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“The STRATCO® Contactor™ reactor and its use in the production of Calcium Sulfonate Based Greases”

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Abstract

Calcium sulfonate based greases are recognized as an excellent technology for grease applications where heat, water, and high or shock loads exist. Their inherent properties are well known and include excellent rust and wear protection, high load carrying capacity, high dropping point, and excellent mechanical stability, even in the presence of water.

Calcium sulfonate based greases are conventionally prepared in atmospheric “open” kettles. This type of production vessel is limited by the basic design in its mixing and heating effectiveness. The lack of a closed system in these kettles allows the volatile promoters used in the calcium sulfonate grease production process to escape. In addition, the slow speed mixing imparted by paddle stirring is not optimal for production of a dispersed micelle structure.

By contrast, the STRATCO® Contactor™ reactor was designed to address the limitations of conventional grease cooking kettles. The STRATCO Contactor reactor’s sealed design, highly efficient rate of heat transfer, turbulent circulation path, and high shear mixing zone make it extremely well suited as a production vessel for calcium sulfonate based greases.

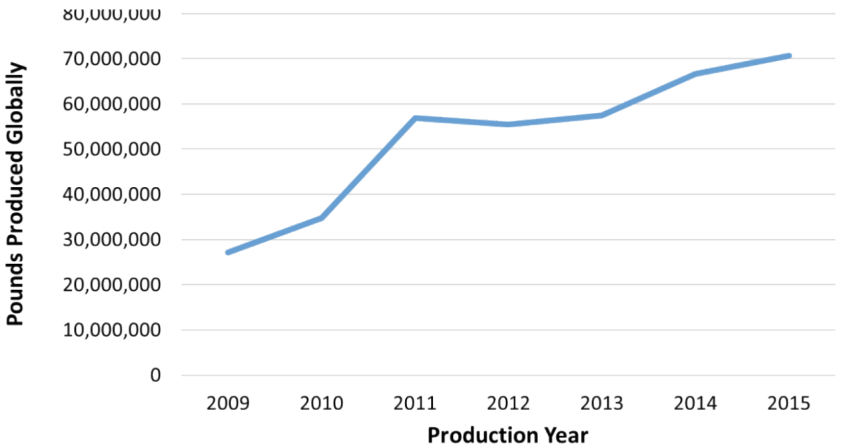
The objective of this project is to successfully manufacture calcium sulfonate based greases using the STRATCO Contactor reactor. The manufacturing process differences between conventional open kettle and the STRATCO Contactor reactor will be discussed in detail. Performance characteristics of the finished calcium sulfonate based greases obtained by each process will be compared.

Introduction

Calcium sulfonate based greases are recognized as an excellent technology for grease applications where heat, water, and high or shock loads exist. Their inherent properties are well known and include excellent rust and wear protection, high load carrying capacity, high dropping point, and excellent mechanical stability, even in the presence of water. Unlike other grease types, these excellent performance characteristics are present in the grease without the use of additional compounding or additives[1].

Calcium sulfonate based greases are frequently found to act as problem solvers in severe service applications where other greases have failed because they could not survive the extreme conditions. Some of the demanding applications that have benefitted from calcium sulfonate type greases are found in steel, pulp and paper mills, off-road construction and mining equipment, marine, and even food processing industries. As shown in ***Figure 1***, the direct result of this successful performance is that calcium sulfonate based greases have become one of the fastest growing types of grease globally[2]. Because of this popularity and high growth rate, grease producers are increasingly looking to produce calcium sulfonate based greases.

Figure 1. Calcium sulfonate type grease global production volumes



Grease production

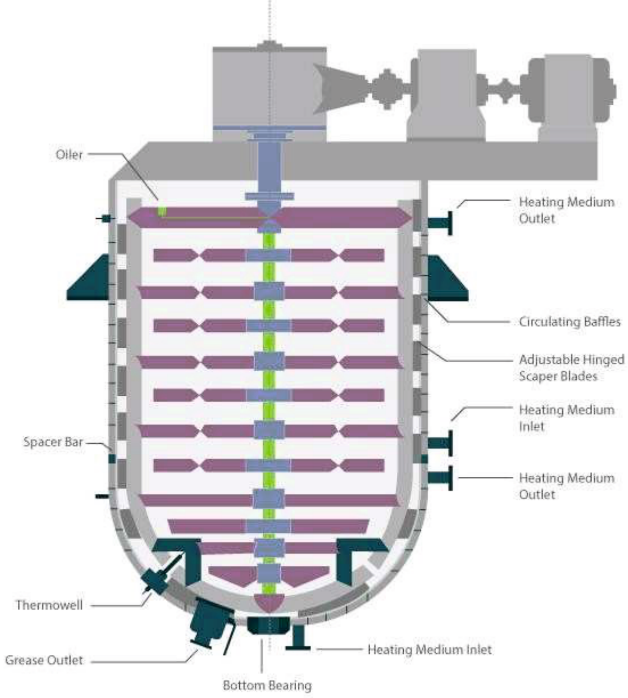
Overbased calcium sulfonates contain a large proportion of non-crystalline calcium carbonate dispersed within the sulfonate matrix. In the presence of suitable promoters such as water, alcohols, and acids, followed by heating within the proper temperature range, the conversion of this amorphous calcium carbonate into its crystalline form calcite takes place. This crystallization causes the rheology of the material to change from a flowable liquid into a viscous or semi-solid gel. At this point, the grease still contains water and must be dehydrated and graded with additional oil to produce a lubricating grease. This is the earliest type of calcium sulfonate grease, commonly referred to as a calcium sulfonate gel or "simple" calcium sulfonate grease.

For the production of a calcium sulfonate complex grease, additional reactions are added after the basic carbonate conversion step to produce a secondary thickener of a compatible soap/salt composition. These soap/salt complex ingredients are typically comprised of 12-hydroxystearic acid and a complexing acid such as boric or acetic, reacted with calcium hydroxide. As with the simple sulfonate grease variety, water must be removed since it is present in the grease due to its use as a conversion promoter. In addition it is also produced during secondary thickener soap forming reactions.

Production equipment

Calcium sulfonate based greases are typically produced in conventional "open" kettles, so called for their operation under atmospheric pressure. This type of production vessel (as shown in ***Figure 2)*** is limited by the basic design in its mixing and heating effectiveness, typically utilizing paddles for stirring, with an external jacket for heat transfer fluid. The agitation, which may be counter rotating, is typically operated at speeds below 20 rpm. The kettle contents may be pumped and recirculated to help turn the product over and encourage better mixing.

Figure 2. Conventional atmospheric kettle



The lack of a closed system in these atmospheric kettles can allow the volatile promoters used in the calcium sulfonate grease production process to escape. This causes the grease to form with reduced structure and produces a soft consistency. In addition, the slow speed mixing imparted by paddle stirring is not optimal for production of a dispersed micelle structure.

STRATCO Contactor reactor

The STRATCO Contactor reactor (as shown in **Figure 3*)*** consists of a pressure vessel, a circulation tube and a hydraulic head assembly complete with the mixing impeller and driver. The STRATCO Contactor reactor by design has a highly turbulent circulation path. All energy input through the mixing impeller is expended within the materials being mixed. The high dispersion mixing in the STRATCO Contactor reactor is achieved by the proprietary hydraulic head assembly. Frequent and forced changes in velocity and direction of flow occur around the impeller area. This results in a zone of high shear and intense mixing, which reduces the time required to complete the saponification reaction.

Figure 3. STRATCO Contactor Reactor

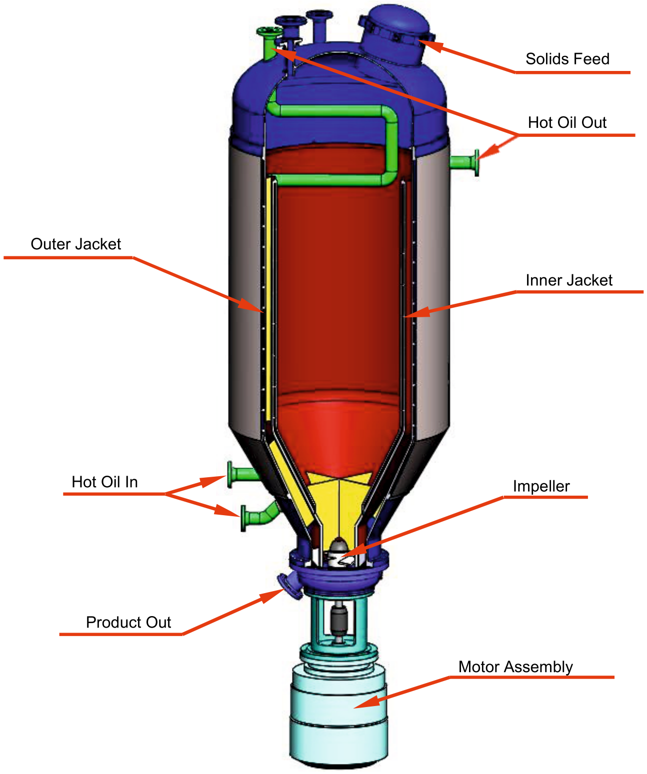
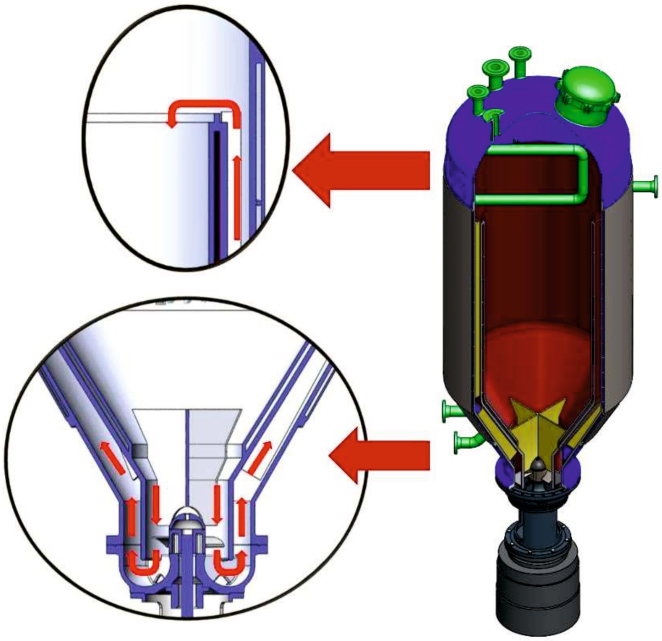


Figure 4 shows the flow through the STRATCO Contactor. Material is pulled down through the center of the circulation tube by the impeller, reversed and then forced up through the annular space. Because the impeller is located on the bottom, dry materials are kept in suspension until they dissolve or are reacted.

Figure 4 - Flow through the STRATCO Contactor



The heating medium is circulated through the double-walled circulation tube inside the STRATCO Contactor. The outside of the STRATCO Contactor reactor is also jacketed. Because of the double-walled circulation tube and the outside jacket on the shell, the STRATCO Contactor reactor has approximately three times the heat transfer area of an open kettle type reactor of the same volume. The flow path forces the circulating material to remain in contact with the total heating surface area at all times. Also, the heat transfer in the STRATCO Contactor reactor is enhanced by the high velocity of material flowing past the heat transfer surfaces.

