 3: Weld points of thiol-ene derivatives at different concentrations in base oil

Tackifiers for High Temperature Lubricants

David DeVore, Erik Willett, Daniel Vargo

Overview

Tackifiers are polymeric additives that add tack, or stringiness, to oil and are typically used to provide lubricant adherence and anti-mist properties to fluids. Conventional tackifiers based on polyisobutylene (PIB) are not thermally stable. Tack and viscosity are lost as PIB begins to spontaneously degrade above 90°C. An increasingly important performance requirement for modern lubricants, however, is better thermal stability and lubricant formulators are turning to API Group III base oils. In this study, components of less refined lubricant oils were individually added to refined Group III oil to isolate the effects of each compound on PIB stability in oil at high temperature. From these results a novel 'preservative' was identified and used to formulate a PIB-based tackified lubricant which greatly resisted loss of tack during high temperature degradation tests.

I. Introduction

Tackifiers provide a unique form of non-Newtonian behavior separate from viscosity that aids a lubricant in remaining on a surface under shear. This is seen as tackiness or stringiness in that the modified lubricant will produce fine filaments of oil due to the tackifier additive. High molecular weight polymers ($M_n > 200k$, $M_v > 1M$) pre-dissolved into oil are the active ingredient in these additives. Large polymers are known for their ability to impart many new properties to their solutions in oil or solvent.[1]

Unlike simple liquids like solvent or water, polymer solutions have unique properties due to the connectivity between many repeat units. The molecules in solution are in constant movement and though they collide there is very little restriction in their motion. Their diffusivity, the ability to diffuse through the molecules of the solution, is very high. These liquids will flow spontaneously. Polymers are linear chains of many small molecules in one large molecule. This much larger particle with a larger cross-sectional area experiences more drag as it diffuses through the solution. As a consequence, its diffusivity is greatly reduced versus the sum of its parts. The diffusivity of polymer chains in an oil-based solution scales by a factor of $N^{-3/2}$, where N is the number of repeat units ($N = M_n/M_1$).[1] [2]

If many sufficiently long polymers are in the solution then the polymer chains create additional obstacles for one another. The chains will become entangled like spaghetti and at this point the polymers cannot diffuse through solution in three-dimensions. The polymers may only travel in a snake-like manner backward or forward in one-dimension through 'tube-like' openings between the many entangled chains. The prevailing theory of how polymers diffuse under these conditions was developed by de Gennes and is appropriately called the 'reptating tube model' after the reptating (the term for how a snake moves) way a chain must travel through a network of tube-like openings created by the other polymer chains in solution.[3] The longer a polymer chain is, the longer it takes for the polymer to snake through the tubes of entangled polymer chains.

This condition greatly slows down the physical response of the polymer solution, such as flow under gravity or response to shear. A given polymer solution with chains of length N and concentration φ has a characteristic timescale, τ, for responding to interactions such as shear, gravity, surface tension, or flow. For a dilute solution or non-polymers τ is negligible and action-reaction occurs 'instantly'. On the contrary, concentrated or polymeric solutions have a noticeable τ value where mundane interactions such as pouring the solution exceed this timescale. Returning to de Gennes's tube-like theory, polymer solutions take a long time to flow because the individual chains must work their way through the entangled network. Very long chains move slowly as it takes proportionally longer for them to travel a distance equal to their own length. The time required for a polymer to diffuse its own length is the fundamental definition of τ.[1] When physical interactions occur faster than τ the solution behaves in a non- Newtonian manner since the polymers cannot flow fast enough to respond. Tack or stringiness in oil is an example of one application of non-Newtonian behavior. Efficient tack-producing polymers achieve this effect at concentrations as low as 0.01wt% for $M_n > 100K$ ($M_v > 1M$).

A tackifier product largely consists of two components: the base oil and a dissolved polymer of high molecular weight. Olefin copolymers (OCP) or polyisobutylene (PIB) at M_n>100K (M_v>1M) are typical polymers in the current state-of-the-art. Their structures are shown below in Figure 1. The tackifier is added to finished lubricants at treat rates of less than 1wt% to provide adherence between the oil and surfaces. The tack of a finished lubricant may be characterized by methods as simple as working the oil between one's fingers to more quantitative methods like ductless siphon.[4] However, tack tests are performed at room temperature and do not encompass the range of conditions the tackifier product will experience during its service life.

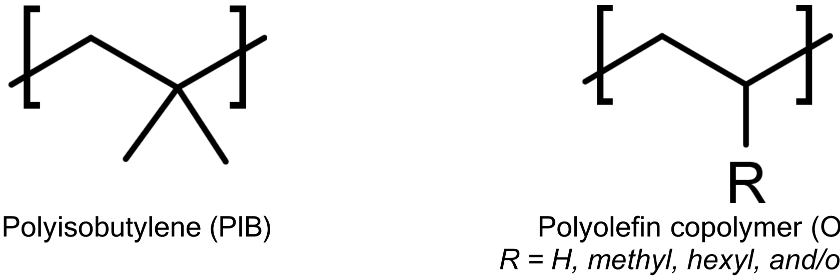

Figure 1: Chemical structure of PIB and OCP polymers

It is well-known that long polymers are sensitive to thermomechanical degradation. Continual shear acting on a polymer coil in solution will stress the chemical bonds along the backbone and cause scission of the bonds.[5] Since viscoelastic properties like viscosity index and tack are inherently tied to chain length this chain scission causes loss of performance.

The thermal contribution to thermomechanical degradation is less studied. Chain scission along the polymer backbone spontaneously occurs beyond a specific temperature for each polymer. This may occur due to reaction with oxygen or thermally generated radicals for olefin-copolymer (OCP) tackifiers. For polyisobutylene (PIB) tackifiers the chain scission occurs as an inherent property of the polymer-monomer chemistry. While PIB, given the same chain length, is more efficient at producing tack than OCP the PIB's structure introduces a critical vulnerability to temperature.

Figure 2 is a plot of % string length remaining versus the time at which a sample PIB tackifier (0.8wt% PIB 600k, 98.2% Group III oil, no antioxidant) has been held at a set temperature. These curves were extrapolated from individual data points to fit the equation

$\%S = 100 — \exp(\alpha t)$, where α is a degradation coefficient that scales exponentially with temperature. String length was measured via ductless siphon.[6] From these curves, high MW PIB-oil solutions will last for months at ≤80°C, weeks from 80-100°C, days from 100-150°C, and hours >150°C in Group III oil. Greater stability is reported for solid, bulk PIB.[7]

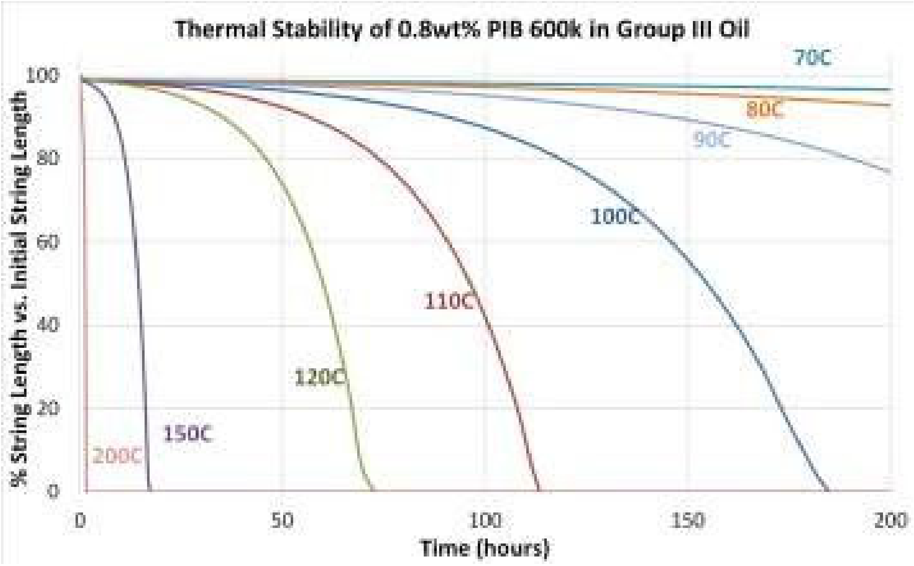

Figure 2: Extrapolated curves of string length versus time for a high MW PIB tackifier show that string length is very stable below 90°C but is rapidly lost at higher temperatures.

PIB is well-known for its unique properties due to the dialkyl substitution at the 1- position of ethylene.[8] Polyethylene and polypropylene possess symmetry in their structures which limits the rotation of C-C bonds along the backbone. As a result the polymer chains do not expand or entangle as readily in oil. Entanglement is critical for viscosity and tack. PIB has two alkyl groups at the 1- position which remove the symmetry bias from the rotation of the C-C backbone and allow it to turn freely. This increases the flexibility of the PIB polymer chain and allows it to entangle more effectively. This polymer also has the benefit of producing water- white solutions in oil with high clarity even at very high molecular weights due to its very low crystallinity. However, the same structural elements in the polyisobutylene chain which allow high tackiness also enable special temperature sensitivity only observed in highly substituted polyolefins.

During polymerization, strong reactive C=C bonds are converted to weaker C-C bonds as monomers are added to the polymer chain. The excess energy is released as heat, called the 'enthalpy' of reaction ($-\Delta H_p$).[9] This confinement of once freely moving monomer units to the polymer chain also causes a loss of disorder or 'entropy' ($-\Delta S_p$). However, the second law of thermodynamics requires *all* processes to increase the total entropy of a system ($-\Delta S_{total}<0$).[10] For polymerization to occur successfully the thermal disorder from the heat released by the reaction ($-\Delta H_p$) must overcome the entropy lost from the monomers ($-\Delta S_p$).[9] This balance is expressed as the Gibbs free energy ($-\Delta G_p$), where T is temperature:

$$-\Delta G_p = -\Delta H_p + T(-\Delta S_p)$$

A process may only proceed forward and yield a stable product while $-\Delta G_p>0$. The process is then called 'favorable'. Polymerization conditions are engineered to achieve $-\Delta G_p>>0$ and one way to do so is by varying temperature, T. If $-\Delta G_p<0$ during or after the polymerization then the process is 'unfavorable' and may spontaneously reverse itself at some rate. This rate is governed by the field of 'kinetics' which describes the speed at which a process moves between the initial and final states of a process that were determined by thermodynamics.[11]

Several key thermodynamic parameters of polymerizations are listed in Table 1 for different polymer families. The general trend is that $-\Delta H_p$, $-\Delta S_p$, and $-\Delta G_p$ of a monomer decrease with increasing 'steric hindrance' from additional alkyl groups on the monomer in polyolefin and polystyrene series. Steric hindrance is an effect of overcrowding in a chemical structure that prevents the structure from rotating into an efficient, energy minimized orientation. As a result, the final polymer structure is higher energy which causes a lower difference in energy between reactants and product. Therefore a lower enthalpy of polymerization is released and less capable of offsetting the loss of entropy. Unsaturated polymers like polybutadiene and polyisoprene benefit from additional alkyl groups due to stabilization of the double bonds in the polymer. As previously stated, higher $-\Delta H_p$ and $-\Delta S_p$ are more thermodynamically favorable.

Table 1: Standard enthalpy, entropy, and free energy of polymerization by monomer, reproduced from Wiley[12]

Monomer	**$-\Delta H_p$ (kJ/mol)**	**$-\Delta S_p$ (J/mol-K)**	**$-\Delta G_p$ (kJ/mol)**
Ethylene	93 — 108	142 — 177	51 — 57
Propylene	87 — 104	167 - 205	37 — 43
Isobutylene	54	120	18
Styrene	70 - 76	105 - 148	31 - 39
α-Methylstyrene	35	104	4
Butadiene	74	86	48
Isoprene	75	101	45

1,1-disubstituted olefins like isobutylene and methylstyrene exhibit low enthalpies ($-\Delta H_p$) of polymerization due to the steric hindrance of two functional groups on the active chain end.[9] Typical monomers have a $-\Delta H_p$ of 80-100 kJ/mol and $-\Delta S_p$ of 100-140 J/mol-K.[12] Isobutylene has a $-\Delta H_p$ of only 54 kJ/mol with a $-\Delta S_p$ of 120 J/mol-K. The resulting temperature-dependent

$-\Delta G_p$ of isobutylene is much lower than usual and $-\Delta G_p<0$ is possible at less than 100 °C. The cross-over point when $-\Delta G_p=0$ is called the ceiling temperature, T_c. Below T_c, depolymerization of PIB to its monomeric units occurs. The equilibrium concentration of monomer, [M], from the depolymerization may be expressed in terms of T_c, $-\Delta H°$, and $-\Delta S°$ as:[9]

$$\ln[M] = -\frac{-\Delta H^{\circ}}{RT_c} + \frac{-\Delta S^{\circ}}{R}$$

Actual T_c may differ from estimated T_c due to additional complex interactions.[12] Depolymerization of a polyolefin backbone is understood to be a homolytic cleavage of the C- C bond into two alkyl radicals. In PIB, these two radicals can reassemble back into bond to restore the original chain. The radicals may also graft to other parts of the polymer to reconstitute the chain in a slightly different, more stable configuration. This effect delays PIB degradation in bulk.[12] However unsaturated compounds and heteroatoms in a PIB-oil solution may scavenge these radicals as chain-transfer agents and prevent reassembly.[9]

Since tackifier additives are two-component systems of oil and polymer it is worth discussing the role of the oil used to dissolve the additive and to prepare the finished lubricant. Previous work has shown that even low (<5wt%) concentrations of Group I/II base oils added to Group III can drastically affect PIB stability at elevated temperatures.[13] These less refined oils may contribute components which disrupt the equilibrium between polymerization and depolymerization of PIB at high temperature and accelerate decomposition.

Group I oils are produced through the cracking of crude oil into lighter products which are solvent refined. This solvent process reduces the content of 'aromatics' like benzene and non- carbon 'heteroatoms' like sulfur (S), nitrogen (N), and chlorine (Cl) but does not eliminate them. Aromatic content may be 10-20% of the oil by weight while S, N, and Cl occur at up to 300 ppm concentration. Group II oils are hydrogenated to >90% saturated hydrocarbons and minimal heteroatom content. Group III oils are hydrocracked using a more aggressive hydrogenation that breaks C-C bonds of cyclic components in the oil. Naphthenic content is greatly reduced. While Group III oils possess high viscosity indexes and purity these oils come at higher cost and often exhibit poor compatibility with additives for Group I/II oils.

As discussed, tackifiers are two-component systems of polymer and oil. This study uses multiple approaches to measure and improve the thermal stability of tack from PIB. In the first section, we focus on base oil impurities as a follow-up to prior work in Group I/III oils.[13] In the second section, we report a 'tack preservative' based on beneficial impurities of Group I oils. In the final section, we describe preliminary work in finding alternatives to OCP and PIB chemistries for use in tackifiers. The goal of this effort is to understand the foundations of tackifier polymer stability, improve on this established technology, and identify new polymer chemistries to advance the state-of-the-art.

II. Experimental

II.a. Base Oil Impurity Study

Polymer-oil solutions were prepared in two stages.

Stock Solutions: Commercial linear PIB and OCP polymers were chosen to examine the effects of composition on viscosity, tack, and thermal stability. A short PIB (M_n = 200k, "PIB 200k") and long PIB (M_n=600k, "PIB 600k") were chosen to examine dependences on molecular weight. A relatively long OCP (M_n=200k, "OCP 200k") was included to compare performance and thermal stabilities with the short PIB of the same molecular weight.

Stock solutions of these three polymers (PIB 200k, PIB 600k, and OCP 200k) were prepared at 1wt% polymer in Group III oil. The same lot number of Group III oil was used throughout the experiments. Due to thermal instability and oxidation the polymers were dissolved into the oil via gentle mixing at 80°C for 72 hrs. No antioxidant was included unless where noted.

Tackifiers with Impurity: Tackifier products containing 0.8 to 1.0wt% polymer and 0.1wt% of one impurity (see below) were prepared from the tackifier stock solutions. Polymer content was varied to obtain initial viscosities of 20-25 cSt at 100°C and initial string lengths of 70 — 99 (via ductless siphon). PIB 200k and OCP 200k solutions contained 1wt% polymer while PIB 600k solutions contained 0.8wt% to account for higher tack with longer chain length. Control groups were prepared for each polymer with no added impurity.

The impurities chosen for this study are single representative species from within varying classes of 'bad actors' in less refined lubricant and crude oil stocks.[14] [15] A bad actor in oil is assumed to cause a qualitative loss in performance or stability in the product. Compounds containing rings, unsaturation, sulfur, nitrogen, and chlorine are known to promote the degradation of polymers and base oils through the formation of radicals or reactions with active ingredients. Four classes of impurity were tested by preparing four tackifiers with impurity, each containing one representative species:

- Monocyclic aromatics – Alkylated benzene (0.1wt% C_6H_5 in tackifier)
- Polycyclic aromatics – Naphthalene (0.1wt% naphthalene in tackifier)
- Sulfur – Thiosulfates (0.1wt% S in tackifier)
- Nitrogen – Primary alkyl amine (0.1wt% N in tackifier)

II.b. Tack Preservative Study

Tackifiers with Tack Preservative: From screening of good and bad actors in the dilute tackifiers a novel additive described as a 'tack preservative' was identified. Tackifiers were prepared from the PIB and OCP stock solutions previously described with varying wt% of the preservative added.

Finished High Temperature Lubricants. Finished lubricants were prepared to assess the performance of the novel tack preservative with both PIB tackifier and OCP-based viscosity modifier. These contain 0.01 — 0.1wt% polymer, 25wt% of a Group II-based OCP viscosity modifier with PSSI 22%, and Group III diluent oil. The dilution of tackifier polymer and tack preservative along with the inclusion of the Group II-based OCP represents a worst-case scenario. This condition aided in optimizing a robust,

II.c. Thermal Degradation Testing

Two methods of high temperature degradation were performed: long-term degradation at 150°C for 16hrs and rapid degradation at 200°C for 2hrs. These two testing regimes were found to induce tack loss to varying degrees. Similar oven-based tests are common in evaluating antioxidants for lubricants under milder conditions (60-70°C).[16] These conditions were sufficient to observe loss of tack across a range of different tackifier products and lubricants. The long-term test is convenient for overnight trials while the high temperature 2hr degradation allows multiple trials per day for rapid optimization of formulas.

Samples were pre-heated in 600mL beakers on a well-ventilated hotplate to the desired oven temperature. Once the temperature was reached each beaker was placed into a PID- controlled heating oven (±1°C) for a period of up to 24hrs. Portions of each sample were taken periodically (90g per string length test; 20g per viscosity test) within minimal disturbance to the samples. It is important to pre-calculate the total sample mass required.

II.d. String Length and Viscosity Testing

Prior studies on tackifier stability at high temperature primarily focused on viscosity to characterize these materials.[13] In this study, string length was chosen to expand on the available data for tack loss at high temperature.

String length was measured on 100mL samples at 25°C via the ductless syphon method.[6] This method was developed by Functional Products Inc. as an arbitrary measure of the tackiness of oil-polymer sample. The reported value is the maximum length of a single thread of tackified oil withdrawn from a standard 100mL graduated cylinder (Kimax 20025-H) by vacuum capillary tube. String lengths are only reported up to 99. Strings longer than 99 tend to be thin enough to be buoyant in air and complicate the measurement.

The finished lubricants were tested for viscosity at 40/100°C using a capillary viscometer (ASTM D445) to ensure similar starting viscosities. Viscosity values are reported as needed.

III. Results and Discussion

III.a. Tackifier Stability

Tackifiers of 1wt% PIB or OCP (M_n = ~200k) in pure Group III oil were initially prepared to demonstrate the short- and long-term temperature stabilities of these major tackifier chemistries. Due to the structure of the oil and polymer, the OCP has better initial string length than the PIB at the same treat rate in oil. It is worth noting that string length and viscosity will vary by the specific compatibility between a given oil and polymer. This compatibility determines K and a in the Mark-Houwink equation, $[\eta]=KM^a$.

Two testing regimes were developed for slow and fast thermal degradation of samples based on the plots in Figure 1. Since the rate constant of reactions scale by $\exp(-\Delta H_{rxn}/T)$ increasing the temperature will cause exponentially faster degradation.[10] 16-24hrs at 150°C and 1-2hrs at 200°C produced adequate string length loss for samples of initial string 60-99 to provide useful information in optimizing formulations.

Figure 3 shows the remaining % string length of M_n=200k PIB and OCP tackifiers held at 150 and 200°C over several hours. While PIB degrades significantly in both cases these two regimes show different behavior in the OCP. 1hr 200°C degradation produces roughly the same remaining string length as 16hrs at 150°C in PIB. This is due to the thermally induced chain scission due to unfavorable thermodynamic stability of isobutylene polymers.

In the OCP sample (Figure 3) the shorter 200°C degradation did not produce the same level of string length loss as the longer, cooler 150°C trials. OCP degradation occurs through slower oxidation of the polyolefin which requires diffusion of polar oxygen through a dense hydrocarbon fluid. Degraded OCP samples were yellowed or light orange while degraded PIB remaining water-white and clear. Mono-substituted polyolefins are more prone to oxidation due to the tertiary carbon, CR_3H, which generates stable tertiary radicals. This is evident in maleated OCP where maleic anhydride is added to the substituted olefin site by radical addition chemistry. Oxidation occurs more readily on that tertiary alkyl site for the same reason. In general, the OCP string length survives thermal degradation better than in PIB of equivalent length. High temperature tackifiers have thus far relied on OCP chemistries for this reason.[17] However, they are not as efficient at producing tack as PIB in most oils at low wt% as demonstrated in Figure 4: below 0.5wt% polymer the PIB 200k polymer provides better string length than OCP 200k, given the same chain length.

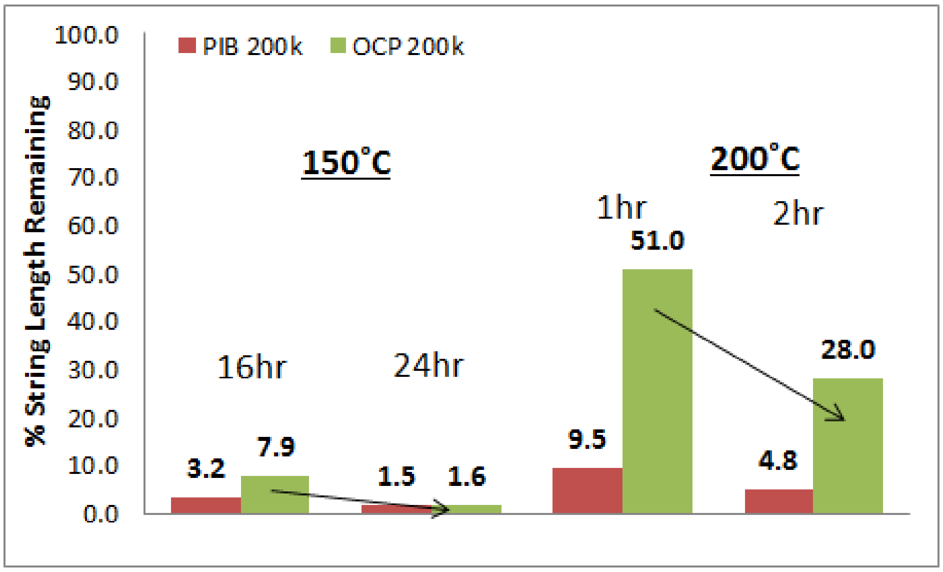

Figure 3: OCP tackifiers possess better high temperature resistance than PIB tackifiers at high, rapid heating (200°C) but fail over long periods of lower heat due to oxidation

PIB remains desirable, despite its temperature sensitivity, due to its production through well-controlled cationic polymerizations which produce extremely high MW grades of pure PIB.[18] PIB-based tackifiers have lower initial color and better oxidative stability than OCP which allows them to remain dominant in non-high temperature applications.

This access to high MW grades of PIB is beneficial to high temperature tackifiers. If string length at high temperature is lost incrementally over time then starting with greater string length would provide a longer time before the polymer is degraded to a length too small to provide sufficient tack. This was tested with a higher grade of PIB (M_n=600k, M_v=6M).

Figure 4 shows the relationship between wt% PIB and string length for two grades of PIB (200k and 600k) in Group III oil. String length by treat rate in very high MW polymers is not a simple exponential curve like viscosity in viscosity modifiers.[19] Tripling the chain length can provide up to twice the string length and produces a viscoelastic plateau from 0.3 to 0.8 wt%. This plateau corresponds to the transition from semi-dilute to dilute concentration regions for an entangled polymer solution.[1] From this plot, the longer polymer (PIB 600k) is obviously better at providing tack however it also possesses this unique plateau where loss of polymer concentration from 0.8 to 0.3wt% does not incur a loss in string length. High temperature tackifiers should target this concentration regime. The tackifier samples produced in this study were prepared with these considerations in mind.

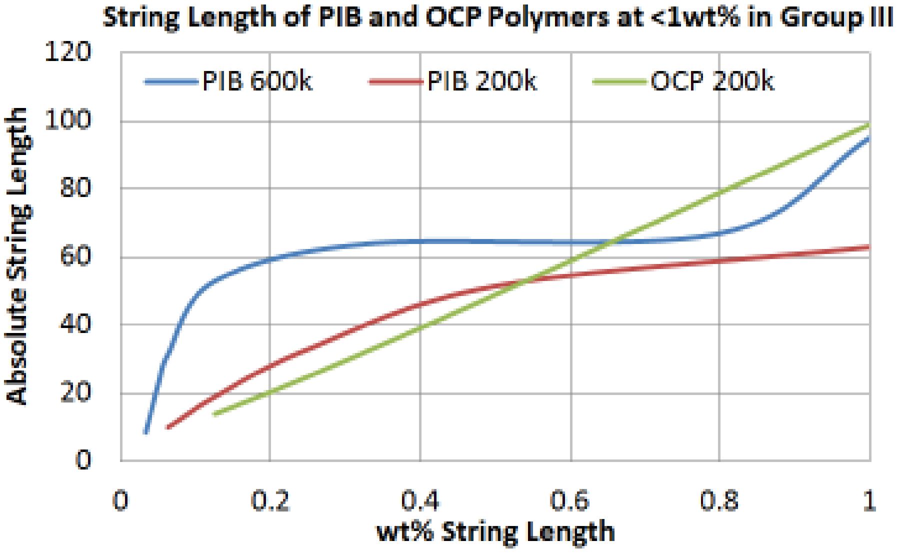

Figure 4: String length for PIB and OCP tackifiers prepared with 0-1wt% polymer. PIB 200k and 600k are better than OCP 200k at providing string length at under 0.5wt% in oil, such as after dilution of the tackifier product in the lubricant; PIB 600k is understandably better at providing tack than PIB 200k. PIB 600k experiences a 'plateau' from 0.3 to 0.8wt% due to its long chain length.

III.b. Base Oil Impurity Study

This work was initiated to complement a prior study on PIB and OCP tackifier stability in pure and impure Group III oils.[13] The results suggested that even low concentrations of impurities present in the Group III diluent oil of a lubricant additive can compromise the tack of a Group III-based lubricant at high temperature.

As discussed in the experimental section, several modified Group III oils containing a single representative species of impurity from Group I and II oils were prepared for tackifier formulation. Monocyclic aromatics (via alkyl benzene), polycyclic aromatics (via naphthalene), sulfur (via thiosulfates), and nitrogen (via alkyl amine) were solubilized in oil at 0.1wt% of the functional group or element of interest. A control with no impurity was also prepared.

Samples of PIB 200k and PIB600k were solubilized at 1wt% and 0.8wt%, respectively, in the Group III oils to initial viscosities 20-25 cSt @ 100°C and string lengths of 63-67. % string length remaining for degraded samples was calculated versus these initial string lengths.

Thermal degradation was performed under the long-term high temperature condition (150°C for 16 and 24hrs) with string length samples pulled from the sample beakers at those prescribed times. Figure 5 shows the 16 and 24hr string lengths for PIB 200k (top) and PIB 600k (bottom) tackifiers.