For the production of calcium sulfonate type grease, there would appear to be several advantages to the use of a STRATCO Contactor reactor instead of the conventional open kettle. Since the STRATCO Contactor is a sealed design, there would be no loss of volatile promoters from the grease mixture. The large heat transfer area would allow quick heating to reaction temperatures. The turbulent circulation path and high shear mixing zone would cause more intense mixing, and could improve micelle dispersion. The operation of the unit under pressure may also be able to provide a faster and more complete conversion of the amorphous calcium carbonate into its crystalline form. Therefore the objective of this project is to successfully manufacture calcium sulfonate based greases using the STRATCO contactor, and understand if any of these equipment differences offer any advantages in the production of calcium sulfonate type greases when compared to the use of conventional open kettle manufacturing methods.

Experimental

Equipment used in the study included a 6-gallon (22 liter) STRATCO Contactor pilot plant reactor and 10- gallon (38 liter) atmospheric finishing kettle. An electric thermal heater and pump supplied heat transfer fluid for product heating up to a top temperature of 275°F (135°C). An air compressor was used to pressurize the contactor during low temperature steps to 50 psi (107 hPa). The equipment configuration isshown in ***Figure 5***.

Figure 5. STRATCO Pilot Plant

The addition of a viewing port to the contactor reactor lid (as shown in ***Figure 6***) allows the grease flow to be observed during pressurized operation (as shown in ***Figure** 7*). This is important as calcium sulfonate type greases can become very thick during the production process. In fact this was one of our concerns going in, and why we chose to make our experimental greases using the full base oil requirement to achievethe NLGI 2 grades up front.

Figure 6. Viewing port

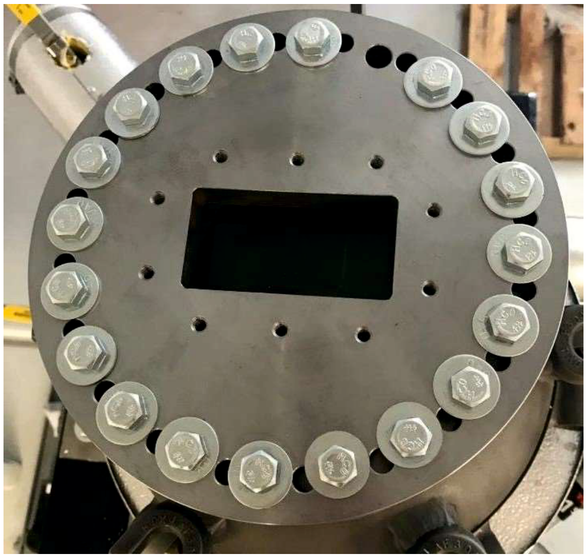


Figure 7. View of grease through viewing port

Techniques for conversion of the overbased calcium sulfonates into multi-purpose lubricating greases is well detailed in the literature[3]. For the production of our experimental greases, two different sulfonate conversion methods from the literature would be attempted. The first approach would use a commercially sourced proprietary overbased calcium sulfonate "pre-mix" designed for easy grease production. In addition to the overbased calcium sulfonate, the mixture also contains a proprietary conversion promoter system. This production method only requires the addition of base oil and water to complete the grease recipe. The second conversion approach was a more conventional one, where the grease is made entirely from individual components, including promoters.

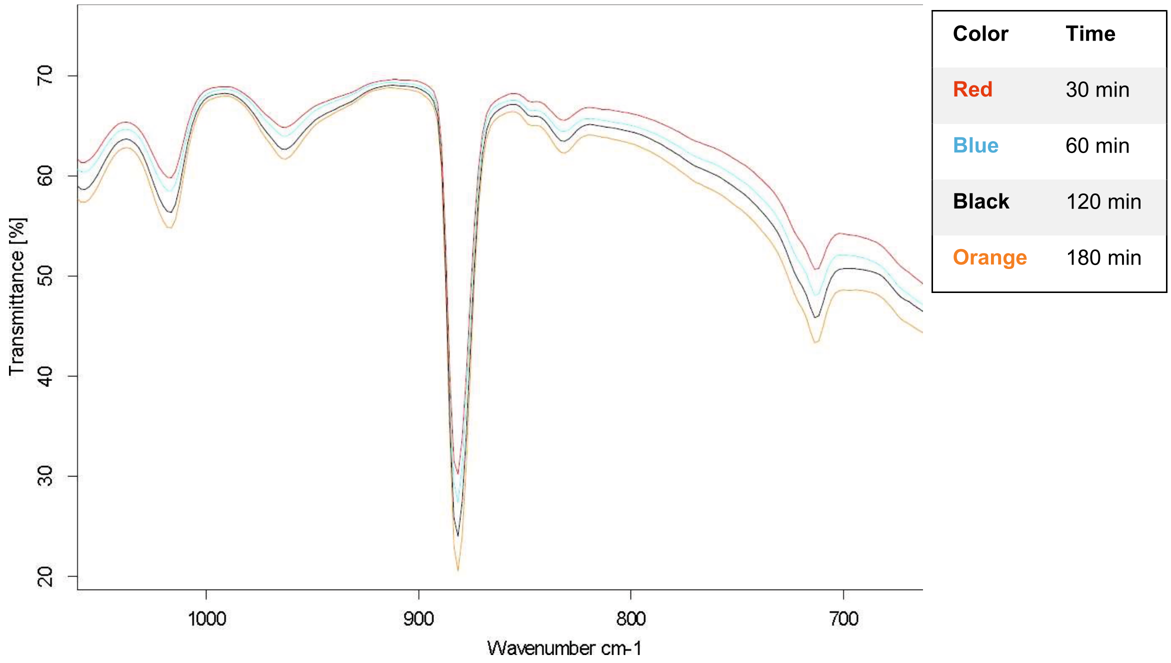
Two types of calcium sulfonate based greases were to be prepared. The first experimental grease would be the production of a "simple" calcium sulfonate grease. This type of grease is based upon the converted calcium sulfonate only, and does not contain any soap forming ingredients. In this system, the grease consistency is based entirely upon the thickening effect of the converted sulfonate. The second and third experimental greases would be the production of calcium sulfonate complex greases. Experimental grease 2 would use the same initial ingredients and gelation procedure as grease 1, but then additionally form a secondary soap based thickener in a separate saponification reaction step. Experimental grease 3 would use a full component based approach for the production of a calcium sulfonate complex grease. In all cases, the specific formulations were designed to achieve NLGI grade 2 consistency.

Experimental Greases

Experiment 1: Calcium sulfonate gel	
Formulation ingredients: • Sulfonate pre-mix • 600N Group I base oil • Water	Manufacturing procedure: 1. Mix sulfonate, oil and water 2. Pressurize STRATCO Contactor to 50 psi (107 hPa) 3. Heat at 193°F (89°C) until conversion to calcite occurs 4. Product is dehydrated by heating to 250-300°F (121-149°C)and transferred to finishing kettle
Experiment 2: Calcium sulfonate complex A	
Formulation ingredients: • Sulfonate pre-mix • 600N Group I base oil • Water • 12-hydroxystearic acid • Acetic acid • Calcium hydroxide	Manufacturing procedure: 1. Mix sulfonate, oil and water 2. Pressurize STRATCO Contactor to 50 psi (107 hPa) 3. Heat at 193°F (89°C) until the conversion to calcite occurs 4. Once gelled, depressurize and add soap formingingredients, repressurize to 50 psi (107 hPa) 5. Hold at 190-200°F (88°C-93°C) to complete saponification 6. Product is dehydrated by heating to 250-300°F (121-149°C) and transferred to finishing kettle
Experiment 3: Calcium sulfonate complex B	
Formulation ingredients: • 400 TBN Ca sulfonate • High boiling glycol • Sulfonic acid • Water • 600N Group I base oil • 12-hydroxystearic acid • Acetic acid • Calcium hydroxide	Manufacturing procedure: 1. Mix sulfonate, oil, promoters and water 2. Pressurize STRATCO Contactor to 50 psi 3. Heat at 193°F (89°C) until the conversion to calcite occurs 4. Once gelled, depressurize and add soap formingingredients, repressurize to 50 psi 5. Hold at 190-200°F (88°C-93°C) to complete saponification 6. Product is dehydrated by heating to 250-300°F (121-149°C) and transferred to finishing kettle

The grease was sampled at various intervals during the pressurized conversion step in order to determine the actual time to convert the amorphous calcium carbonate into its crystalline calcite form. These samples were kept and analyzed after the production had taken place. As shown in ***Figure 8***, upon checking the samples by FT-IR for conversion, it was found that the actual conversion had taken place within the first 30 minutes of the 3 hour hold time. This represents a significant change from conventional open kettle manufacturing, where the conversion time can take anywhere from 3 to 6 hours. As such, it was determined that an optimized process would only require a 30-minute conversion step.

Figure 8. FT-IR spectra comparison of gelation time



Manufacturing process comparison

The manufacturing process steps and timing between conventional open kettle and optimized STRATCO Contactor process were recorded in ***Figure 9***. The red color blocks indicate events occurring in the heated vessel, and the blue color blocks indicate those events occurring in the cooling vessel. As shown, the conventional open kettle cooking process can produce a single batch of calcium sulfonate complex grease over two standard 8-hour shifts. By comparison with an optimized STRATCO Contactor reactor cooking process, the shorter process cycle time could allow the production of up to two batches of calcium sulfonate complex grease during the same two 8-hour shifts.

Figure 9. Manufacturing process comparison

Conventional open kettle cooking process

	0.50	1.00	1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	5.50	6.00	6.50	7.00	7.50	8.00	0.50	1.00	1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	5.50	6.00	6.50	7.00	7.50	8.00
Charge oil, sulfonate, water & promoters	🟥																					🟥										
Heat from ambient to 89°C		🟥																														
Hold at 89°C to convert to calcite			🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥																			
Once converted, add soap forming ingredients														🟥																		
Heat to 89°C to 93°C and hold for saponification															🟥	🟥																
Ramp temp 93°C to 135°C																	🟥	🟥	🟥	🟥												
Transfer to Finish Kettle																					🟥											
Cooling oil addition																						🟦										
Cooling 121°C down to 90°C																						🟦	🟦	🟦	🟦							
QC penetration check																										🟦						
Additives and grading oil																											🟦	🟦				
QC final check																													🟦			
Packaging																														🟦	🟦	🟦

STRATCO Contactor reactor cooking process

	0.50	1.00	1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	5.50	6.00	6.50	7.00	7.50	8.00	0.50	1.00	1.50	2.00	2.50	3.00	3.50	4.00	4.50	5.00	5.50	6.00	6.50	7.00	7.50	8.00
Charge oil, sulfonate, water & promoters	🟥										🟥																					
Heat from ambient to 89°C while pressurizing		🟥										🟥																				
Hold at 89°C to convert to calcite			🟥										🟥																			
Once converted, depressurize and add soap forming ingredients				🟥										🟥																		
Repressurize and heat to 89°C to 93°C					🟥	🟥									🟥	🟥																

and hold for saponification					🟥	🟥									🟥	🟥																
Ramp temp 93°C to 135°C							🟥	🟥									🟥	🟥														
Transfer to Finish Kettle									🟥										🟥													
Cooling oil addition										🟦										🟦												
Cooling 121°C down to 90°C										🟦	🟦	🟦	🟦							🟦	🟦	🟦	🟦									
QC penetration check														🟦										🟦								
Additives and grading oil															🟦	🟦									🟦	🟦						
QC final check																	🟦										🟦					
Packaging																		🟦	🟦									🟦	🟦			

Comparison of finished grease properties

As previously reported, the grease formulations were identical to those expected to achieve NLGI grade 2consistency at 100% yield in an open kettle process. In the case of experimental greases 1 and 2 based upon the sulfonate pre-mix, this was exactly what was obtained. However, in the production of experimental grease 3 using the component approach, the grease at 100% yield unexpectedly had the consistency of NLGI grade 4 grease. This grease would require an oil extra addition of 20% by weight to reach NLGI 2 consistency.

Once all greases were at the same relative consistency, the performance characteristics of the finished calcium sulfonate based greases obtained by each process were compared by standardized ASTM test methods. The results are shown in ***Table 1***. In our experience, the performance test results are similar towhat would be expected from the same greases manufactured in a conventional open kettle process.

Table 1. Performance characteristics of finished calcium sulfonate greases obtained by each process

ASTM Method	**Test Description**	**Units**	**Exp. 1 CaS Gel**	**Exp. 2 CaSX A**	**Exp. 3 CaSX B**
D217	60X Worked Penetration	dmm	292	291	295
D217	10K Worked Penetration	Δdmm	+3	+12	+18
D217	100K Worked Penetration	Δdmm	+9	+25	+35
D2265	Dropping point	°C	>316	>316	270
D2266	4-Ball Wear, Scar diam.	mm	0.33	0.42	0.45
D2596	4-Ball EP, Weld Point	kgf	500	400	400

Conclusions drawn from the experimental work

The STRATCO Contactor reactor was designed to address the limitations of conventional grease cooking kettles. The STRATCO Contactor reactor's sealed design, highly efficient rate of heat transfer, turbulent circulation path, and high shear mixing zone make it extremely well suited as a production vessel for calcium sulfonate based greases. During the process, we observed faster conversion of the amorphous calcium carbonate into calcite for the contactor process. In one case, we measured an improvement in grease yield over the conventional process. The resulting greases obtained from the STRATCO Contactor process were demonstrated to have similar overall performance to the greases obtained from more conventional manufacturing equipment.

For the full scale manufacturing plant, we have shown that the use of the STRATCO Contactor has potential to improve process speed in the production of calcium sulfonate type greases. This improvement may allow improved equipment utilization, improved labor efficiency, and reduced energy consumption. We believe that with a shorter process cycle there is clear potential for increasing manufacturing output, producing more batches in the same time.

Acknowledgements

The authors wish to acknowledge Nathan Claycamp of AXEL Americas, LLC for his contribution in the performance testing of the finished greases.

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The synergistic effect of PTFE with Extreme Pressure additives in Lithium complex/clay greases under elastohydrodynamic lubrication condition

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Abstract

Industrial greases are one of the most important fluids extensively used by a large variety of industry branches. Industrial greases are showing a systematic growth, additionally, it is supported by technological improvements, Innovative solutions upcoming new industry sectors that look for the best performing products economical and environment friendly. As a result, there is a need of high performance grease to achieve tribological properties like low co-efficient of friction; low wear rate and high load bearing capacity under sever operating condition. Polytetrafluoroethylene (PTFE) is synthetic fluoro polymer, which is chemically inert in nature show superior properties like low friction co-efficient and high temperature stability. PTFE has tendency to enhance the desired tribological properties of lubricating grease. This paper presents the comparative effect of PTFE as EP additive and the synergy with Zinc dialkyldithiophosphate (ZDDP) & conventional EP additive like Sulfur phosphorus (SP) in comparison with Molybdenum (MoS_2) in candidate greases under rolling/sliding friction condition. The tribological results reveal that the PTFE improve anti-wear and extreme pressure property than MoS_2. On further addition of ZDDP and SP additive in PTFE lithium complex grease, significantly improve extreme pressure property.

Keywords: Lithium complex/clay based Greases, PTEF, MoS_2, ZDDP, SP, wear Rate, load wear index.

1.0 Introduction

Lubrication is one of most promising way to enhance the life of machining tools. The use of proper lubrication reduces not only cost but also effect the natural environment in positive way. Grease has gained importance in lubricant industry since the beginning of the industrial revolution wherein machine components had to be lubricated. In industry greases are used in application wherein lube oils cannot provide lubrication frequently. Greases provide prevention from upcoming contaminants and resisting water. Unfortunately lubricating greases are cheaper than other lubricants. However, on the basis of application, addition of extreme pressure additives in grease increases the cost of final product. Now days increasing the demand for long life and high load industrial grease applications.

More than 90% of rolling bearings are grease lubricated [1]. As a result, understanding of grease frictional performance can offer an important way to reduce power losses in rolling bearings. The base oil, thicker and additive in typical greases is obvious more complex rheological system than simple base oil. So it is difficult to ascribe lubricant film formation and bearings friction behaviour for grease component. But it is determine by interaction between all grease elements which in turn strongly depend on the specific operating conditions. However, only a few works have explored the effect of grease composition on its friction behaviour on thrust ball bearing [3-4], four ball machine [5] and ball on disc machine [6]. The friction behaviour of grease lubricated bearing system explains under elsatohydrodynamic lubrication (EHL) regime [2]. In EHL regime, as loads and speeds increases dynamic pressure, and greases is compressed to a point behaving like a solid. Under this condition, surface component elastic deformed and helps to predict friction behaviour of roller bearing system.

Researchers have been blended MoS_2, elemental Sulfur, ZDDP and other EP additive in different concentration in greases and greases samples have been tested under EHL conditions. Laurentis et al. (2015) studied the effect of mineral oil, synesthetic or ester based grease with different thickener for high temperature and heavy duty application [7]. Neyman et al. (2008) studied the effect of graphite, MoS_2, molybdenum dithiocarbamate and ZDDP in mineral oil lithium complex and synthetic grease. His studied concluded that synthetic grease effectively improves fretting wear property. Further addition of anti-wear additive prevents material loss [8]. Munot et al. (2005) used PTFE for low coefficient of friction, ZDDP for anti-wear properties and MoS_2 for high load application in lithium complex grease [9].

Due to environment concern, ZDDP, MoS_2 & SP additive are toxic [10-12]. On the other hand PTFE has been introduced as effective friction modifier in solid and semi lubricants. Due to its high softening point and chemical inertness make it a choice in many extreme conditions. In a study by Stolarski et al. (2002) it was seen that a thin layer of PTFE adheres to the interacting surface due to a physical reaction between PTFE and metal surface. It was also shown that due to the mechanical fracture of PTFE chain, chemical reactions are induced on the interacting surface where asperity contact is the highest [13,14]. Some of the recent studied shown that a combination of ZDDP and PTFE is known to be synergistic that yield superior wear and weld load performance. In a study by Aswath et al. (2012), strong interaction between fluorinated-ZDDP and PTFE was shown to be the reason for the superior wear and weld performance for oils and greases [14].

Hence the present work is a systematic comparative approach on friction, wear and behavior of load wear index of PTFE and MoS_2 in different greases and also evaluate the synergic effect of PTFE with ZDDP or SP additives under EHL regime. The present research extended the application of PTFE in grease. The reported results in the present paper will help to grease manufacturers to incorporate the PTFE as additive for grease ingredient.

2.0 Experimental

2.1 Materials

In the present paper the commercially available lubricant additives MoS_2, ZDDP and SP were used as such. High molecular weight PTFE after irradiation using E – beam, and micronization (high pressure air micronization) results in fine micronized powders which are useful in applications like Inks, Coatings, Lubricants, elastomers and personal care products for blocking moisture and improve the slip properties.

PTFE powders for the current study were manufactured at Apar Industries Limited (1.5 MeV and

3.0 MeV Electron Beam Accelerators along with most modern high air pressure micronizer). Typical properties of the PTFE powders are given in Table 1. In the current study Grade 210 PTFE powders are used in the experimentation.

Table 1: Typical Grades of PTFE Properties

Properties	Test Methods	Units	210	230	290	M230
Color		Visual	White	white	white	white
Physical Form		Free flowing powder				
Bulk Density		g/L	400	900	700	900
Specific Gravity		g/cm3	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

2.2 Preparation of Grease Samples

Lithium complex grease was used as the starting material. The micronized PTFE powder, MoS_2, ZDDP and SP (sulfur-phosphorous) were used as extreme pressure (EP) additives in lithium complex grease. The selected concentrations of EP additive were chosen to prepare grease samples. The preparation of grease from PTFE and other reported EP additives involved vigorous mixing of EP additives at room temperature by Mechanical Grease Worker (MGW). 200 strokes were given with MGW for uniform mixing. The prepared grease samples are tabulated in table 2.

Table 2: list of prepared grease samples

S. No.	Base Grease	Prepared Sample Coded as
1	Li complex grease	A
2	Li complex grease + 4% MoS_2	B
3	Li complex grease + 4% PTFE	C
4	Li complex grease + 4% PTFE + 3% ZDDP	D
5	Li complex grease + 4% PTFE + 2% SP	E

2.3 Anti-Wear Test

A four tribo tester has been used to analyse the anti-wear property of prepared grease samples as per ASTM D 2266 test condition. The E-52100 steel balls were used in point contact geometry as shown in figure 1. The four ball tribo tester utilizes 4 ball in which top ball is held in collet and rotated at desired speed with the help of electric motor. The bottom three balls are fixed in cup assembly and emerged in lubricating grease. Each grease samples were tested five times to check the repeatability of wear behaviour.

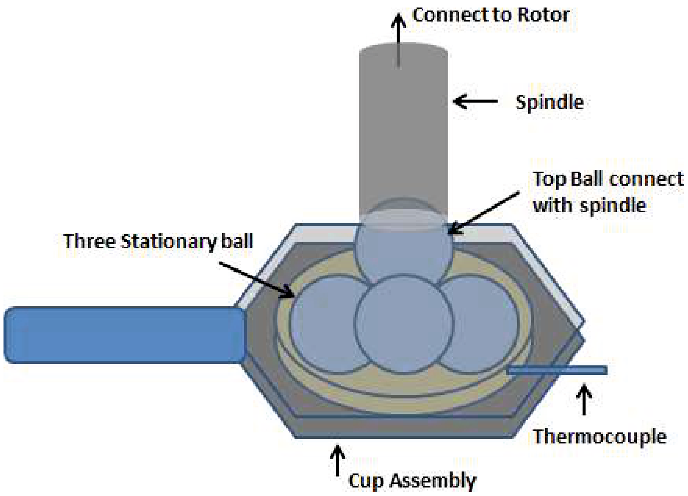


Figure 1: The systematic representation of 4 ball tetrahedral geometry used in 4 ball tribo tester.

2.4 Wear Rate Determination

Wear rate describe sliding wear based on the theory of asperities contact. Archard's formula [9] and Wear scar diameter were used to determine the wear rate of formulated grease samples. The formula was used to observe volume of wear debris on friction force. Wear depth, wear volume and sliding speed are important parameters which help to calculate wear rate. The wear depth of the ball was deduced using WSD as shown in figure 2.

$$\boldsymbol{The\ Wear\ Depth\ (h) = DB = R - R\ Cos}\ [(\mathbf{sin^{-1}}\frac{\boldsymbol{WSD}}{\boldsymbol{2R}})] \qquad (1)$$

Where, R is the radius of the ball. The wear volume and wear rate of the ball is given by,

$$\boldsymbol{Wear\ Volume\ (V) = \frac{\pi h}{6}\ [\frac{3\ (WSD)^2}{4} +\ h^2]} \tag{2}$$

$$\boldsymbol{Wear\ Rate\ (Q) = \frac{Wear\ Volume\ (V)}{Sliding\ Distance\ (X)}} \tag{3}$$

Where X is the sliding distance and calculated using,

$$\boldsymbol{X = \frac{\pi DNt}{60} = Sliding\ Distance, mm} \tag{4}$$

Where, t is the time for test duration in second, D is the pitch circle diameter (PCD) in mm and N is the rotational speed of the top ball in RPM.