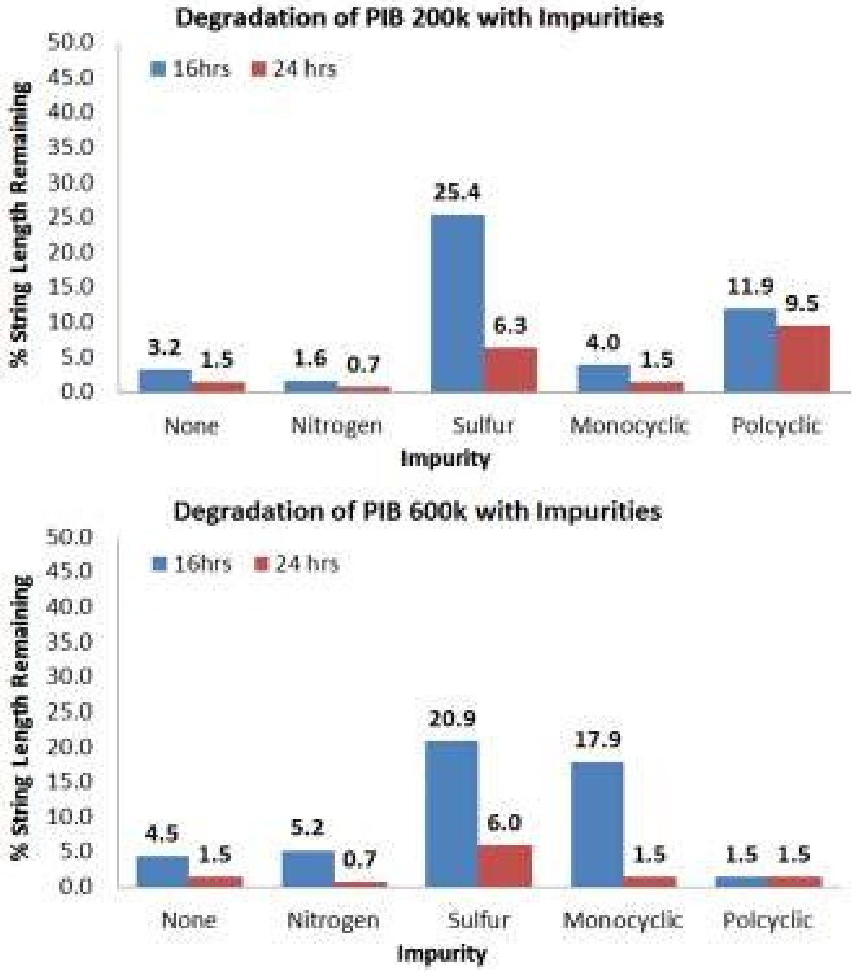

Figure 5: % string length results from PIB 200k and PIB 600k tackifiers degraded at 150°C show a benefit from heteroatoms and aromatic compounds at 0.1wt% over 16-24hrs of thermal treatment. This is contrary to the conception of these compounds as 'bad actors'.

Without any impurity, both PIB 200k and 600k degrade to 1-5% of their initial string lengths in 16hrs. The PIB 600k maintains better string length in 16hrs however they both reach the same negligible string length by 24hrs. These results are expectable based on the difference in initial chain size. The addition of heteroatoms (N and S) and aromatics (monocyclic and polycyclic) produced varying effects in the two PIB samples.

Heteroatoms accelerated string loss in PIB 200k but reduced string loss in PIB 600k at 16hrs. Phenolic compounds like butylated hydroxytoluene (BHT) use oxygen as a heteroatom to abstract and stabilize radicals from interacting with lubricants.[16] Nitrogen and sulfur compounds are generally reserved for anti-corrosion and extreme pressure additives but their electronegativity would grant them some affinity for the spare electron on radicals.[20] This would slow the attack of thermally generated radicals on the large PIB 600k chains. 0.1wt% nitrogen reduced both PIB string lengths below the pure Group III (none) PIB samples by 24hrs. Nitrogen compounds are oxidized to reactive nitrates species over time. Nitrogen may initially absorb radicals from the oil to initially slow degradation but will later be easily oxidized by addition of O_2 to give the reactive oxides. NO_2 will proceed to oxidize the alkyl chains and its effect will add to the thermal chain scission breakdown of PIB.

Sulfur-treated PIB 600k maintained high string lengths for 16 and 24hrs. Sulfides and thiols have high affinity for radicals due to their electronegativity, multiple lone pairs, and ability to form bonds to many atoms at one time. Like nitrogen, sulfur compounds are eventually oxidized to reactive SO_2 however sulfur did not produce the same degree of string loss as nitrogen. The slower rate of string length loss may be due to nitrogen and sulfur intercepting oxygen before it react with the polymers, essentially acting as antioxidants.

Aromatics, both mono- and polycyclic, had an inverse effect with respect to MW. PIB 200k string length loss was reduced during150□C treatment with mono- and polycyclic aromatics impurities. PIB 600k was generally unaffected after 24hrs though the benzene- doped sample gave a high % string length value at 16hrs. The results for these two categories are shown in Figure 5. Lower MW PIB produced lower string length loss after the 150□C. This was unexpected since aromatic compounds have been identified as promoting the formation of radicals in oil.[14] The difference in outcome may be due to the fixed 0.1wt% concentration used for all the modified Group III oils prepared. Unsaturation may be as high as 10-20% in some base oils. Aromaticity of a compound stabilizes the radical, making it easier to form, through resonance which disperses the high energy radical over a large area.[9] Aromatic compounds tend toward generating radicals through breakage of the C-H bond but also tend to recombine with alkyl radicals rather than hydrogen radicals.[9] Recombination occurs when two radicals, essentially two half bonds, react to form a stable single bond. Multiple PIB radicals attacking the same aromatic compound could temporarily build chain length and prolong tack loss in principle. This would occur, for example, when the larger portions of two broken PIB chains attached to a single aromatic molecule to produce a chain of similar or larger size than the original PIB chains. If this effect occurs then it is observed more prominently in the shorter PIB chain with polycyclic aromatics where the % string length remaining after 16 and 24hrs was the highest among degraded PIB 200k samples.

Further study is needed to determine the concentration limits for the benefit effects of heteroatoms and aromatic impurities. Both types of impurities have some interaction with radicals generated from the oil or polymer at high temperature. As discussed, PIB is continually breaking bonds into radicals and recombining radicals back into chains in a temperature-dependent equilibrium. Above its ceiling temperature the breakage is favored and a net amount of radicals is generated as the chains revert to monomer. These excess radicals may proceed to accelerate degradation by attacking other sections of polymer. When impurities that interact with radicals are added this complex exchange of reactions becomes much more complicated. Impurities may help prevent further attacks on the PIB chains by PIB radicals but the additives will also prevent reassembly of broken chains when two PIB radicals recombine. There is precedent for this type of reaction in polymerization and it is the basis for the field of ‘reversible addition-fragmentation (RAFT)’ polymerization.22 RAFT agents work by selectively binding (“addition”) and releasing (“fragmentation”) alkyl radicals to sulfur groups at high temperature to control the speed of radical-initiated polymerizations and produce narrow molecular weight distributions. Many such RAFT agents are capable of adding two or more alkyl radicals. In effect, these sulfur-based compounds add two alkyl radicals together. Since PIB breaks down at high temperature into multiple radicals a compound with two or more sulfur groups could potentially reconnect the PIB chain at the site of breakage.)

This study did not include species which are a combination of the different impurity types. Crude oil feedstocks contain many species of heteroatoms and unsaturated components but also combinations of unsaturated heteroatom compounds.[15] Aromatic nitrogens like aniline will have a different interaction than alkyl amines, for example. It is difficult to establish a representative sampling of all these components for testing since there are very few published works about the composition of lubricant base oils at the molecular scale.

From these results we may draw a few conclusions. First, the representative species of impurities in less refined oils (Group I and II) are not equally or always responsible for the degradation of PIB tackifiers at high temperature. Cases were observed with neutral, positive, or negative outcomes to the addition of the impurities at 0.1wt%. These effects are summarized in Table 2. Polycyclic and sulfur compounds had beneficial effects on the string length of PIB 200k and 600k with long- and short-term thermal degradation. Second, 24hrs at 150°C appears to be sufficient in determining the long-term stability of tackifiers with impurities at high temperature. Multiple samples gave higher % string length remaining than the pure control group but gave the same or worse results after 24hrs. A 16hr overnight trial is not sufficient for anticipating this loss. Third, this work has shown that there are alternative chemistries to butylated hydroxytoluene (BHT) in preserving the string length of tackifiers at high temperature.

Table 2: Summary of the observed effects of 0.1wt% impurity in PIB-based tackifiers

Impurity Group	**Representative**	**Effect on PIB 200k**	**Effect on PIB 600k**
None	None	Loss of tack	Loss of tack
Monocyclic Aromatics	Alkyl Benzene	No Change	Reduced Loss (temporary)
Polycyclic Aromatics	Naphthalene	Reduced Loss	No Change
Sulfur	Thiosulfate	**Reduced Loss**	**Reduced Loss**
Nitrogen	Alkyl Amine	Increased Loss	Increased Loss

III.c. Tack Preservative

Based on the initial findings from the base oil impurity study a larger selection of ‘beneficial’ impurities was surveyed for their effectiveness in preserving tack at high temperature. Upon further review it was determined that one compound in particular showed promise as a new type of additive.

This novel ‘tack preservative’, TP, acts partially as an antioxidant however its structure also provides additional functions specific to PIB-based tackifiers at high temperature unlike butylated hydroxytoluene (BHT) tested in a prior study.[13] While BHT added to PIB tackifiers in Group III reduced string loss considerably it did not confer high temperature resistance at 0.001wt% BHT after addition of a few percent Group I oil. High treat rates of BHT may have been effective but BHT has poor compatibility

Optimization of this high temperature tack preservative was performed using results from the fast 1hr and 2hr 200°C degradation method. This is reliable for generating substantial PIB string length loss and observing any effects of an additive. Throughout a series of different experiments we can propose how and under what conditions this tack preservative operates.

PIB 200k, PIB 600k, and OCP 200k were compared as simple two-component polymer-oil tackifiers with and without the new additive using the long- and short-term thermal treatments. The resulting string lengths after thermal degradation, shown in Figure 6, were used to assess the effectiveness of the additive for varying tackifier polymers.

Figure 6 compares the % string length remaining versus OCP and PIB tackifiers containing 0 and 0.1wt% of the tack preservative. In the 150°C trials, top of Figure 6, the tack preservative provides long-term stability of tack for both OCP and PIB chemistries. The preservative’s chemical structure allows some anti-oxidant behavior. Remarkably, in the case of the high MW PIB there is no loss of string length versus the original unheated PIB tackifier. The performance is similar between OCP 200k and PIB 200k, both having roughly the same chain length, but works best with longer chains (PIB 600k). It is also notable that the % string length value is stable between 16 and 24hrs for PIB while OCP varies over time.

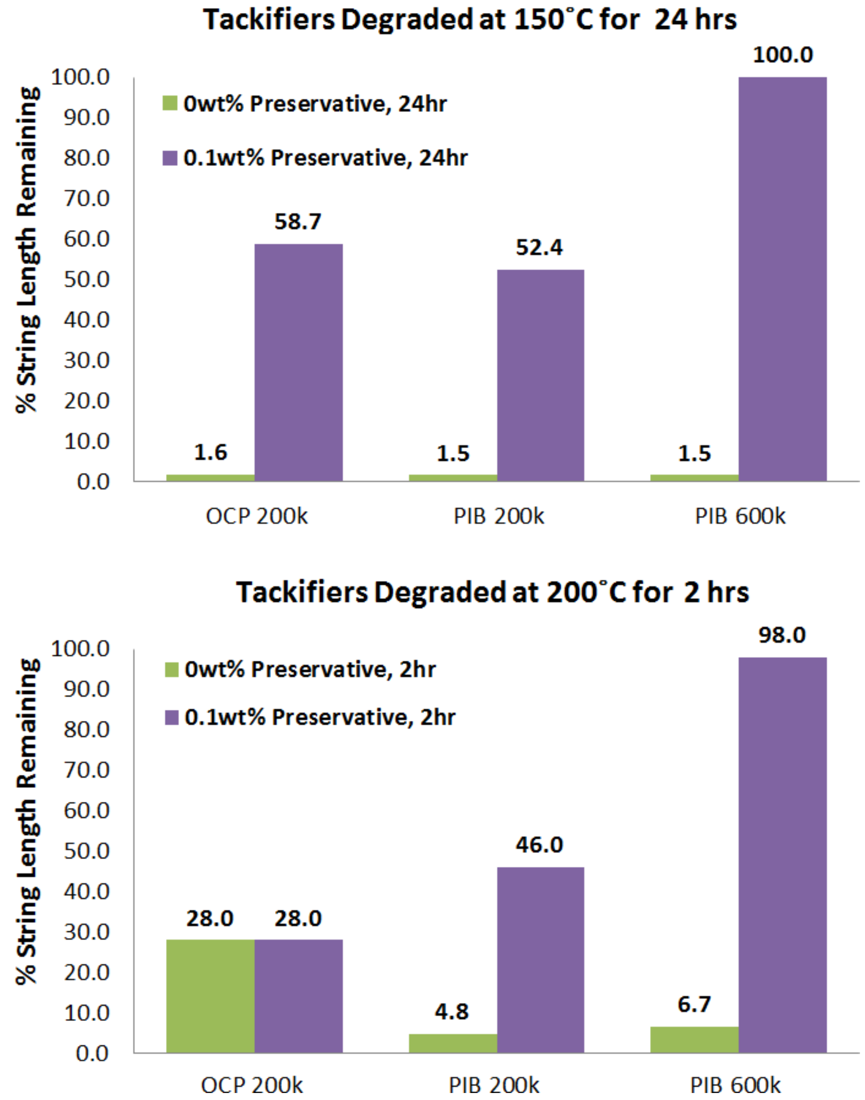

Figure 6: The tack preservative provided high temperature resistance to the tackifiers which allowed high retention of string length after 24hrs at 150°C and 2hrs at 200°C. PIB-based tackifiers exhibit the most dramatic improvement suggesting that the tack preservative is specific to PIB. The behavior of OCP between 150°C and 200°C suggests an antioxidant effect over long-term, lower temperature heating for OCP tackifiers.

Initial treat rates for the tack preservative were based on the 0.1wt% treat rate from the base oil impurity study. A series of varying treat rates in 0.8wt% PIB 600k in Group III oil were prepared. PIB 600k was chosen since it provides the highest tack and had the best performance with the new additive. The results in Figure 7 show the robust performance of this additive from high to low concentrations. No string length loss was observed for any concentration of the additive from 0.001 to 0.1wt% at 200°C for 1hr. A concentration of ~0.05wt% is required to also resist string length loss over 2hrs. This concentration regime is possible even at low treat rates in a finish lubricant through a tackifier modified by this additive.

While high treat rates provide better heat resistance to the tack the extra tack preservative content contributes additional color after degradation. 0% preservative gives an ASTM D1500 color of <0.5 after 2hrs at 200℃; ≤0.01% is 0.5 — 1.0 in color; 0.05% is 1.5 in color; and 0.1% is 2.0.

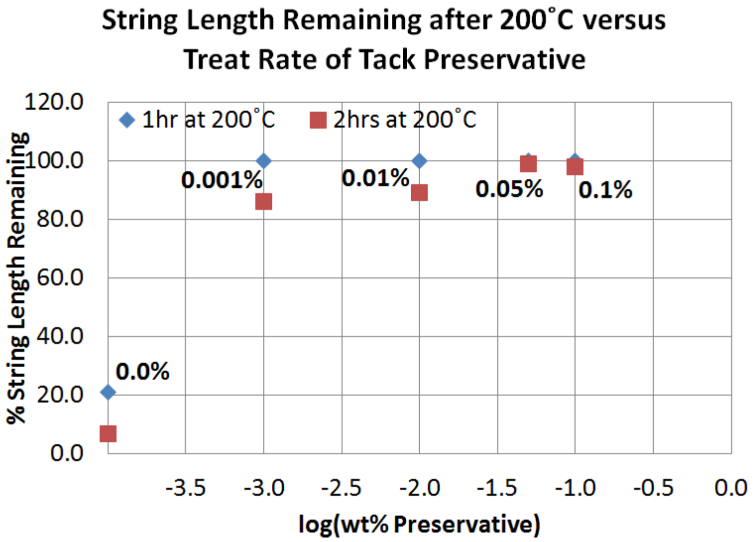

Figure 7: The tack preservative is effective in the PIB 600k tackifier over a very wide range of treat rates from 0.001wt% (10 ppm) to 0.1wt%. No improvement was observed at >0.05wt%.

The tackifiers discussed thus far have only been two-component solutions of PIB or OCP polymer and Group III oil. A finished lubricant often includes polyolefin viscosity modifiers to improve the viscosity index and achieve a more stable viscosity across a large temperature range. A series of tests were performed to show the robustness of the tack preservative with mixed PIB and OCP polymer chemistries in a finish lubricant.

The PIB 600k polymer and tack preservative were added to Group III-based oil with an OCP-based viscosity modifier. As shown in Figure 6, olefin copolymers are not affected by the tack preservative due to the difference in chemical structure between PIB and OCP. It is important to note that increasing the viscosity of a tackified oil multiplies the string length though no additional tackifier is added.[6] Obviously the addition of the OCP viscosity modifier will improve the initial string length of the finish lubricant but it will also dilute the concentration of tackifier and tack preservative and physically block the interaction between those two components. An excess of this OCP-based viscosity modifier was included (25wt%). The oil in this modifier was Group II to further demonstrate the improved performance above simply adding BHT. As previously shown, BHT greatly reduces string length loss at high temperature when only Group III oil is used with PIB.[13] Impurities from less refined oils compromised the effect of BHT.

In short, the finished lubricant using the tack preservative was formulated in Group III oil with a Group II-based commercial OCP viscosity modifier to test the operation of the tack preservative in a sample finished lubricant. A series of these lubricants with viscosities from 26-30 cSt at 100℃ and initial string lengths of 75-80 were prepared to optimize the content of tackifier polymer and tack preservative for a sample high temperature tackifier product. These sample formulations are described in Table 3. They do not specify the wt% Group II oil in the OCP viscosity index improver ("OCP VII").

Table 3: Formulations prepared to test and optimize the performance of the novel tack preservative in a realistic finished lubricant containing OCP viscosity modifier, Group II oil, and diluted tackifier. Performance was maximized by doubling the tackifier polymer content and raising the level of preservative by an order of magnitude.

Sample	**A0**	**A1**	**A2**	**B0**	**B1**	**B2**
Note	1x PIB **Control**	1x PIB 1x TP	1x PIB 10x TP	2x PIB **Control**	2x PIB 1x TP	2x PIB 10x TP
wt% PIB 600k	0.08	0.08	0.08	0.17	0.17	0.17
wt% OCP VII	25.00	25.00	25.00	25.00	25.00	25.00
wt% Preservative	0.00	0.02	0.17	0.00	0.02	0.17
wt% Group III Oil	74.92	74.90	74.75	74.83	74.82	74.67
%String, 1hr at 200°C	90	82	100	91	100	100
%String, 2hr at 200°C	71	82	60	81	94	100

Sample A0 is the control group: a Group III lubricant with PIB tackifier and OCP viscosity modifier. The % string length after 2hrs at 200°C is 71% which is greatly improved over the simple 0.8wt% PIB 600k tackifier with 0% additive in Figure 6. This is due to the contribution of larger percentages of shorter OCP polymer to provide viscosity in addition to the small percentage of long PIB tackifier. As the PIB tackifier degrades due to thermal instability the viscosity of the degraded lubricant is maintained by the more stable OCP viscosity modifier. When the PIB tackifier is used as the sole source of viscosity improvement (without an OCP viscosity modifier) then viscosity will decay exponentially under heating as the small concentration of highly effective tackifier chains break down into a small concentration of short pieces that do not provide tack or viscosity. The oxidation-prone nature of the OCP viscosity modifier may also help prevent oxidation of the PIB.

When the tack preservative was added at a treat rate based on Figure 7 (Sample A1) it reduced 1hr % string length and increased 2hr % string length versus the initial string length. The string length was stabilized between the two measurements but an 18% loss of string was still observed. In prior samples from Figure 6 and 7 no string length loss was observed. It was hypothesized that the preservative required some minimum concentration in the oil to affect the PIB and survive radicals generated by the oil. The treat rate of tack preservative was increased by an order of magnitude to produce Sample A2. This increase in additive improved 1hr heat resistance but greatly reduced 2hr heat resistance versus samples A0 and A1. Higher preservative to PIB ratios appear to accelerate degradation of string length. The initial improvement at 1hr may have been the preservative acting as an antioxidant prior to accelerating degradation.

The hypothesis guiding formulation was adjusted to consider both the ratio of tack preservative and PIB and their overall concentration in the lubricant. Sample B0 was produced as the control group for the B series of samples with double the PIB content versus the A0-A2 samples. This gave the same 1hr % string length remaining value as sample A0 with half the PIB. B0 had better 2hr % string length remaining as A0 but not better than additized A1. Tack preservative was added to the control, B0, to produce additized sample B1. This was an improvement on string length stability at high temperature versus the A0-A2 series. However string length stability remained lower than the results with the simple

PIB 600k tackifier in Figure 6. Sample B2 was prepared using an order of magnitude more tack preservative to achieve no string loss after 1hr and 2hr at 200°C.

In summary, we have demonstrated a novel tack preservative which prevents the measurable loss of tack during long-term (16-24hrs at 150°C) and short-term (1-2hrs at 200°C) thermal degradation experiments. This new additive is capable of operating in Group III base oil with an OCP viscosity modifier. Additionally, less pure Group II diluent oils do not prevent the tack preservative from functioning, unlike BHT in prior studies.

III.d. Preliminary Investigation of High Temperature Polymers

OCP and PIB polymers are only a small part of the commercial polymer sector. There are roughly thirty polymers common in industrial applications and these are separated into four tiers.[21] Several inherently high temperature polymers with working temperatures ranging up to above 200°C were obtained to prepare high temperature polymer-oil solutions. Polyethylene terephthalate (PET) is an engineering polymer with very low cost containing aromatic terephthalate in its backbone. Polysulfone (PSU) is known for its relatively weak solvent resistance. Polyphenylsulfone (PPSU) was chosen due to its lower polarity and higher hydrocarbon content than polysulfone. Polyetherimide (PEI) is a high performance polymer with high polarity which is attractive for ester-based Group V oils. Standardly available extrusion grades of polymer were obtained to avoid the cost of specialized formulations.

Engineering and high performance polymers are typically polar with ether, amide, or ketone linkages between subunits of benzene. These linkages have positively and negatively charged bonds which cause a strong attraction between chains to neutralize these charges.[22] ‘Pi-pi stacking’ occurs between the non-polar benzene units and further strengths that attraction.[22] Solvents and oils to dissolve the high polymers must then interact with both the polar linkages and non-polar benzene backbone to disrupt the attraction between chains.

The most effective solvent was a mixture of toluene and methyl ethyl ketone (MEK). The two components of this co-solvent system contribute both the polar and aromatic solvency required. This solvent system produced a range of effects on the polymers. PET was dissolved in toluene:MEK at room temperature to concentrations as high as 10wt% to form a gel. PSU with toluene:MEK formed an interesting free-flowing latex phase. PEI gave a similar effect with much greater viscosity with toluene:MEK. PPSU turned from clear to white from the toluene:MEK but did not flow.

While the toluene:MEK blend is effective in some cases it has a low boiling point (90°C) that limits its application and creates the issue of flammable vapors. Elevated temperatures used in lube oil (~80°C, 180°F) and grease (~200°C, 400°F) production would not be compatible with this method. Dissolution of the polymers in high solvency base oils like Group I, naphthenic, bright stock, and esters near the flash point of the oil (150-200°C) was not successful.

Based on this initial inquiry there are several recommendations for future work. Most high performance polymers only begin to melt above 200°C and though many high solvency base oils can approach this temperature the oils will become oxidized. Nitrogen blanketing or autoclaving is necessary. Another consideration is the initial form of the polymer. Extruded polymer may be ground down but powdered grades for applications like rotomodeling offer high surface areas to accelerate the rate of dissolution. Greater solubility may also be accomplished by selecting special grades of polymer with some fraction of the benzene backbone replaced by more soluble C4-C6 alkyl units.[22] For example, nylon, polyphthalimide, and Kevlar are all polyamides which differ primarily by aromatic content from 0-100%.

IV. Conclusions

Lubricant additives are most often needed in extreme, high temperature conditions when they are most likely to be degraded. Tackifiers based on polyisobutylene chemistry are especially sensitive to long- and short-term periods of heating due to their chemical structure. Improving the state-of-the-art for high temperature tackifier stability was approached from three areas in this investigation. Conventional wisdom guides high temperature lubricant formulation toward Group III oils due to lower impurities like aromatics and heteroatoms.

We have demonstrated, through studying individual impurity species added to Group III oil, that base oil composition versus thermal stability of PIB is more complicated than originally thought. Some 'bad actors' exhibit a stabilizing effect for PIB at 0.1wt% (1000 ppm) concentration. More work is needed to tell if this trend continues for high or lower concentrations of impurity. Lessons learned from the base oil impurity study helped develop a novel tack preservative which greatly stabilized string length in PIB-based tackifiers over 2- 24hrs of high temperature treatment. This new additive can correct for the thermal instability of PIB and serve as the active ingredient in new high temperature tackifier formulations

Preliminary work on expanding the library of polymers suitable for tackifier products did not identify a promising candidate from the high performance polymer family. Polymer physics predicted effective viscosity modification and tack if such polymers could be dissolved. Based on this work it appears that PIB modified with the tack preservative is the most cost-effective and readily available way to advance the current performance of tackifiers at high temperature.

Acknowledgements

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Extended Bearing Life Greases – “Tried and True” or New Technology?

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Abstract

An experimental calcium sulfonate complex (CSC) grease and standard lithium complex grease (LiCx) were produced with the same base oil composition. The base greases were then formulated with two additive systems. The additive systems consisted of a primary antioxidant component and a multifunctional component containing antiwear and extreme pressure additives with secondary antioxidant function. The two base greases were treated with the single components and a combination of the two components. High temperature bearing performance of the six formulated greases was evaluated using ASTM D3527 wheel bearing life(WBL) test. Greases were also evaluated by a protocol designed to study the effect of thermal aging on the oxidative and shear stability of the greases. Specifically, the greases were statically aged at the same temperature (160 °C) and in the same inboard roller bearings used in the WBL test. Bearings were weighed before and after aging to determine weight loss. Pressure Differential Scanning Calorimetry (PDSC) was used to monitor oxidation stability before and after aging, and infrared (IR) spectroscopy was used to measure extent of oxidation. Changes in grease shear stability were measured using oscillatory shear rheology strain sweeps performed at 160 °C. The WBL data showed that CSC and LiCx greases had similarly short-lived performance when greases were treated with each of the single components while greases treated with the combined components produced extended lives. Although antioxidant synergism is expected between the two components of this study, the rheological analyses of the fresh and statically aged greases suggest that the additives can alter the thermal and mechanical stability of the greases in ways that positively and negatively impact grease life in high temperature wheel bearings.