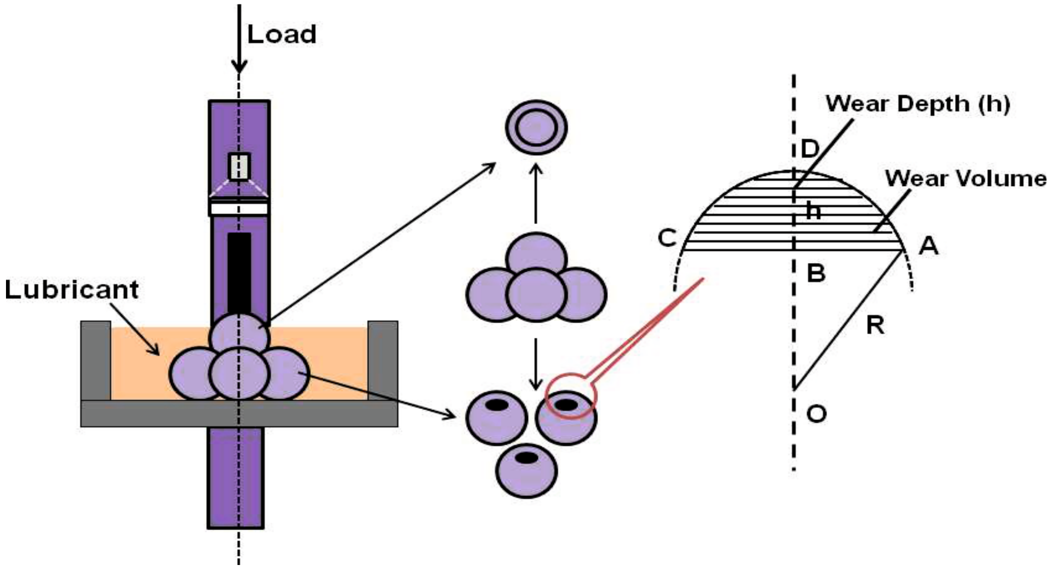


Figure 2: Determination of wear volume using wear scar on ball specimen.

2.5 Load Wear Index.

The ability of lubricant to prevent wear at applied loads is measure by load wear index (LWI). High LWI indicates lubricant effectively improve anti-wear properties of lubricating grease. The load wear index of prepared grease sample has been evaluated by using 4 ball tribo tester. The grease samples were tested as per standard IP-239 test method. The test was conducted for 10 second with a spindle speed of 1450 rpm. The load wear index of grease is to prevent the wear at applied load. All steel balls were thoroughly cleaned before and after the experiment with hexane. The test conditions of standard tests are tabulated in table 3.

Table 3: Test conditions of standard test methods

Test Method	Speed (rpm)	Load (kg)	Temp (^{0}C)	Time Duration, Second
ASTM D 2266	1200	40	75	3600
IP-239	1450	16, 18, 20, 22, 24, 28, 32, 36, 40, 45, 50, 56, 63, 70, 80, 90, 100, 112, 126, 140, 160, 180, 200, 225, 250, 280, 315, 355, 400, 450, 500, 560, 620, 700, 800	27	10

3 Result & Discussion

3.1 Physicochemical properties of grease samples

The consistency of grease and high temperature resistivity were determined by using cone penetrometer and drop point measurement apparatus. The fresh lithium complex grease has NLGI number 2 and drop point 180°C. On additive of EP additive there is no change in consistency and drop point of lubricating grease.

3.2 Tribo performance of grease samples

The tribo performance behaviour of greases samples has been performed as per ASTM D 2266 procedure is shown in figure 3. The tribo performance tests reveal that on addition of ZDDP or SP additive in 4% PTFE lithium complex grease, the friction force reduces. The kinetic friction represent by the friction at the end of the test reveals that there is significant reduction in friction for the 2% SP additive in 4% PTFE lithium complex grease. The average value of friction and wear scar diameter in mm has been tabulated in table 4. The table 4 clearly indicate that 4% PTFE significant improvement in anti-wear property then moly lithium complex grease. Furthermore addition of ZDDP and SP additive in PTFE lithium complex grease gives significant improvement in anti-wear property as well when compared with fresh Li complex grease and 4% Moly Li complex grease.

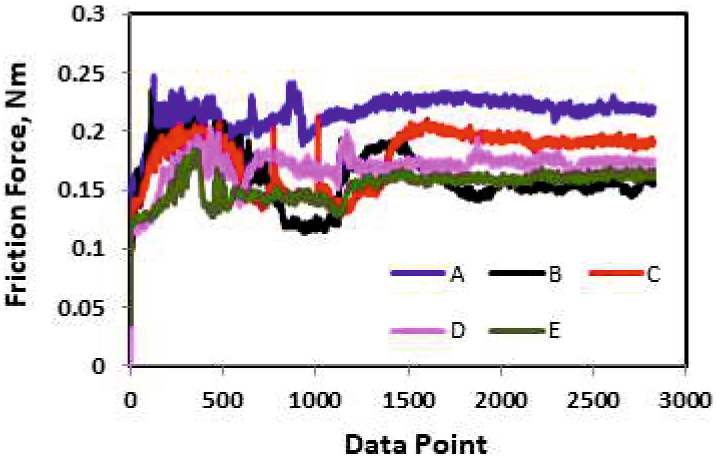


Figure 3: Friction behaviour of prepared grease samples

Table 4: The variation of Friction and wear behaviour of prepared grease samples

S. NO	Prepared Grease	Average Value		% Change in COF & WSD	
1	A	COF	WSD	COF	WSD
2	B	0.122	0.778	-	-
3	C	0.092	0.716	24.6	7.96
4	D	0.100	0.626	18.0	19.53
5	E	0.096	0.609	21.3	21.72

The variation of wear rate of prepared grease is shown in figure 4. The result show that fresh lithium complex contain high wear rate as compared to EP additive containing lithium complex grease. The 2% SP and 4% PTFE containing lithium complex grease show minimum wear rate. The minimum wear rate clearly indicates during operational condition formulated grease reduces the material loss and improves the life of the machining component.

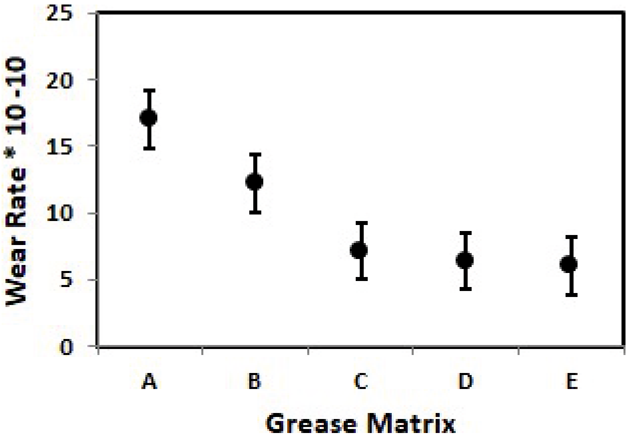


Figure 4: variation of wear rate of grease samples

3.3 Extreme Pressure and Load Wear Index of grease samples

Bearing and gear systems while in operation are loaded by intermittent heavy loads due to operational abnormality. Under such condition EP additive containing grease form a film of sufficient thickness and bear the applied load. In case of fresh greases, they form a film but it cannot able to sustain the load and increase contact friction and wear. In order to assess this characteristic behaviour of formulated grease samples were tested under extreme pressure condition. Furthermore, to investigate the wear behaviour at different applied load in term of load wear index. The weld load & load wear index of formulated grease samples are tabulated in table 5.

Table 5: The variation of Weld Load and Load Wear Index of grease samples

S. NO	Grease samples	Weld Load (WL), Kg	Load Wear Index (LWI), Kg	% Change in WL & LWI	
				WL	LWI
1	A	160	42.84	-	-

2	B	355	40.85	121.8	4.64
3	C	560	74.13	250.0	73.0
4	D	620	98.82	287.5	130.6
5	E	800	123.4	400.0	188.0

The table 5 clearly reveal that EP additives has tendency to sustain heavy load during operational condition. On the addition of 4% PTFE and 2% SP additive significantly improve weld load and load wear index by 400% and 188% respectively when compared with fresh lithium complex grease. The variation of WL and LWI with different EP additives in lithium complex grease is shown in figure 5.

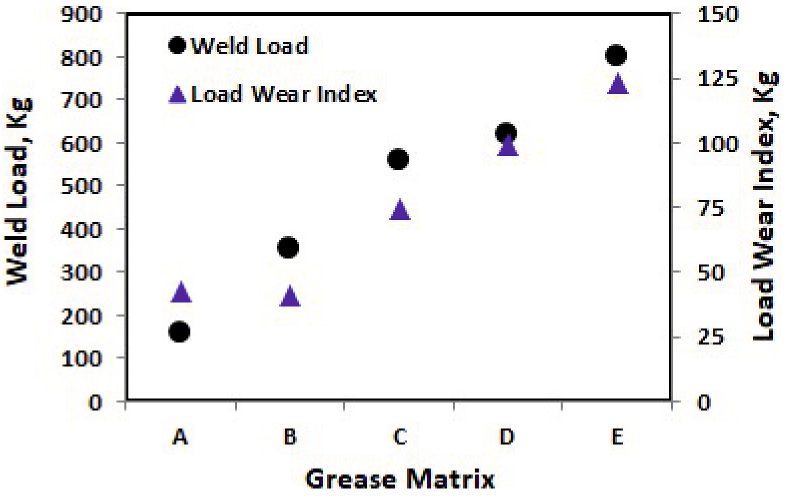


Figure 5: Variation of WL and LWI in different formulated grease samples with different combination of EP additives.