Introduction

As machinery is built to be more efficient and transmit more power, rolling bearing elements are increasingly required to operate at higher loads, speeds and temperatures[1]. The steady rise in bearing operating temperature has gradually expanded the demand for greases with improved oxidative and thermal stability. To enhance oxidation resistance, grease manufacturers have turned to higher quality base stocks such as Group II and III mineral oils and synthetic fluids like PAO’s and esters. To improve thermal stability, the use of thickeners that impart higher dropping points is also trending upwards[2-3]. Two grease types that have seen noticeable growth in their production volumes are lithium complex (LiCx) and calcium sulfonate (CS) greases. This increase is demonstrated in Figure 1, which compares production volumes in 2004 versus 2014[4-5]:

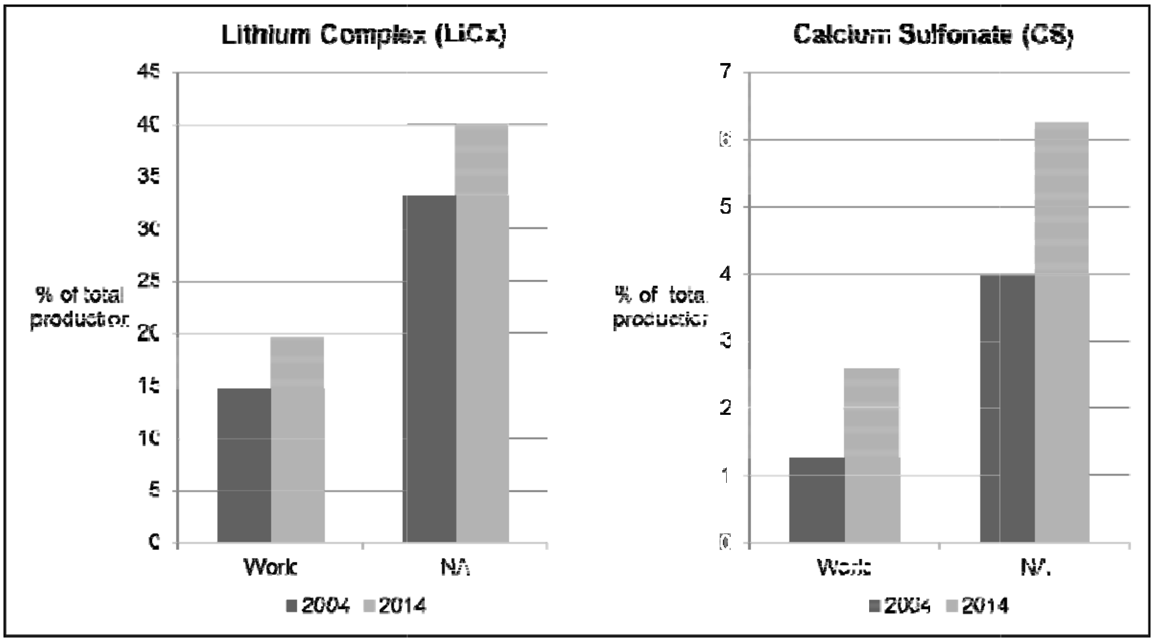

Figure 1: Data from 2004 and 2014 NLGI Annual Production Surveys[3-4].

LiCx grease is an established commodity with a proven service record while CS grease, although not new to the industry, is considered an up and coming technology. Greases based on lithium soap are good all-around performers that have excellent pumpability, shear stability and water resistance. The ability to complex simple lithium soaps and raise dropping points from about 200 °C to >260 °C have made LiCx greases the conventional choice for high temperature applications including automotive wheel bearings[3].

To achieve their high dropping points, the production of LiCx greases involves the use of complexing agents such as boric acid, salicylic acid and di- carboxylic acids. Of these complexing agents, the di-carboxylic acids, azelaic acid and sebacic acid, are the most widely used. With di-carboxylic acids, the manufacturing process typically involves in-process saponification of the fatty acid, typically 12-hydroxystearic acid (12-HSA) and the complexing agent followed by heating and a cooling step that co-crystallizes both thickener components into micron sized fiber network[2-3]. Due to incorporation of the dibasic salt, it can be ascertained that the thickener network will have higher ionic character that increases melting/dissolution temperatures of the soap fibers and amplifies inter- and intra-fiber interactions that strengthen thickener network.

CS greases are thickened by overbased calcium sulfonates. The technology date back to 1960’s and recent NLGI papers by Denis et al. and Waynick offer excellent overviews on their compositions and preparation methods[6-7]. Overbased calcium sulfonates are lubricant additive that find their highest use in combustion engine oils where they neutralize oxidation-derived acids as well help suspend polar oxidation products. Their compositions are generally describedas colloidal dispersions of amorphous calcium carbonate particles stabilized in carrier oil by sulfonate surfactant, typically calcium alkybenzene sulfonates[8]. CS greases are formed when the amorphous calcium carbonate particles are converted to the crystalline allotrope calcite. This process is carried in base oil to form greases with gel-like structure that typically require 40 to 50 mass percent of the overbased calcium sulfonate raw material to produce NLGI 2 consistency grade greases. The high calcite content of CS greases provides excellent EP, AW and rust inhibiting properties. CS greases are also recognized for their shear stability, water resistance and high dropping points that commonly exceed 300 °C. On the other hand, the high demand and low thickening efficiency of overbased calcium sulfonates makes CS greases relatively expensive[9]. In addition, the gel-like structure of CS greases negatively affects their pumpability and limits oil release that is deemed an important property in bearing lubrication[10].

In 1985, the first CS grease classified as calcium sulfonate complex (CSC) grease was patentedby Muir and Blokhuis. The development involved the use of relatively low levels of calcium soap thickener and boric acid complexing agent to reduced overbased calcium sulfonate content to levels approaching 30 mass percent. Further refinements have followed and calcium sulfonate contents have continued to drop mitigating issues with cost, pumpability and other drawbacks that hindered the use of CS greases in the past[6-7; 9-11].

The focus of this paper is a preliminary assessment of an experimental CSC grease in the ASTM D3527 high temperature wheel bearing life (WBL) test. A fair amount of work has been done with this test. This includes Rhee’s use of PDSC and a modified Thermal Gravimetric Analysis (TGA) procedure to build a “decomposition kinetic model” to predict performance in the WBL test[12]; Ward and Fish’s use of PDSC and the WBL test to guide the development of greasewith extended life in FAG FE-9 bearing rig test[13]; and the use by Kaperick et al. of high temperature oscillatory shear rheology to assess the ability of greases to perform in the WBL test[14].

The first part of this paper involved WBL testing of the experimental CSC grease and LiCx benchmark both produced with the same base oil composition and formulated with same antioxidant systems. The second part of the paper involved measuring the effect of thermal aging on weight loss, oxidative stability, extent of oxidation and rheological properties of the formulated greases with the goal of finding the factors that most influence performance in the WBL test. Specifically, the greases were statically aged at the same temperature (160 °C) and in the same inboard roller bearings used in the WBL test. Bearings were weighed before and after aging to determine weight loss. PDSC was used to monitor oxidation stability before and after aging, and infrared (IR) spectroscopy was used to measure extent of oxidation. Changes in grease shear stability were measured using oscillatory shear rheology strain sweeps performed at 160 □C.

Experimental

Materials

Base Greases: Two base greases, one LiCx and one CSC, were prepared for this study. Both greases were produced with the same base oil composition. The base oil used consisted of 3 parts of a 600 SUS Group I base oil and 1 part of a 2500 SUS Group I bright stock. The final viscosity grade of the base oil was ISO VG 150.

The two base greases were made by batch processes. The preparation of the LiCx grease was based on a procedure described in Example 1 of U.S. Patent Number 3,791,973[15]. The procedure used 12-hydroxystearic acid and azelaic acid at 2 to 1 mole ratio and the saponification of the acids was done in two steps. The experimental CSC base grease was prepared using a proprietary process. Basic properties for both base greases are provided in Table 1.

Table 1: Base grease properties.

Properties	**Method**	**CSC**	**LiCx**
Dropping Point, °C	ASTM D2265	>307	306
NLGI Grade, mm^{-1}	ASTM D1403	279	274
Oil Separation (40 °C; 168h), % wt. loss	IP 121	1.1	6.5
Roll Stability (4h; 80 °C) , % change in Pen	ASTM D1831	0.7	14
Four-Ball EP (Weld Point), kgf	ASTM D2596	315(280)*	200 (200)*
Four-Ball Wear (1200rpm, 40kg, 75C, 1h), mm	ASTM D2266	0.500	0.88

*Actual weld point when measured 10 kgf intervals

Additives: The base greases were formulated with two additive systems. The additive systemswere selected based on recognized performance in LiCx greases. The additive systems consisted of HT-1, a multifunctional component that is composed of zinc dialkyl dithiophosphate (ZDDP) and a sulfurized compound and HT-2, a primary antioxidant component. For the study, the two base greases were treated with the single components and with a combination of the two components to produce three LiCx and three CSC greases as summarized in Table 2:

Table 2: Grease Formulations

Components	**CSC-1**	**CSC-2**	**CSC-3**	**LiCx-1**	**LiCx-2**	**LiCx-3**
CSC base grease (wt. %)	97	99.2	96.2			
LiCx base grease (wt. %)				97	99.2	96.2
HT-1 (wt. %)	3		3	3		3
HT-2 (wt. %)		0.8	0.8		0.8	0.8

Test Methods

Wheel Bearing Life: The high temperature life of the formulated greases prepared from the experimental CSC base grease and conventional LiCx base grease was compared using ASTM D3527 WBL test method. The method is a measure of service life for automotive service grease and is part of NLGI GB and GC wheel bearing grease specification. The test evaluates greases under high temperature and high shear conditions using tapered roller bearings operating in a modified front wheel hub-spindle-bearing assembly. A light axial load of 111 N is applied to the bearings while the hub is rotated at 1000 rpm and spindle temperature is maintained at 160 °C. The test duration consists of a 20 hour running period followed by a 4 hour resting period. This cycle is repeated until grease deterioration causes the drive motor torque to exceed a cut off that is calculated from an initial two hour running period. Failures normally occur after the resting periods and test results are typically reported in 20 hour intervals. GB and GC specification limits are 40 and 80 hours respectively.

Static Grease Aging: Formulated greases were aged at 160 °C in the inboard wheel bearings that are used the ASTM D3527 test rig. The bearings are the same as the bearings utilized in ASTM D1743 Bearing Rust Test. Thus, cleaning and packing of the bearings was done by ASTM D1743 procedures. Heating of the packed bearings was accomplished in an oven in a vertical position. Packed bearings were held in the oven by sliding them onto a horizontal bar held by a vertical stand. Three bearings per experiment were used to collect sufficient sample to conduct other testing. Grease from the three bearings was joined together to make acomposite sample for ensuing evaluation.

Weight Loss: Bearings used for grease aging were weighed before and after packing and then again after aging. For each experiment, composite weight of the three bearings used per experiment was used to determine percent weight loss data. Percent weight loss was calculatedby subtracting the total weight of the packed aged bearings from the total weight of packed un- aged bearings and dividing this value by total amount of grease packed into the bearings. The latter value was calculated by subtracting the total weight of unpacked bearings from the weight of packed un-aged bearings.

Oxidative Stability: The oxidative resistance of the formulated greases before and after aging was measured following ASTM D5483, Standard Test Method for Oxidation Induction Time(OIT) of Lubricating Greases by Pressure Differential Scanning Calorimetry (PDSC). The test temperature selected for this study was 180 °C.

Extent of Oxidation: Infrared (IR) analysis of the aged greases was conducted using Perkin Elmer FT-IR Frontier Spectrometer with Universal ATR Sampling Accessory. IR absorbance for carbonyl (C=O) bonds is excellent indicator of oxidation product build-up in the grease. As oxygen attacks hydrocarbon parts of the grease, products containing carbonyl bonds such as ketones, aldehydes, carboxylic acids and carboxylic acid esters are formed and produced a broad absorbance peak that ranges from 1700-1800 wavenumber. For this study, the relative intensity of this peak was used to determine the extent of oxidation of the formulated greases after aging.

Shear Stability: Oscillatory shear rheology was used to measure yield point, which is the shear stress where grease loses resistance to flow, and storage modulus at the flow point (flow point for short), which is the shear stress where grease loses structural stability and becomes fluid. An Anton-Paar oscillatory rheometer (MCR301) was used to measure these rheological properties of the base greases and formulated greases before and after aging. For each analysis, the greases were compressed between a temperature controlled Peltier bottom plate and a parallel top plate. A hood that contains a temperature controlled Peltier device was placed over the assembly and a strain sweep ranging from 0.01% to 1000% strain at 160 °C was performed. The yield point was measured at the point where the storage modulus (G') deviated from the linear viscoelastic (LVE) portion of the sweep. Also, from the strain sweep, the place at which storage modulus (G') and loss modulus (G”) are equal was determined (flow point). This is the stress at which the internal structure of the grease moves from grease-like material to a liquid-like material. An example of this strain sweep procedure is illustrated in Figure 2:

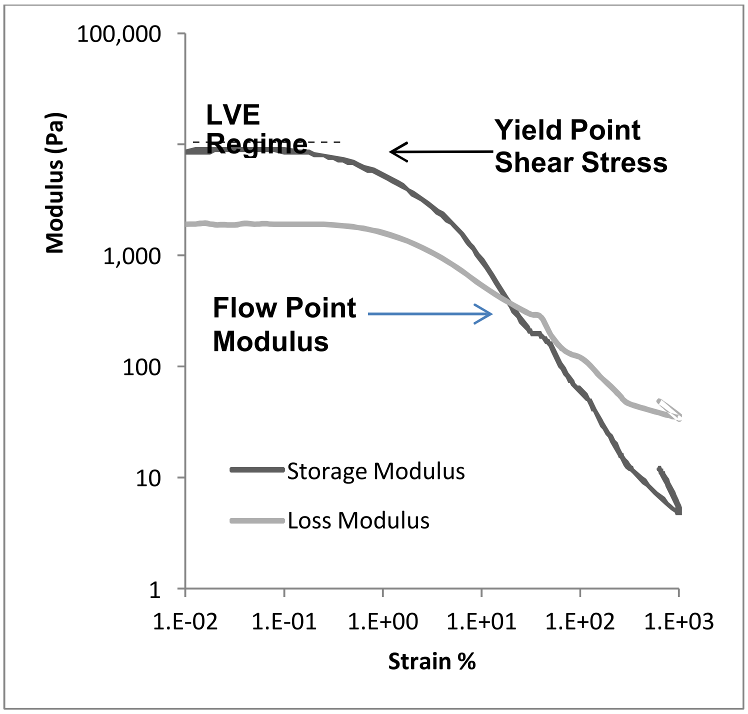

Figure 2: Plot of oscillatory shear rheology strain sweep (0.01% to 1000%)

Results

The additives used to formulate the greases of this study were selected based on the established performance in other LiCx greases. Specifically, the use of primary antioxidants to supplement the antioxidant capacity of ZDDP and sulfur compounds is a well-established approach to extending the high temperature life of LiCx greases and lubricants in general[13&16]. Therefore, one goal of the study was to determine if the same approach was applicable to the experimental CSC grease.

As summarized by Figure 3, the CSC greases had very similar WBL performance to that of the LiCx greases. Therefore, it can be deduced that the use of the primary and secondary antioxidant combination is also an effective way to prolong the WBL of the experimental CSC base grease. On the other hand, PDSC data, also shown in Figure 3, did not detect the antioxidant synergy in the CSC grease although the synergy was evident in the LiCx grease. Specifically, the long OIT but short WBL of the CSC-2 grease suggested that the extended WBL of the CSC-3 grease could not entirely be attributed to oxidation stability.

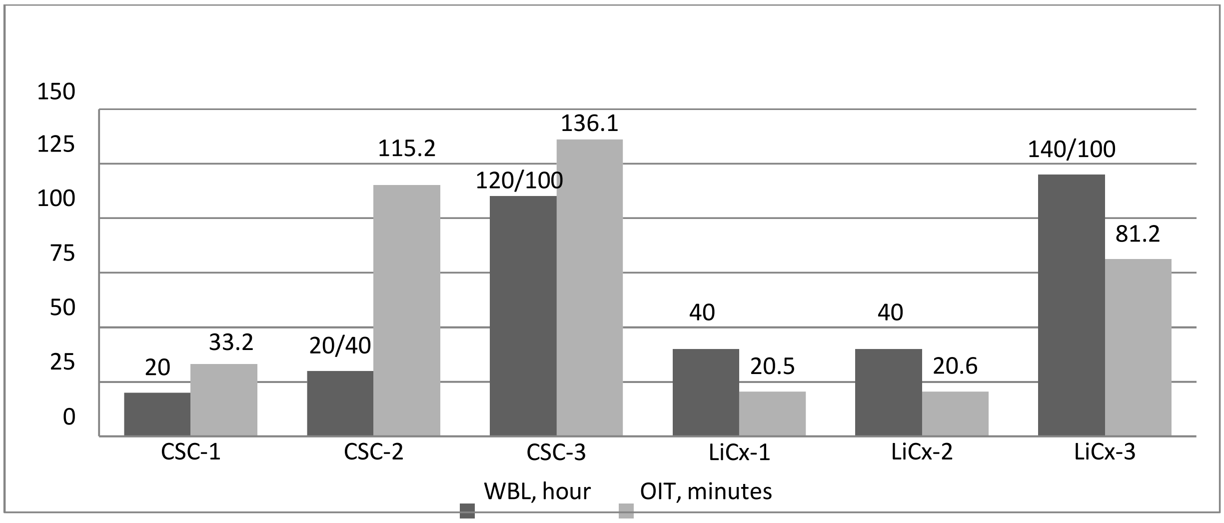

Figure 3: WBL and PDSC OIT data

To further investigate the role of oxidation resistance, the formulated greases were statically aged at same temperature and in the same bearing assemblies that are used in the WBL test. An aging time of 40 hours was selected since 4 of the 6 greases failed to surpass 40 hour of grease life in the WBL test. The aged greases were then analyzed for weight loss, PDSC OIT, intensity of the IR oxidation peak and changes in oscillatory shear rheology behaviour.

As per Table 3, weight loss data correlated well with the OIT data collected on the un-aged greases with the greases with the longest OIT's (CSC-3 and LiCx-3) having the least weight loss. As with the PDSC data, weight loss data for the CSC greases did not relate well with WBL and the data implied that other factors besides weigh loss impacted grease life. This conclusion specifically applied to the CSC-2 grease that tested well for oxidation stability and weight loss but had a short life in the WBL test.

Also in Table 3 is the OIT data for the greases after 40 hours of aging in static bearings. The data revealed that the antioxidant capacities of all the greases were significantly depleted, this included greases with the longest before aging OIT's (CSC-2, CSC-3 and LiCx-3). These PDSC results were unexpected as they denote that static aging was more severe than the dynamic WBL test. Aging to 80 hours on the greases with longest WBL's (CSC-3 and LiCx-3), further supported the severity of the static aging as these greases became hard, unpliable and impossible to completely remove from the bearings. Although no further aging experiments were conducted, the accelerated degradation of the greases under static conditions could be linked to the procedures used to remove rust preventive from the bearings. In the ASTM D3527 WBL test, the bearings are only washed several times with n-heptane while bearings used for the static aging studies were cleaned by the ASTM D1743 Bearing Rust Test procedure. The latter procedure included two washings with hot mineral spirits and wiping of the assemblies after each washing to assure complete removal of the rust preventive. After the hot mineral spirit washes, the bearings were also rinsed two times with 1% ammonium hydroxide in isopropyl alcohol/water solution. Therefore, it is possible that the more complete removal of the rust preventive from the bearings used in the static aging experiments led to steel corrosion that accelerated oxidation due to Fe ion catalyst.

Table 3: Weight loss and PDSC OIT data after grease aging at 160 °C

Components	**CSC-1**	**CSC-2**	**CSC-3**	**LiCx-1**	**LiCx-2**	**LiCx-3**
Weight Loss (wt%)						
Aged (40h bearings)	38.6	19.6	11.4	24.5	25.1	16.0
Aged (80h bearings)			29.2*			30.7*
PDSC OIT, minutes						
Un-aged	33.2	115.2	136.1	20.5	20.6	81.2
Aged (40h bearings)	<10	<10	<10	<10	<10	<10

*Grease severely degraded; tested no further

FT-IR spectra for greases after 40 hours of static aging are shown in Figures 4 and 5. Figure 4 shows full IR scans for the LiCx greases and Figure 5 compares the oxidation peaks of the LiCx greases to those of the proprietary CSC greases. Figure 4 also includes a spectrum of LiCx grease that failed the WBL test at 120 hours. The purpose of this spectrum is to provide an example of grease with a high degree oxidation. As per Figures 4 and 5, the oxidation peak of the grease that was degraded for 120 hours in the WBL test was much more intense than the peaks of statically aged greases. This meant that of none the aged greases reached a point of severe oxidization and complete antioxidant depletion although their PDSC OIT's at the 180 °C test temperature were not significant as per the ASTM D5483 test method. The oxidation peak data also correlated well with un-aged OIT's for both grease types. Specifically, the greases thatgave the longest OIT's (CSC-3 and LiCx-3) were also least oxidized. However, it should be stated none of the statically aged greases were severely oxidized although static aging was more severe than the WBL test. This again inferred that grease life in the WBL test is not solely dependent on controlling oxidation.

Rheology data is summarized in Figures 6 and 7. Figure 6 provides yield points of the un-agedbase greases, un-aged formulated greases and aged formulated greases. A comparison of the un-aged greases revealed that the CSC grease produced higher yield points than the LiCx counterpart but was more affected by additives than the LiCx grease that gave stable yield points regardless of formulation. Although the yield points measured on the un-aged greases did not relate to WBL performance, the data provided evidence that additives affect the structural integrity of greases, especially at high temperature and high shear conditions. After aging, the CSC greases with poor WBL performance exhibited larger variability in yield points. Specifically, the CSC-1 grease lost resistance to flow and CSC-2 become much stiffer than all the other greases. Based on these results, it can be concluded that the poor WBL performance for the CSC-1 grease was due to a lack of thermal and shear stability. CSC-1 also showed the largest weight loss, another sign of structural instability. In the case of the CSC-2 grease, the poor WBL performance corresponded to a loss of fluidity that decreased the ability of grease to flow into bearing contact zones. The yield point data for the LiCx greases was not as conclusivewith the exception of the LiCx-2 grease. As was the case with the CSC-1 grease, the LiCx-2 grease also lost its resistance to flow with aging, an indication of reduced thermal and mechanical stability that in turn leads to poor WBL performance.

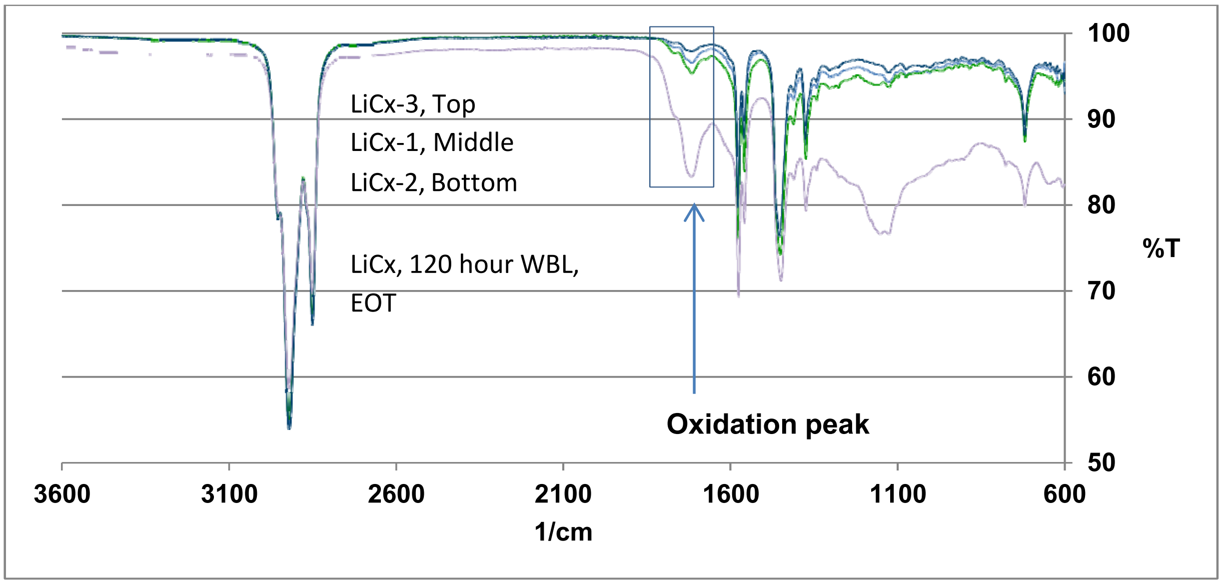

Figure 4: IR spectra of LiCx greases aged in static bearings for 40 hours.

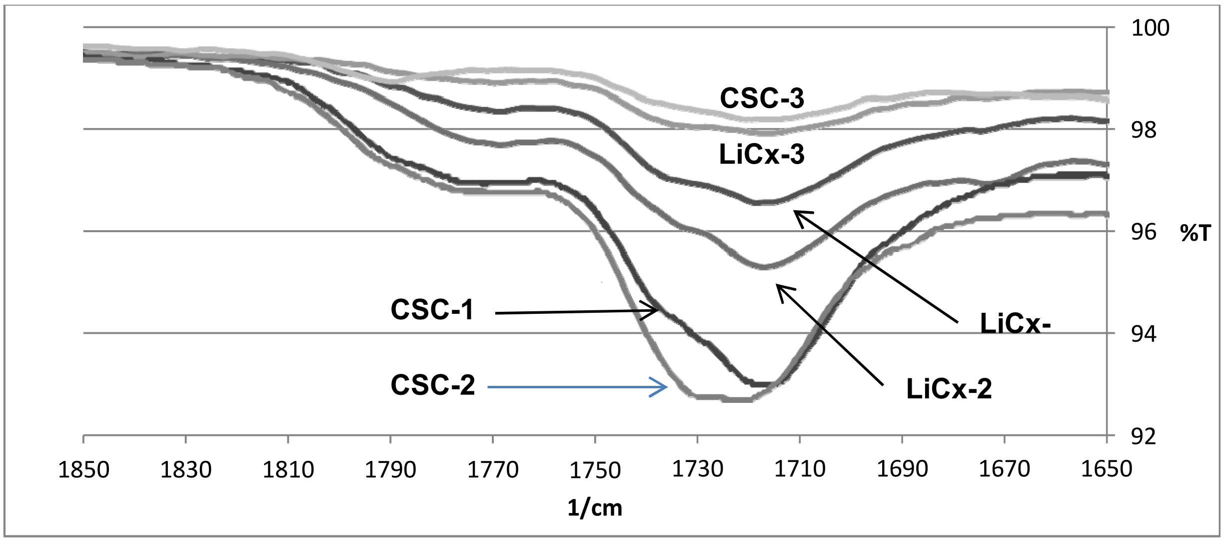

Figure 5: IR spectra for greases aged in static bearings for 40 hours.

Modulus at flow point data is given in Figure 7. A comparison of data collected on the un-aged greases that included unformulated base greases reveals that the LiCx grease produced higher and more stable flow points than its CSC counterpart. Although higher and more stable flow points for the un-aged greases was not a predictor of WBL performance, the data implied that the LiCx greases were more shear stable over a wider range of shear stresses and were less likely to bleed out of the bearings. After aging, the key observation was an intermediate increase in the flow points of the two greases with longest WBL's (CSC-3 and LiCx-3). This behavior indicated that these greases had the ability to flow into the contact zone without an excessive rate of bleeding that might lead to premature bearing starvation and failure. It should also be noted that these greases produced the least amount of weight loss and were the least oxidized. Therefore, the increases in flow points that occurred with aging were not completely attributed to these degradation factors. A possible explanation for this unique behavior is that thickener network was strengthened by interactions with the additives. As for CSC-1, LiCx-1 and LiCx-2, their flow points did not change with aging despite significant amounts of weight loss that should have increased their thickener content and consistency. This response suggested a lack of structural stability that caused faster bleed rates and early bearing starvation. Finally, the flow point of the CSC-2 grease, like its yield point, showed that this grease became significantly stiffer than all the other greases. The loss of fluidity decreased theability of the CSC-2 grease to flow into and adequately replenish bearing contact zones with lubricant, thus, explaining the short WBL of this particular grease.

Summary

The study demonstrated the importance of additives in determining the high temperature performance of greases regardless of thickener type. Specifically, it showed that additives influenced both oxidation and shear stabilities of greases, two critical properties in determining grease life in high temperature wheel bearings. In addition, the study showed that the effect of additives on the high temperature shear stability of grease was measurable by a combination of static aging and oscillatory shear rheology experiments.