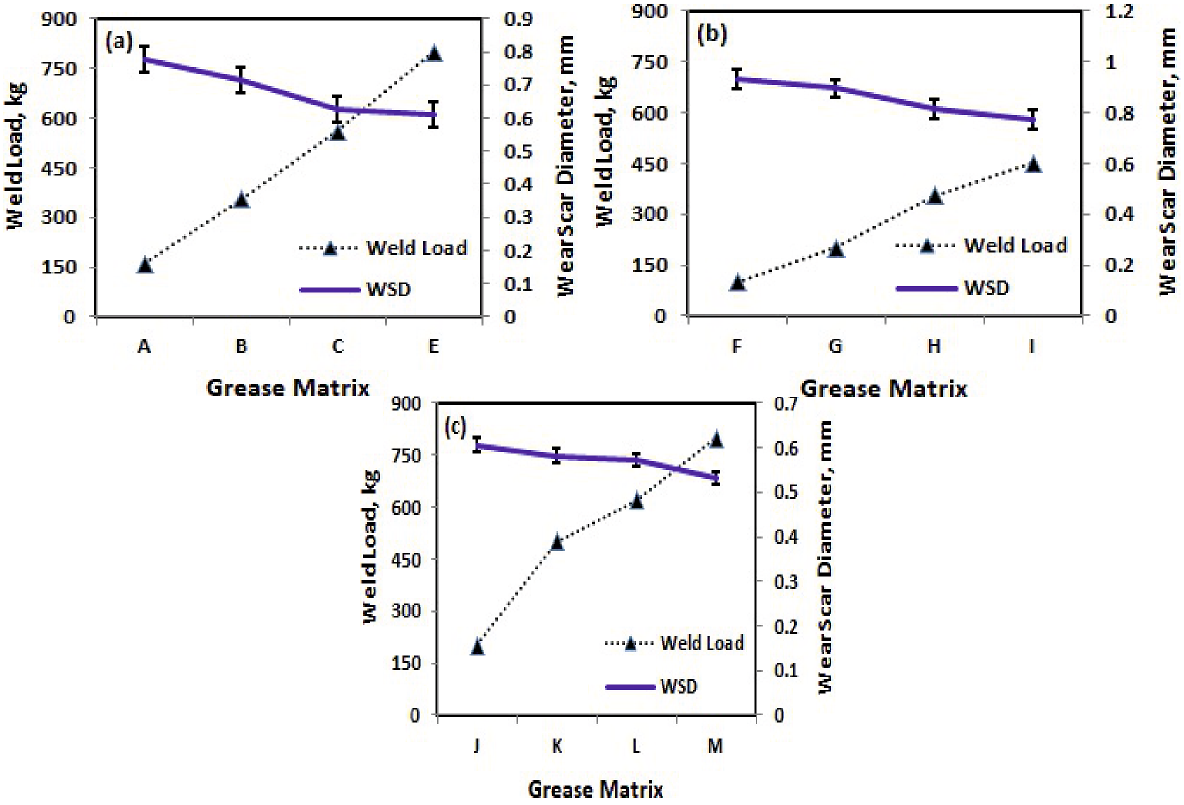
3.4 Effect of EP additive in lithium complex, organic clay base and poly urea grease

The effect of EP additive in term of weld load and wear scar diameter in different industrial grease is shown in figure 6. The figure 6 clearly indicates that on addition of 4% PTFE significantly improved the weld point and reduces the wear property as compared with addition of 4% MoS_2 in different industrial greases. Furthermore, addition of 2% SP additive with 4% PTFE in industrial greases remarkably improves the weld load and anti-wear properties. Overall the reported concentration of PTFE and SP additive is also cheaper than concentration of MoS_2. The comparative results of weld load and WSD are tabulated in table 6.

Table 6: The variation of Weld load and WSD in different greases

S. No.	Grease Sample	Weld Load (WL), Kg	WSD, mm	% Change in WL or WSD	
				WL	WSD
1	A	160	0.778	-	-
2	B	355	0.716	121.8	7.96
3	C	560	0.626	250.0	19.53
4	E	800	0.609	400.0	21.72
5	F	100	0.931	-	-
6	G	200	0.895	100	3.86

7	H	355	0.813	255	12.67
8	I	450	0.772	350	17.07
9	J	200	0.605	-	-
10	K	500	0.581	150	3.96
11	L	620	0.572	210	5.45
12	M	800	0.531	300	12.23



Notation* -See Annexure A

Figure 6: Effect of variation of EP additives in term of weld load and WSD (a) Lithium complex grease (b) organic clay based grease & (c) poly urea based grease

4.0 Conclusion

The present paper has investigated the effect of different EP additives in different grease. This paper also focused on environment concern and cost effectiveness. PTFE is environment friendly and chemically inert in nature. The present study clearly reveals that PTFE is much more effective than MoS_2 and ZDDP. Therefore, we focused blending of PFTE in spite of MoS_2, ZDDP and other toxic lubricant additive in greases. On the basis of tribo performance the following point are concluded as following:

- The PTFE added greases were tested for the other properties like oil leakage tendency, extended work rheology properties, water wash out attributes. The changes are well within the specified limits.
- The tribological results show PTFE is more effective
- Addition of PTFE in grease significantly improves the load wear index than MoS_2.
- PTFE give synergetic effect with SP & ZDDP to improve the load wear index and reduces the wear property at applied loads.
- 4% PTFE containing Lithium complex grease improved anti-wear and weld load property by 19.53% and 250% respectively.
- On addition of 2% SP additive in 4% PTFE containing Lithium complex grease improved anti-wear and weld load property by 21.72% and 400% respectively.
- The load carrying capacity of 2% SP additive containing 4% PTFE containing Lithium complex grease is improved by 188%.
- Due to high inert nature to chemicals and environment and its pleasant color, Greases for long life and high load application PTFE may be a good choice.
- PTFE grease is environmental friendly than other MoS_2, ZDDP and other EP additive containing commercial greases.
- To improve the weld load of a grease one can keep an option of PTFE as one of the EP additive while formulating the grease.
- PTFE addition test details verified in plain Lithium, lithium complex, poly urea and clay based greases as these greases represent more than 85% market share of the grease.

Annexure A

Table : list of Formulated clay or polyurea grease samples

S. No.	Base Grease	Formulated Sample Coded as
1	Clay Base Grease	F
2	Clay Base Grease + 4% MoS_2	G
3	Clay Base Grease + 4% PTFE	H
4	Clay Base Grease + 4% PTFE + 2% SP	I
5	Poly urea Grease	J
6	Poly urea Grease + 4% MoS_2	K
7	Poly urea Grease + 4% PTFE	L
8	Poly urea Grease + 4% PTFE + 2% SP	M

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Investigation of VI Improver Blends for Improved Low Temperature Lubricants

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Abstract

Polymeric viscosity index improvers (VII) are routinely used to modify oils to the proper viscosity and VI for an application. There are many commercially available polymer chemistries (PMA, PB, OCP etc.) to choose from when selecting a VII product for formulation. Improper selection of a polymer in a formulated oil can reduce pour point, raise Brookfield viscosity, and inhibit the pumpability of the product in cold climate conditions. Oils formulated with shear stable polymers are more prone to this issue due to the higher treat level required.

This study investigates the appropriateness of different polymer chemistries in Group II, Group III and PAO fluids and the polymers' effect in low temperature pour point testing. Technical discussion will cover viscosity and gelation of polymers in oil. Based on these fundamental principles, several strategies for synergistic combinations of VII for maximum VI improvement and minimal effect on low temperature viscosity are proposed.

1. Introduction

1.1 Viscosity Index and Lubrication

The viscosity of oil decreases temporarily as temperature increases. This occurs due to the increased thermal (kinetic) energy allowing the individual oil molecules to move faster and overcome the internal attraction or 'cohesion' between molecules. Variation in viscosity with temperature during start-up, operation, or wear of a lubricant can cause a lubricant's viscosity to fall out of grade for a particular application. The desired viscosity is dependent on intended operating temperature, load, and speed.[1] The rate at which viscosity declines with temperature, from 40˚C to 100˚C, is expressed as the viscosity index (VI). Most base oils have a VI of 90 – 110. An oil with VI 100 has a KV100 roughly 1/10th the KV40. An oil with VI 200 has a KV100 about 1/5th the KV40.

Commercial lubricant VI varies widely. ANSI AGMA 9005 specifies four distinct ranges of VI for industrial applications: 90, 120, 160, and 240.[1] A review of 200 commercial motor/gear oils demonstrates that VI is critical for multi-grade oils. Roughly, a VI of 120 - 140 can be expected for 20W-X and 15W-X oils, 140 – 160 for 10W-X and 5W-X oils, and 160 – 180 for 0W-X oils. Exceptions apply depending on conventional, synthetic, or blended formulas.

In many cases, a low VI (50 – 90) or mono-grade (90 – 110) lubricant is sufficient for a simple application where there is no fluctuation in temperature from weather, operation, or wear. However, vehicles, mobile equipment, and areas that experience wide seasonal temperature swings benefit from multi-grade ("all-season") oils. Low VI products operating in varying temperature environments require replacement to meet changing lubrication requirements. Every 15-20˚C variation in operation temperature necessitates roughly one ISO grade up or down in a mono-grade VI 100 oil.[1] This shortens oil drain intervals, increases downtime, and poses the risk of cross-contaminating old and new lubricants.

Higher VI fluids also benefit from requiring lower viscosity grades to achieve the same lubrication. For example: the lubrication guidelines in AGMA 9005 (Table B.1-3) for spur/helical/bevel gears operating at 65˚C with a pitch line velocity of 10 m/s specify a VI 90 ISO 220, VI 120-160 ISO 150, or VI 240 ISO 100 oil. Lower viscosity, high VI products require lower treat of thickener since higher ISO VG is avoided.

1.2 VI and Grease

It is important to remember that oil is an integral part of grease lubrication. While the basis of this work - simple formulations of VI improvers in various fluids - applies directly to oil-based lubricants these concepts apply to the mobile oil phase of greases. The majority of grease is produced using an ISO 220 base oil for both general use and EP applications.[2] Higher or lower viscosity grades are advisable depending on the application speed with high viscosity base oils being favorable in low speed applications and vice versa. This work produced a range of oils with varying VI and low temperature performance as quantified by ASTM D97 pour point. High VI fluids would be excellent for greases intended to operate at elevated temperatures – aluminum complex, clay, and polyurea greases – which may benefit from the lower change in oil viscosity with temperature. Low pour point formulations present here would be best in cold weather greases – lithium complex and calcium sulfonate – where pumpability is a key concern.

1.3 VI Improvement

Viscosity index improvers (VII) are low to high molecular weight (1,000 – 250,000 g/mol) polymers which are added to oil to counteract the effect of oil thinning as temperature increases.[3] Polymers are large molecules prepared from connecting many individual repeat units, called ‘monomers’, into single structure.[4] This structure may be very linear like a chain or highly branched like a tree. The structure and choice of monomers determines the behavior of a polymer.[5]

Polymethacrylates (PMA) were one of the first VI improver polymers in the early 1900’s.[3] [6] Motor oils benefited from higher VI products which allowed a single oil to operate across many different seasons and climates. Polyisobutylene (PIB) gained favor due to greater cost effectiveness which in turn was later replaced by polyolefin copolymers (OCP). Each chemistry continues to be used to this day for applications that best fit each polymer’s advantage. The use of polymers has expanded from motor oil to hydraulic fluids, gear oils, and other lubricants.

The mechanism for polymer-based VI improvement is due to the thermally responsive behavior of polymers when dissolved in solution or a lubricant.[7] Polymers exist in solution or lubricant as very large coiled chains and occupy large spaces in the oil.[8] According to Stokes-Einstein theory, large molecules like polymers experience drag while they drift through oil due to continuous collisions with many smaller oil molecules.[9] These collisions slow the overall motion of the oil and raise the viscosity. The increase in viscosity increases with the cross-section of the polymer coil.

Conveniently, the size of a polymer coil increases with temperature.[8] Increasing temperature causes the polymer to uncoil into a larger sphere with larger cross-sectional area. **Figure 1.1** demonstrates this principle. The larger coils undergo more collisions across the larger cross-sectional area and produce greater enhancement of viscosity. A suitable VI improver polymer will overcompensate for the loss in oil viscosity at high temperature (KV100) relative to lower temperature (KV40). This temperature- sensitive effect produces a net increase in the viscosity index (VI).