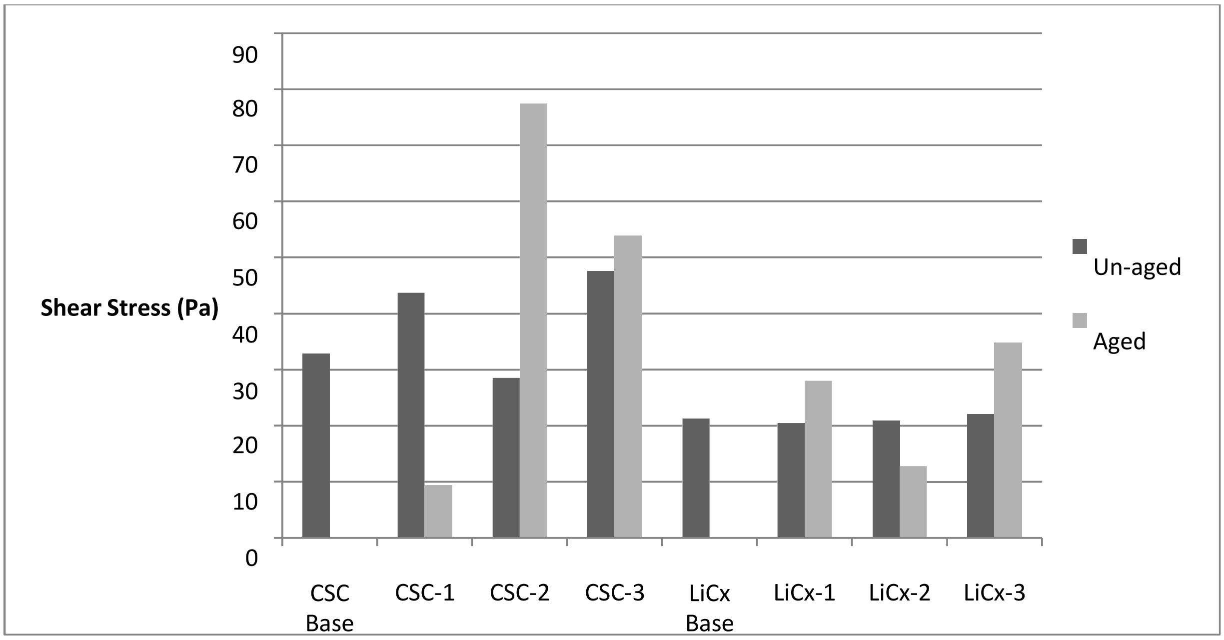

Figure 6: Yield points for un-aged greases and greases aged in static bearings for 40 hours.

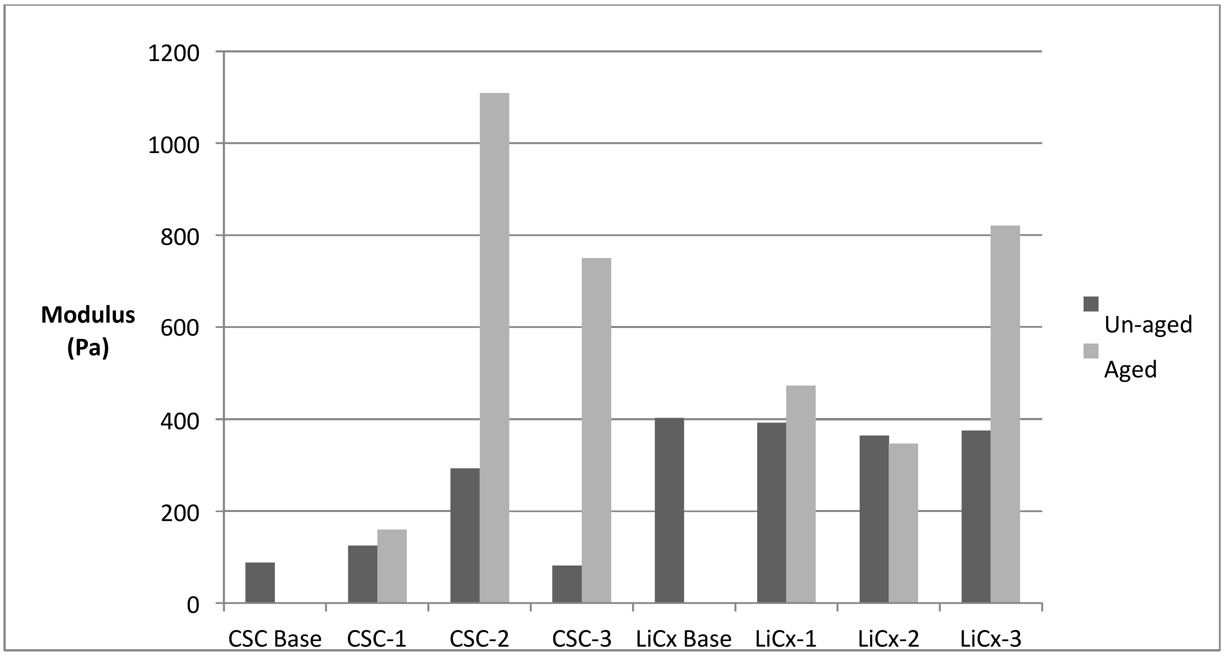

Figure 7: Flow point data for un-aged greases and greases aged in static bearings for 40 hours.

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Synergistic performance of Micronized PTFE powder along with ZDDP in Lithium complex greases for automotive application

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1. ABSTRACT

Automotive is the largest and fastest-growing end-use industry for grease. The need for high performance grease is rising for the increasing manufacturing of machines and equipment in end-use industries. So, the primary goal of grease development is to minimize friction and improve on wear and load bearing capacity at high temperature. Micronized PTFE powders due to exceptional temperature withstanding and load bearing properties plays fundamental role in meeting the greases requirements both in EP as well as performance greases. ZDDP works in synergy with PTFE to enhance wear scar properties and load bearing properties. In current study, along with conventional tribological methods of wear scar and weld load of high performance grease, 'cyclic loading' test is conducted where load was varied keeping other parameters fixed. Analysis of Wear scar diameter after performing 'cyclic loading' test is done and compared with moly grease.

Keywords: Grease, Micronized PTFE powder, ZDDP. Molybdenum Disulphide, Cyclic Loading

2. INTRODUCTION

Greases are one of the oldest forms of lubricants used by mankind. Greases can be defined as thickened oils with added performance additives for the definite purpose. Greases are composed of soap-thickener fibers which forms long network of oil entrapment pockets. The most commonly used greases consist of mineral oil and lithium based soap-thickener fibers. According to a recent NLGI Grease Production Survey, approximately 70 percent of the grease sold worldwide is based on either simple lithium soap or lithium complex thickener. Greases based on lithium soap possess many improved properties compared to the other alkali metal soaps that existed in 1942. They have better water resistance properties compared to sodium soap greases, better high-temperature properties compared to calcium soap greases, and excellent mechanical properties (both resistance to shearing and good ability to be pumped).[1]

PTFE acts as an EP additive and ZDDP as an anti-wear agent, improving load bearing and wear preventive characteristics of lithium complex grease. Weld load test ASTM D2596 and IP 239 is used to evaluate extreme pressure properties of greases to withstand high load at high speed. Wear scar test (ASTM 2266) can be used to determine the relative wear-preventing properties of greases under the test conditions in sliding steel-to–steel applications. Wear Scar test is performed under fixed set of test parameters: 75ºC, 1200 rpm, 40 kg load & 1 hour test. [2]

The industry today strives to develop and test high performance greases which have wide application versatility and a longer service life. Many of the times greases are applied where varying load condition exists. In current Study, to verify grease's performance at varying load and varying speed, **Cyclic Loading** test has been introduced. EP performance in cyclic loading test was already established for moly grease for industrial applications. Present work highlights PTFE's performance in cyclic loading test to verify its application as an EP additive for different industrial applications at varying load. PTFE synergy along with ZDDP has comparatively showed excellent cyclic load results and weld load than Moly grease with ZDDP. In Cyclic loading test greases are subjected to varying load ramp up (40-80-40-80) and ramp down (80-40- 80-40) and scar is checked. [3]

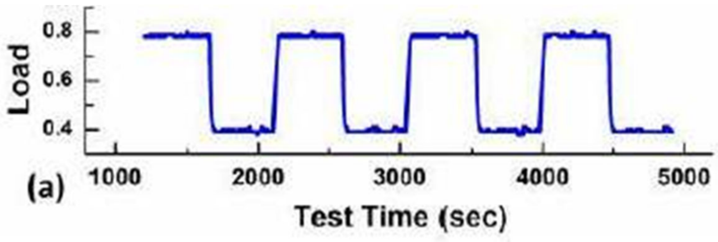

Figure 1: Graphical representation of cyclic load test

However, actual applications may require bearings to be subjected to varying loading conditions where-in speed, time and load are variables.[4] To evaluate grease's performance at spectrum loading condition, generally high and fluctuating load conditions are created in continuous casting machines, Wheel bearing of trucks and heavy vehicles and rollers of fork lift trucks.

In the current study different performance additive chemistries were blended and tested for extreme pressure and anti-wear properties. Performance additives used for the study are PTFE, ZDDP and molybdenum disulphide. Grease containing PTFE micronized powder and ZDDP was compared with moly grease along with ZDDP. Weld load and Wear Scar test were performed for grease having synergy of PTFE and ZDDP as well as molybdenum disulphide and ZDDP. Test was also conducted under spectrum loading conditions wherein the load is systematically varied and the wear outcome is studied. Functionalization of PTFE particles with electron beam irradiation makes the PTFE particles highly polar and increases the surface affinity of the particles leading to a better tribofilm resulting in significantly reduced wear. Mixture of PTFE and ZDDP as compared to that of molybdenum disulphide with ZDDP, further reduces friction and wear due to its synergistic interaction with the additives.

PTFE is a fluorocarbon consisting wholly of carbon and fluorine. PTFE is hydrophobic: neither water nor water-containing substances wet PTFE, as fluorocarbons demonstrate mitigated London dispersion forces due to the high electronegativity of fluorine. PTFE has one of the lowest coefficients of friction values [2].

Types of PTFE and its Production

Poly tetra fluoro ethylene is broadly divided into two types, high molecular weight and low molecular weight PTFE.

PTFE MICRONIZED POWDER

Micronized Polytetrafluoroethylene (PTFE), also known as PTFE micro powder, is used where higher surface lubricity and anti-blocking properties are required. Micronized PTFE is prepared by the utilization of pre-sintered PTFE resin or recycled PTFE.

Fluoroadditives, or micro powders, are finely divided low-molecular-weight (MW) PTFE powders by molecular weight reduction through electron beam radiation and thermal cracking. In the thermal method, the polymer is exposed to high temperatures beyond its degradation point, whereby covalent carbon carbon bonds in its backbone are broken. The cleavage of a long chain results in several smaller molecules. The same result is achieved by exposing PTFE to gamma rays, X-rays, or electron beams. The most common commercial method to produce fluoroadditives is by electron beam exposure. After the irradiation, the PTFE resin is ground into micro powders.

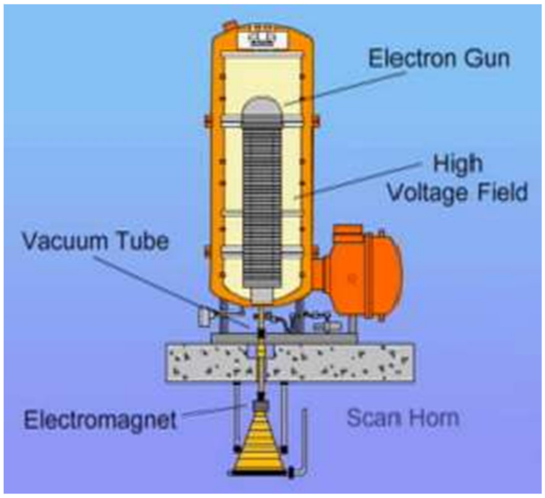

Figure-2: Schematic set up of EBM process

Figure-3: Sample image of APAR PTFE powder 210 grade

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PTFE Micro powder of APAR 210 grade is manufactured in-house by radiation degradation and pulverizing technique. APAR 210 PTFE micronized powder have uniform particle size distribution with average particle size of 5-10 microns, thus APAR 210 grade found to be more suitable for grease study. Characteristics of various grades of PTFE powder are mentioned in Table 1.

Table 1: Characteristics of PTFE grades

Properties	**Test Methods**	**Units**	**210**	**230**	**290**	**M230**
Color	Visual		white	white	white	white
Physical Form	Visual		Free Flowing Powder	Free Flowing Powder	Free Flowing Powder	Free Flowing Powder
Bulk Density	D4894	g/L	400	900	700	900
Specific Gravity	D2320	g/cm^3	2.16	2.16	2.16	2.16
Particle Size	D90	µm	<10	<25	<18	<25
Particle Size	D50	µm	<6	<12	<10	<15
Melting Point	DSC	°C	322	322	322	322

3. EXPERIMENTAL SECTION

3.1 Sample Preparation

Addition of PTFE and ZDDP additives 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 PTFE and ZDDP were blended with grease using Mechanical Grease Worker. 200 strokes were given with mechanical grease worker for uniform mixing. 4-6% PTFE and 2-3% of ZDDP was incorporated in thickener system of EP2 greases and its key properties were measured and evaluated.

Base Grease 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. Wear Scar, Weld load and cyclic load characteristics was analyzed. 4-6% of PTFE and 2-3% ZDDP were added in thickener system of Base Grease. All key properties of Base Grease were compared with, grease having Mos2 additive.

Table 2: Sample details: treat-rate; types of additive

Sr.No.	Samples Name
1.	Base Grease
2.	Base grease+1% ZDDP
3.	Base Grease+3% ZDDP
4.	Base Grease+2% PTFE
5.	Base Grease+4% PTFE
6.	Base Grease + 4% Molybdenum disulphide
7.	Base Grease + 4%PTFE +3%ZDDP
8.	BaseGrease+4% Molybdenum disulphide+3%ZDDP

3.2 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 PTFE along with ZDDP. 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 of moly grease was also measured. Wear scar diameter measurement results of Base Grease combinations are presented in Table 3

Table 3: Wear Scar Diameter measurement (Base Grease)

Sr. No.	PRODUCT	WEAR SCAR DIAMETER(mm)	% Reduction in Wear Scar Diameter
1.	Base Grease	0.62	-
2.	Base Grease+ 1% ZDDP	0.441	29
3.	Base Grease+ 3% ZDDP	0.318	48
4.	Base Grease+2% PTFE	0.49	21
5.	Base Grease +4% PTFE	0.50	19
6.	Base Grease+4% Molybdenum disulphide	0.66	No reduction
7.	BaseGrease+4%PTFE +3%ZDDP	0.48	23
8.	Base Grease+ 4%Moly grease+3% ZDDP)	0.54	13

GRAPH

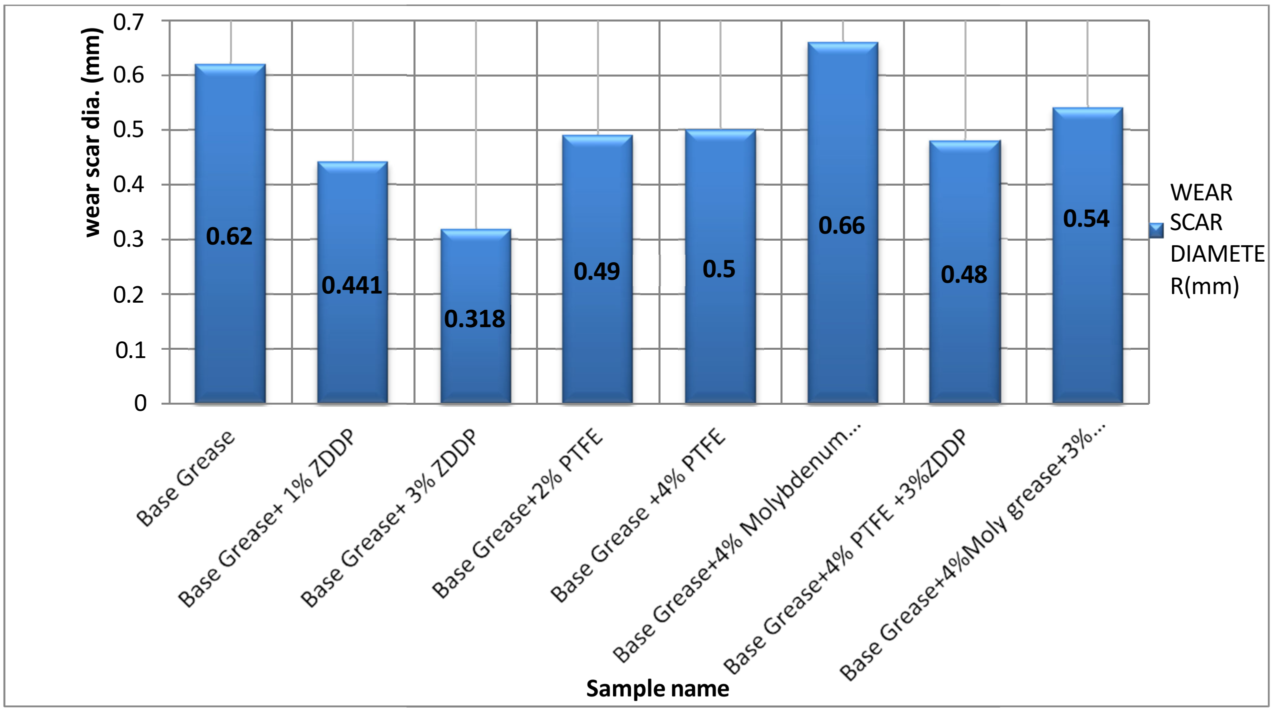

Figure 4: Wear-prevention –change in wear scar diameters on addition of performance additives

Remark

ZDDP reduced scar by 48% and ZDDP along PTFE reduced scar by 23% whereas Molybdenum disulphide didn’t contribute for scar reduction.

3.3 Extreme pressure (Weld Load Test) (IP 239)

The 4-ball weld load test rig uses three steel balls held in a cup. A fourth ball is rotated against the three balls at a given speed. A starting load is applied and increased at pre-determined intervals until the rotating ball seizes and welds to the stationary balls. Weld load characteristics of Base Grease along with ZDDP and PTFE additives is compared with Sample 2 grease containing molybdenum disulphide additive. The rotating speed is 1450 ± 50 rpm. Lubricating greases are brought to 27 °C and then subjected to a series of tests of 10-s duration at increasing loads until welding occurs.

Table 4: Four Ball EP Weld Load (IP-239)

Sr. No.	SAMPLE	Weld load IP-239
1	Base Grease	180
2	Base Grease+ 1%ZDDP	180
3	Base Grease+ 3%ZDDP	180
4	Base Grease+ 2% PTFE	315
5	Base Grease+ 4% PTFE	400
6	Base Grease+4% Molybdenum disulphide	355
7	Base Grease+4% PTFE +3% ZDDP	580
8	Base Grease+ 4% Molybdenum disulphide + 3%ZDDP	400

GRAPH

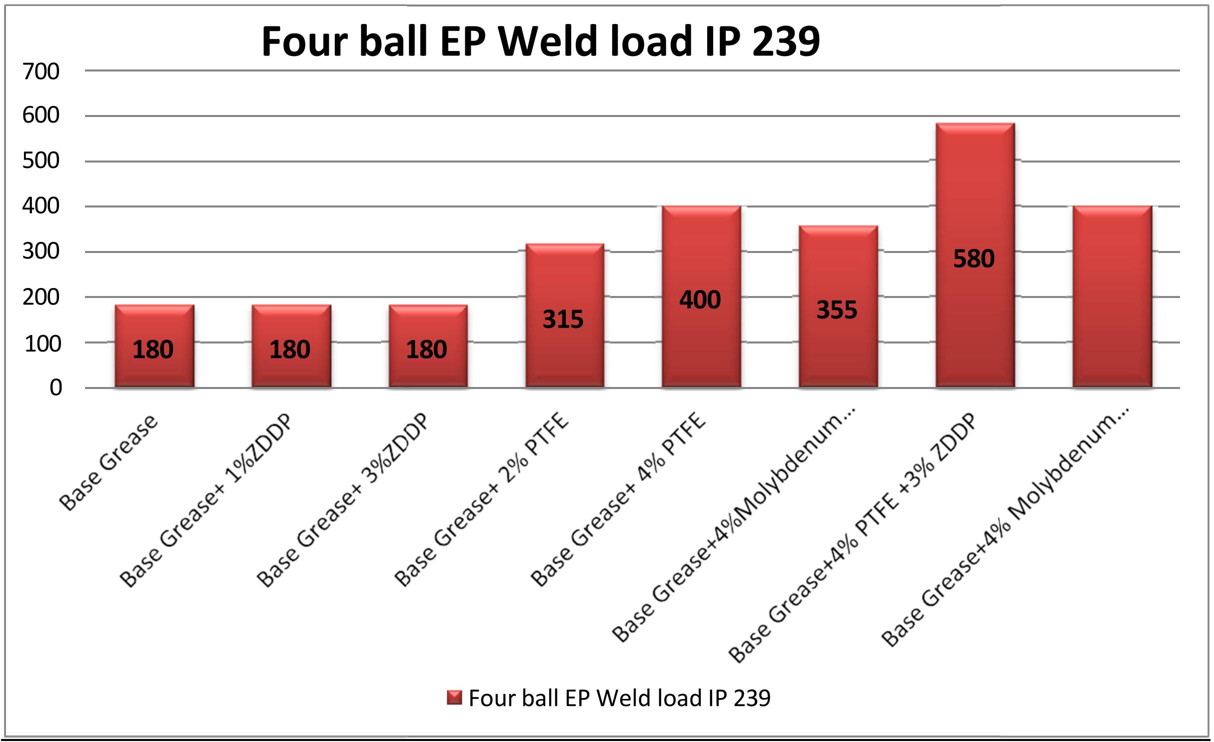

Figure 5: Extreme pressure properties –Change in weld load with addition of performance additive

Remark

Addition of PTFE increased base grease's weld load from 200 kg to 580 kg. Addition of moly increased weld load from 200 to 400 kg.

3.4 CYCLIC LOAD TEST

The cyclic loading tests were grouped under Ramp-up & Ramp-down conditions wherein the tests were started with initial load of 40Kg and were increased up to 80 Kg in the Ramp-up tests and vice versa. These tests were further classified on the basis of load step sizes of 7.5 min and 15 min each for each cycle. The rpm and test temperature were maintained at 1200 rpm and 75ºC in the cyclic loading test. Lubrication of wheel bearing at fluctuating loading is a critical issue, normal wear scar test and weld load test of greases cannot reflect actual condition while applications of greases. **Cyclic loading** test reflects actual condition and can provide significance data of grease performance at varied loads. Typical grease applications where fluctuating load conditions are there are Mobile and stationary instruments in construction, Rally and off road cars bearings, Racing wheel bearings.

Table 5: Cyclic Loading Test Condition

TEST NO.	**TEST CONDITIONS**	**TYPES OF TEST**	**CONSTANT VALUES**
TEST 1	40—80-40-80(KG)	Ramp up	1200 rpm,75ºC, 15 min
TEST 2	80-40-80-40	Ramp down	1200 rpm,75ºC,15 min

Table 6: Cyclic Loading Testing Result

BLEND	**Wear Scar diameter after cyclic loading Ramp up**	**Wear Scar diameter After cyclic loading Ramp Down**
BASE GREASE	0.90	0.91
BASE GREASE+1%ZDDP	0.82	0.83
BASE GREASE+3%ZDDP	0.85	0.88
BASE GREASE+4% PTFE	0.94	0.95
BASE GREASE+4% Molybdenum Disulphide	1.10	1.07
BASE GREASE+2%PTFE+3%ZDDP	0.93	0.90
BASE GREASE+4%PTFE+3%ZDDP	0.71	0.72
SAMPLE2+4%MolybdenumDisulphide+3%ZDDP	0.96	0.920

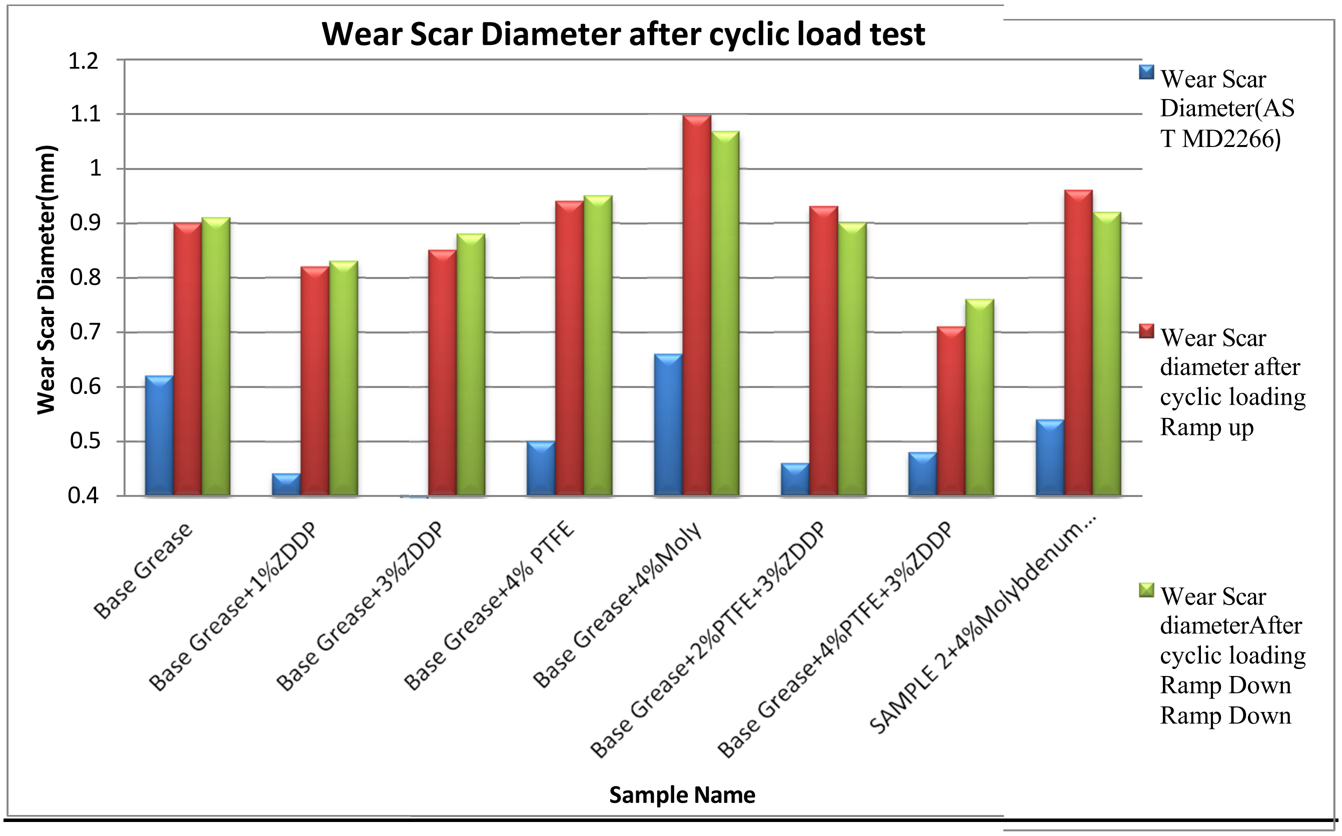

Figure 6: Wear Scar Diameter after Cyclic load test

Remark

PTFE along with ZDDP in lithium complex grease showed better anti wear property in cyclic loading test than molybdenum disulphide along with ZDDP.

4 CONCLUSION

4.1 Synergy of Micronized PTFE with ZDDP in lithium complex grease show better anti wear compared to Synergy of Moly and ZDDP.

4.2 Synergy of PTFE and ZDDP showed excellent EP properties than Moly grease as PTFE acted as an EP additive and it enhanced load bearing properties of grease.

4.3 Wear Scar results with standard test and Cyclic loading test differed in wear readings and showed clear difference of additive performance.

4.4 Under practical conditions like cyclic load conditions combination of ZDDP with micronized PTFE, results in improving the shock loads and load carrying capability of the grease.

5 REFERENCES

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