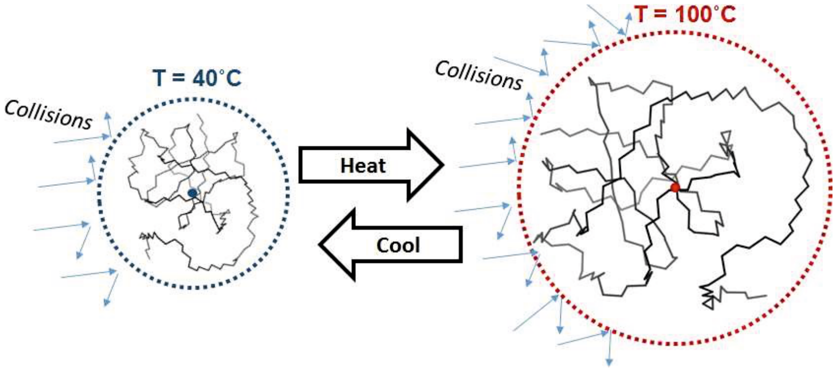


Figure 1.1: The classic depiction of a VI improver in oil by expansion of a polymer coil is shown above. At high T, polymer coils will absorb more oil and expand in solution to counter-act the effects of decreasing base oil viscosity. The depiction is very simplistic and evidence shows it is not always true.[10] This study will focus on when and why VI improvers deviate from this behavior.

1.4 Low Temperature Behavior and Pour Point

The behavior of oil at low temperature (below room temperature to -70˚C (-94˚F) or colder) is far less predictable than behavior at 40˚C and 100˚C due to the gradual solidification of the oil. As oil cools, wax (linear alkanes) form a network of fine crystals which traps the remaining oil in a rigid gel.[11] Upon heating the solid reverts to the original liquid lubricant. This process is highly complex and risks extensive damage to equipment if the lubricant is not carefully selected for anticipated cold conditions.[12] Extensive testing of lubricants under various circumstances at low temperature is required to circumvent this risk.

ASTM D97 pour point is one of the most well-known low temperature tests routinely performed on lubricants. Pour point (p.p.) is defined as the temperature at which an oil will not flow under its own weight while cooling quickly (~1˚C/minute). The manual test (D97) is performed by progressively cooling a tube of oil via a series of baths or environmental chambers until the oil does not flow when the tube is tilted. Several automatic methods (ASTM D5949, D5950, D5985, D6749) have been devised with varying degrees of automating temperature and tilt of the sample.[13] Oil at temperatures below the pour point becomes a semi-solid which will not pour from drums, cannot be pumped or risk damage to pumps, and will starve lubrication systems by remaining in the sump.[12]

Pour point for a given lubricant is roughly set by the pour point of the base oil which comprises the majority of the formulation. Higher refinement of oil (Gr. II or III) or synthesis from alpha-olefins (polyalphaolefin, PAO) produces high amounts of isomerized or branched alkanes which resist the tendency to gel. The wax that facilitates the pour point effect is attributed to long, linear alkanes (C18 to C30) that result from processing of crude oil into lubricant oil. Any additive used in the oil to produce a fully formulated lubricant can contribute additional wax from the diluent oil or the active ingredient may act inherently as a wax.

Pour point depressants (PPDs) are additives designed to reduce the pour point of an oil to allow it operate at lower temperatures.[14] This is achieved by modifying the shape and size of the wax crystals that develop in the oil under low temperatures. For this reason PPDs are also called ‘wax crystal modifiers’.

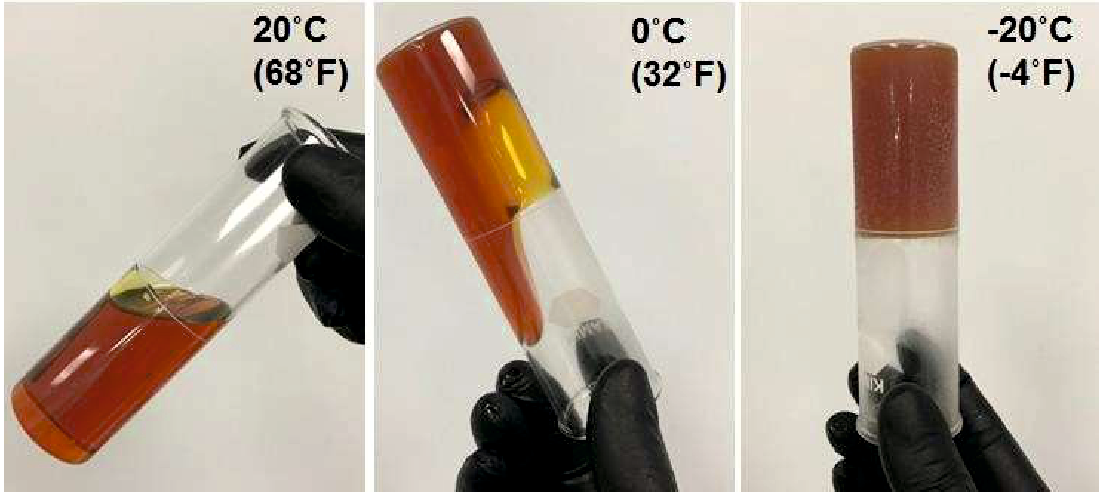


Figure 1.2: A single oil sample (p.p.=-15 ˚C) is shown at multiple temperatures above and below the pour point to demonstrate the significance of pour point on the flow of oil. The vial shown is a standard ASTM D97 pour point tube for performing the manual tilt test method (tilting of the oil sample is exaggerated to show viscous behavior).

2. Experimental

2.1 Materials

Three VI improvers (VII) were chosen to represent major commercial VI improver chemistries. Typical properties of the three products used in this study are listed below in Table 2.1. PB, PMA, and OCP products were selected with the same thickening efficiency (10% in Group I ISO 32 = 9.0 – 9.5 cSt @ 100˚C).

Table 2.1: Typical properties of the three VI improvers (VII) studied in this work

VII	Chemistry	%Polymer wt%	MW (g/mol)	PSSI ASTM D6278	KV100 cSt	Application
"PB"	Polybutene	100%	2,000 – 3,000	0%	4000	Gear
"PMA"	Polymethacrylate	50 - 80%	10,000 – 30,000	1%	1100	Hydraulic
"OCP"	Olefin Copolymer	5 – 20%	50,000 – 100,000	22%	3500	Crankcase

Polybutene (PB) is pure low molecular weight (< 3000 g/mol) polymer in the form of a viscous liquid. PB is prepared from the low temperature polymerization of butene isomers including isobutylene and 1-butene. Various grades of PB are assigned by molecular weight and correspond to handling viscosity, thickening efficiency, and shear stability. The advantage of PB is excellent shear stability and low cost. The disadvantage is that the high treat required to improve viscosity and VI can often lead to worse low temperature properties and lowering of base oil solvency (i.e. haze).

Polymethacrylates (PMA) are highly branched copolymers of short (C1 – C5), medium (C6 – C11), and long (≥C12) methacrylate esters.[6] Uniquely, PMA includes the polar ester functional group. The advantage is very high VI improvement and excellent improvement of low temperature properties by pour point depression. The disadvantage is cost and moderate thickeningefficiency. PMA was prepared in highly refined mineral oil with monomers and MW optimized for high thickening and VI improvement relative to its high shear stability.

Olefin copolymer (OCP) is a copolymer of ethylene and one of more olefins including propylene, butylene, or octene. OCP polymers are very long molecules with low branching and high molecular weight. The advantages are high thickening efficiency and low cost. The disadvantages are poor shear stability and some OCPs can behave like wax if ethylene content is too high (>50%). Solutions of OCP were prepared in paraffinic Group II oil.

Table 2.2 lists typical properties of three different base oils used to test the PB/PMA/OCP blends. Each base oil possessed substantially different wax characteristics. Viscosity grades were limited to lighter grades from ISO VG 22 to ISO VG 32. PAO was based on C10/polydecene chemistry. Each paraffinic oil was treated with 0.2wt% PPD.

Table 2.2: Typical properties of the three base oils tested

Oil	**API Group**	**KV40** cSt	**KV100** cSt	**Viscosity Index**	**Pour Point, ˚C** No PPD	**Pour Point, ˚C** 0.2wt% PPD
"Group II"	II	31.9	5	113	-18	-39
"Group III"	III	19.6	4	122	-15	-42
"PAO"	IV	30.2	6	137	-61	N/A

2.2 Methods

2.2.1 Sample Preparation

Varying combinations of two VI improvers in one of three base oils produced 81 unique formulations. Blended VI improver formulations were prepared for PB-OCP, OCP-PMA, and PB-PMA combinations using 5/10/20% of each product (10 – 40% total) in each base oil. Samples were prepared at 100 gram scale. Nine formulations were prepared for each pair of VII (5%+5%, 5%+10%, 5%+20%, 10%+5%, etc.). Treat level of each VII was labeled as "low" (5wt%), "medium" (10wt%), and "high" (20wt%). Appendix A lists each formulation and the measured data.

Group II formulations were treated with 0.2wt% of Group I/II-specific PPD while Group III formulations were treated with 0.2wt% of Group III-specific PPD. Both PPD were based on polymethacrylate chemistry with the blend of monomers designed to treat the different species of saturated waxes in Group II and III oils.[6,15] No PPD was added to PAO formulations to emphasis the wax contribution of each VII.

No additive packages were included. This study focuses on the viscometrics and low temperature properties of VII in oil as baseline for further formulation. Formulations presented in this work are starting points for low temperature industrial and/or automotive lubricants. Commercial additive packages are available to easily produce a finish product.

2.2.2 Visual Inspection

Visual inspection of sample clarity occurred after storage at room temperature (20˚C) for one week. Multiple formulations produced haze upon cooling to room temperature or after 24-48 hours. These formulations were marked as "Haze" in appearance in Appendix A. High PB or PMA content in PAO separated into two separate liquids after standing at room temperature. These samples received a rating of "Separation" in appearance.

Samples marked for "Haze" were included in the discussion of results. However, these formulations must be further treated by replacing 5% of the base oil with a synthetic ester or alkylated naphthalene for improved solvency. Saturated dibasic esters (adipate), trimethylol propane (TMP), or pentaerythritol esters are suggested. Samples marked for "Separation" are not considered as formulations in the following results and discussion sections.

2.2.3 Viscometrics

Kinematic viscosity at 40˚C (KV40) and 100˚C (KV100) were measured using a Cannon capillary viscometer in a Koehler liquid mineral oil bath per ASTM D445. Viscosity index was calculated from KV40 and KV100 data according to ASTM D2270. Pour point for each blended oil formulation was measured by ASTM D97 (Group II and III) or ASTM D6749 (PAO) method. Haze and separation in each oil was evaluated by visual inspection.

2.2.4 Viscosity Grade Assignment

ISO VG (ISO 3448, ASTM D2422) and AGMA (ANSI AGMA 9005) viscosity grades were assigned on the basis of KV40. SAE J300 Crankcase and SAE J306 Gear viscosity grades were assigned on the basis of KV100. Many formulations were observed with both an ISO/AGMA viscosity grade (KV40 specification) and SAE crankcase/gear grade (KV100 specification).

3. Results

3.1 Viscosity and grades

Appendix A (attached) contains the formulas and experimental data for all 81 samples prepared for this work.

Table 3.1 summarizes the range of viscometric and pour point data for the various formulations by base oil. Formulations were observed with KV40 from 37 to 764 cSt and KV100 from 7.3 to 75.1 cSt. This covered the majority of ISO/AGMA and SAE Crankcase/Gear viscosity grades as shown in Table 3.2. ~41% of samples conformed to an ISO 3448 or AGMA 9005 viscosity grade.
~54% conformed to SAE J300 Crankcase and ~78% to J306 Gear. All formulations conformed to at least one grade. These assessments were made by simple comparison to KV40 or KV100 requirements. In many cases, a single formulation met an ISO/AGMA grade, an SAE Crankcase grade, and an SAE Gear grade. For example, Formulation 5 in Appendix A (10% PB / 10% PMA in Gr. II) met the required KV40 and KV100 for ISO 100 / AGMA 3 / SAE 40 / SAE 90 viscosity grades.

Table 3.1: Statistics on KV 40, KV100, VI, and p.p. of the 81 samples prepared in this study, arranged by base oil, to demonstrate trends in viscometrics and VI due to the choice of base oil

		Group II	**Group III**	**PAO**
KV40	Min	62.8	36.9	61.2
	Max	763.7	557.4	423.9
	Average	192.0	137.5	193.8
KV100	Min	10.0	7.3	10.8
	Max	75.1	61.2	47.1
	Average	24.3	19.9	25.4
VI	Min	130.3	145.0	153.6
	Max	179.4	211.4	194.0
	Average	161.2	178.1	170.2
p.p.	Min	-45.0	-45.0	-52.0

	Max	-24.0	-24.0	-38.0
	Average	-35.5	-37.2	-47.1

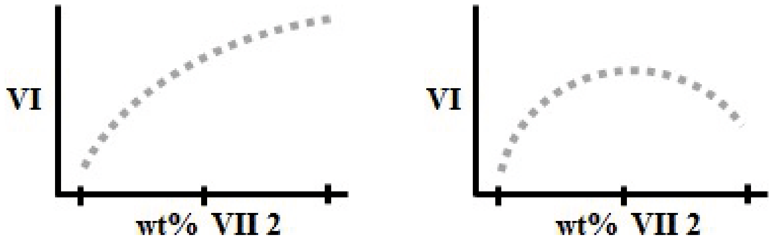
Table 3.2: Statistics on ISO/AGMA/SAE viscosity grades obtained from the 81 blended VII samples prepared in this study. Multiple formulations qualified for several viscosity grades based on KV40 and/or KV100.

Visc. Grade		#	**Visc. Grade**	#	**Visc. Grade**	#
ISO 46	**/ AGMA 1**	2	**SAE 20**	2	**SAE 80**	5
ISO 68	**/ AGMA 2**	8	**SAE 30**	13	**SAE 85**	11
ISO 100	**/ AGMA 3**	7	**SAE 40**	13	**SAE 90**	12
ISO 150	**/ AGMA 4**	2	**SAE 50**	12	**SAE 110**	13
ISO 220	**/ AGMA 5**	6	**SAE 60**	4	**SAE 140**	10
ISO 320	**/ AGMA 6**	6			**SAE 190**	9
ISO 460	**/ AGMA 7**	2			**SAE 250**	2
ISO 680	**/ AGMA 8**	0				
Total:		32		44		63
% of Samples:		40.7%		54.3%		77.8%

3.2 Viscosity index trends

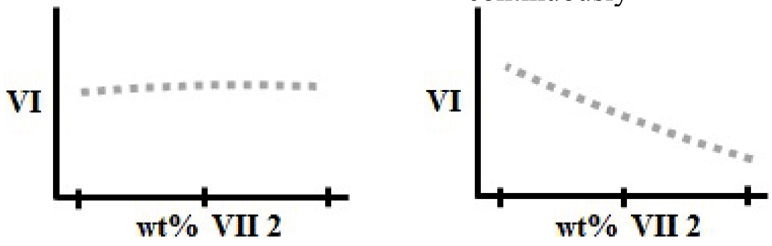
Viscosity index (VI) in the formulations ranged from 130 to 211. Average VI of tested formulations in Table 3.1 increased from Group II (base VI =113) to Group III (base VI =124) base oil. VIs in PAO (base VI = 137) were lower than expected due to separation in several high PB/PMA samples which would have otherwise increased the average VI. These samples produced high VI in Group II/III but were not included as PAO formulation due to drop-out.

Formulations were compared in groups of three with low/medium/high (5%/10%/20%) treat of one VII varied to demonstrate trends in viscosity and VI with the combination of a second VII. Blending different classes of VI improver (PB, PMA, OCP) produced complex trends in VI with treat level. **Figure 3.1** demonstrates the four observed cases for change in VI with increasing wt% VI improver. KV40 and KV100 increased in all cases when blending PB, PMA, and/or OCP. However, KV40 and KV100 increased at different relative rates with increasing treat. A large different in the relative change of KV40 and/or KV100 produced a changed in VI.



Case 1
VI increases continuously

Case 2
VI increases, then decreases or remains constant



Case 3
VI remains same

Case 4
VI decreases continuously

Figure 3.1: The VI of a formulation with increasing treat of VII responded in one of four qualitative cases (1 – 4). Generic plots above demonstrate the response in VI to VII relative to the initial VI. Absolute VI is not compared and, for example, a formulation with Case 4 behavior may have a higher VI than a Case 1 formulation.

3.3 Pour point trends

Pour point (p.p.) showed strong contrast between mineral oil and PAO-based formulations. In Group II and III, pour point was limited from -24 to -45˚C. PAO produced pour points from -38 to -52˚C. Pour point was generally independent of VI with several instances where VI increases with treat of VII and pour point decreased and vice versa. In commercial products, pour point varies over a range of 20-30˚C for a given VI. However, p.p. generally improves (decreases) with VI.

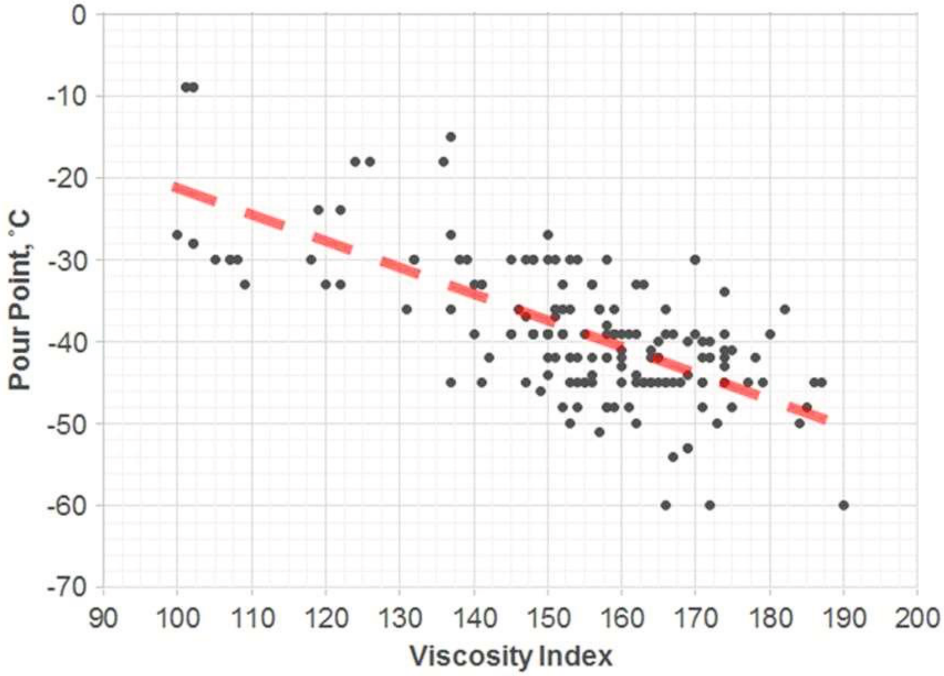


Figure 3.2: Pour point of commercial motor oils plotted against the corresponding viscosity index. This demonstrates the variability in required pour point to achieve commercial low temperature specifications. However, higher VI products tend to yield better p.p.

The pour point is a separate phenomenon from the measurement of VI at 40˚C and 100˚C. Oil undergoes complex and chaotic physical processes during the pour point test. The simple exponential curve of viscosity versus temperature, which can be obtained from VI and KV40 or KV100, simply does not anticipate the viscosity increase and change in flow at low temperature.

The change in pour point with varying treat of a second VII in a formulation was straightforward and followed one of three cases (A, B, C) as shown in **Figure 3.3**. ASTM D97 pour point was reported with a precision of +/- 3˚C. Any variation of 3˚C or less between two samples was regarded as negligible.

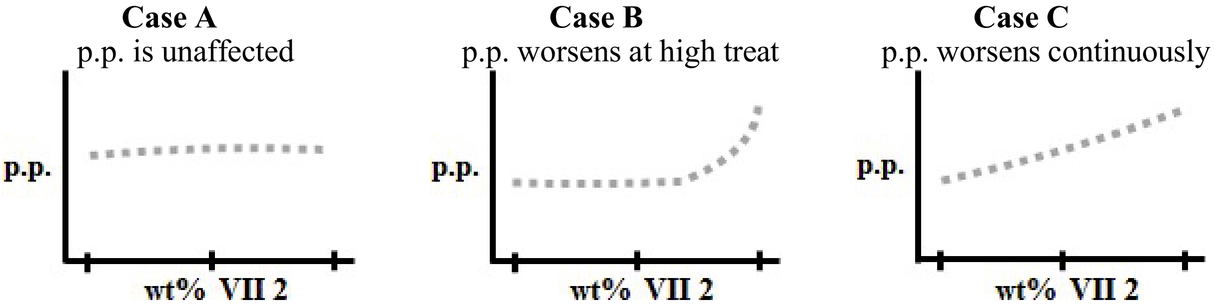


Figure 3.3: The relative change in pour point with varying amount of VII was assigned to one of three qualitative cases (A, B, or C) to simplify the analysis of a complex phenomenon. Generic plots for Case A/B/C are shown above that demonstrate the relative change in p.p. with VII. Absolute p.p. was not compared (i.e. a Case C formulation may have better p.p. than a Case A formulation however the Case A formulation pour point is more stable with VII)

4. Discussion

4.1 Trend in VI with blending VII

Due to limitations in cost or demanding specifications like shear stability it is often attractive to blend multiple types of VI improver to achieve the desired properties in a lubricant. The goal of this work was to blend VII with separation advantages and disadvantages to investigate opportunities for synergy.

Synergy occurs where two or more formulated components provide better performance (higher VI and/or lower pour point) than either product individually. The opportunity for synergy occurs because each VI improver chemistry tested (PB, PMA, OCP) contributes to the VI differently due to different molecular weights and chemical structure. Blending multiple polymers in solution can produce non-intuitive effects on the expected viscosity or VI since polymers in solution interact.[16] These effects can be positive or negative. Section 3.2 identified four different cases for the change in VI with blending two VII improver chemistries (**Figure 3.1**).

Case 1 – continuous increase in VI with treat – is the most desirable situation for a formulator since using more product to achieve high viscosity will also provide improved VI. Case 1 is the ideal situation for polymer-based VI improvement as described previously. The basic explanation of VI improvement requires the individual polymer coils in oil to expand with increasing temperature to counteract the thinning of oil under heat.[7] Higher treat of the polymer increases the number of coils in oil and multiplies the effect of thermal expansion in the coils. Case 1 behavior for VII is the generally accepted understanding for how polymers behave in oil. However, this picture is often not true.[10] [17] The exact performance of VII polymers is highly variable and three other responses to VII blending were observed: Case 2, 3, and 4.

Case 2 – initial increase in VI at low/medium treat with a decreasing or constant VI at high treat – tended to occur exclusively with adding PMA or OCP at 5-20wt% to another VII. Bell-shaped or parabolic responses of performance versus wt% of an additive is common when formulating lubrications and this over-treat effect is often called ‘reversion’. The difference between the ideal Case 1 (continuous improvement with added VII) versus the reversion seen in Case 2 can be explained by considering effects not shown in the simple VI improvement explanation (**Figure 1.1**). Reversion (Case 2) occurs most often for higher MW polymers, PMA and OCP, which have MW on the order of 10,000 and 100,000 g/mol respectively. The lower MW polymer PB (roughly 1,000 g/mol) generally expressed Case 3 or Case 4 change in VI (**Figure 3.1**). This suggested the Case 2 behavior related to polymer size in solution. Polymer behavior in solution is known to be dependent on concentration and size.[8]

Polymer solution theory, the understanding of how polymers behave in solution, is divided into three regimes: dilute, semi- dilute, and concentrated.[8] Dilute polymer solutions is defined as the concentration range where polymer coils are sufficiently diluted to avoid contact with other polymer coils in solution. This is the ideal condition assumed in Case 1. Semi-dilute polymer solutions occur when the concentrate of polymer coils achieves a critical concentration where polymer coils regularly contact one another in solution. Concentrated polymer solutions occur when the concentration of polymer coils causes polymer coils to overlap extensively in solution and form entangled networks. These conditions are directly dependent on the molecular weight of the polymer which defines the size of the polymer coil. Very small, low MW polymers require higher concentrations to reach the semi-dilute range while very large, ultra-high MW polymers can exhibit semi-dilute behavior at fractions of a percent by weight.

The three VI improvers use polymers of different MW at different wt% to deliver roughly the same thickening efficiency in paraffinic oil as previously summarized in Table 2.1. Polymer MW and concentration are important and proprietary information for an VI improver formulator. Knowing both pieces of information would allow the transition between dilute and semi-dilute polymer behavior for the polymers at treat to be calculated. However, the wt% at which this transition occurs can be identified for a given polymeric VI improver by plotting the log of specific viscosity (KV of oil+VII / KV of oil – 1) and log of wt% VII.[8] A change of slope in the log-log plot indicates a transition from dilute to semi-dilute. **Figure 4.1** below demonstrates a qualitative plot for the PB, PMA, and OCP products tested.

From **Figure 4.1**, it is apparent that the high MW OCP (~100,000 g/mol) creates a semi-dilute condition at 4-5wt% in oil.

Most examples of Case 2 VI behavior with increasing treat occurred with OCP VII. The explanation is that increasing contact between the large polymer coils inhibits coil expansion at high temperature. Coils cannot expand through another coil. The loss of expansion reduced the VI improvement in the thinning base oil and lowered VI with high treat. PMA (on the order of 10,000 g/mol) also exhibited Case 2 behavior and **Figure 4.1** shows that the dilute/semi-dilute transition occurred within the 5-20wt% treat tested in this study.

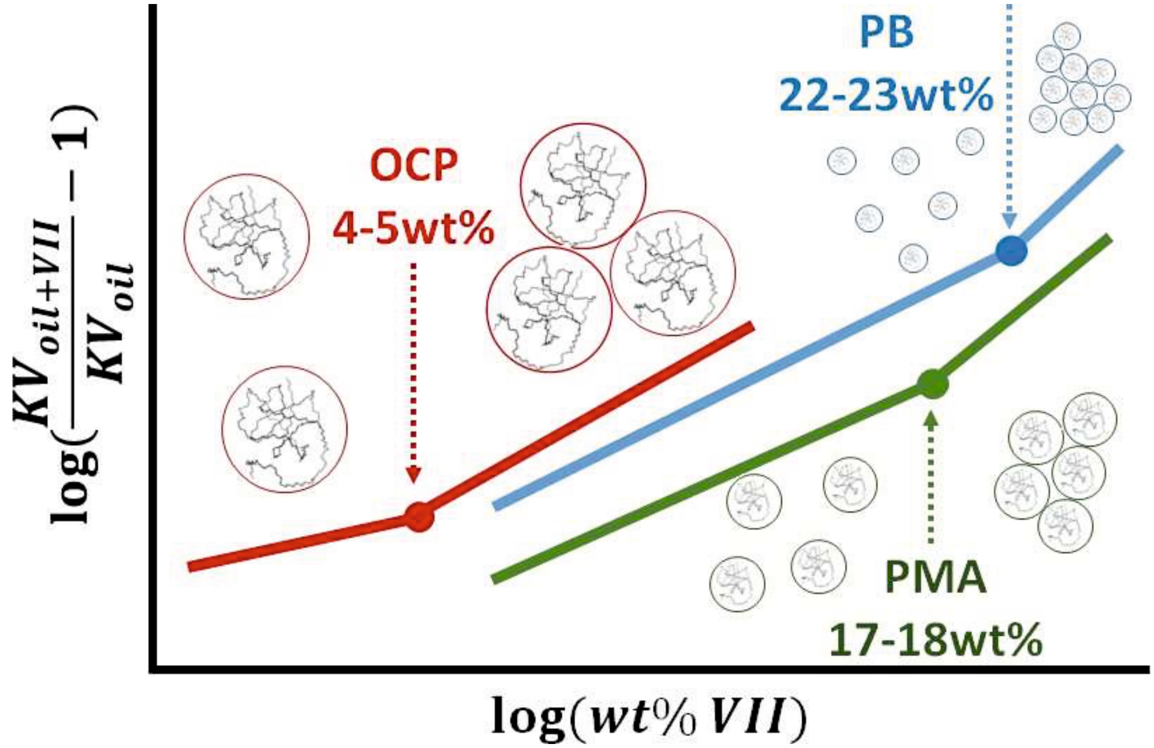


Figure 4.1: Plotting specific viscosity (KVoil+VII/KVoil-1) versus wt% VII on a log-log plot reveals a critical concentration where the slope of the line suddenly increases. This inflection point indicates that polymer coils sufficient large and/or concentrated enough for polymer coils to contact in solution. 'Dilute' solution theory handles polymer solutions below this critical concentration while 'semi-dilute' solution theory treats concentrations above this transition. Individual polymer coils are shown before (dilute, isolated) and after (semi-dilute, in contact) the critical concentration.

Case 3 – VI remains same with varying wt% – is useful for high VI base fluids whose VI is already appropriate for an application. A formulator may wish to further increase the viscosity within affecting the VI. Case 3 occurred most often in cases of varying PB in the formulation (Table A-2 in Appendix A). PB is unique among the three VII improver chemistries due to its very small molecular weight and high shear stability. The fundamental explanation for Case 3 is based the different ability of small or large polymers to coil or uncoil with temperature.

Liquid PB additives are typically found up to 2,800 g/mol or less which consists of a mere 50 butylene units or less. As demonstrated in **Figure 4.2**, it is intuitive that longer polymers have a greater potential to coil and uncoil: where N is the number of repeat units, an average polymer coil is proportional to $N^{1/2}$ in size and a fully stretched chain's length is proportional to N.[5] The size ratio between the fully extended polymer chain and its coil size is therefore depending on MW and is proportional to $N^{1/2}$ (or, N / $N^{1/2}$). Real polymer chains do not fully extend to the straight 'zig-zag' alignment shown in **Figure 4.2** but the visual aid is intended to demonstrate the potential for long polymer chains provide the VII effect. For low MW PB, N is typically <50 units while ethylene- based OCP may have N from 1k to 10k units. Case 3 likely occurs where low MW polymers approach the size of the base oil and the size of the expanded (KV100) and contracted (KV40) coil are not sufficiently to overcompensate for the thinning of base oil with temperature. In this case, low PB acted more as a thickener or high viscosity base oil than a VII.

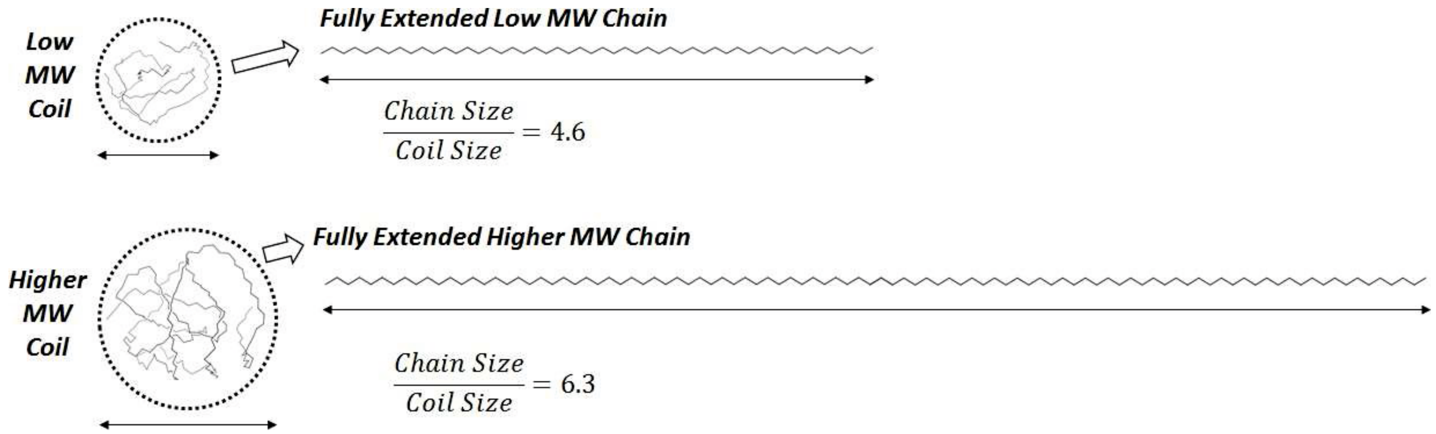


Figure 4.2: Higher MW polymers contract into a coil in solution to a greater degree than lower MW polymers as demonstrated by the ratio of end-to-end chain length versus coil diameter. This ratio scales by $N^{1/2}$ where N = number of monomers. If ideal VII behavior is dependent on coil expansion then more contracted, high MW polymers will provide better VI improvement. Case 3 behavior occurs when polymers are low MW and cannot provide sufficient expansion to compensate for base oil thinning.

Case 4 – continuous decrease in VI with added VI improver – was not an expected outcome of adding VII may be acceptable in the case of a high VI base oil like PAO. The Case 4 trend suggested that the addition of polymers could directly reduce VI unlike all other Cases. This case occurred most often in low solvency (Group III, PAO) base oils and with varying PB VII. The origin of VI decrease may be attributed to the overall solubility of polymers in solution.

Polymer-oil compatibility is a critical issue in high performance oils. The formulation for these products generally uses high treat of shear stable VII and a highly refined or synthetic base oil with poor solvency. The strain on compatibility produced by this strategy is two-fold: 1) higher wt% polymer means lower wt% base oil; 2) polymer which has replaced the oil is a poor solvent for other polymers or additives and reduces solvency of the oil.

A robust framework for approaching polymer-solvent compatibility was developed by Hansen in the 1960's to aid in the formulation of solvent-based products like paint, cleaners, and halogen replacements.[18] This mathematical model considers the balance of different molecular interactions (non-polar, polar, and hydrogen bonding) and the molar volume of each component in the oil or solvent.[19] Molar volume defines the molecular weight of a component divided by its density (MW/ρ) and is a rough estimation of the size of a molecule in solution. Hansen solubility calculation takes parameters from a given polymer and each component of the solvent or oil and returns a 'relative energy difference' ("RED") value for that combination of materials. RED ranges from < 1.0 (very good solvent) to 2.0 – 3.0 (borderline) or higher. **Figure 4.3** shows the calculated RED (from 1.0 – 1.5) for an arbitrary VII polymer of 100,000 MW in an example oil containing 0-30% polybutene of varying molecular weight. As MW of PB increases, the RED increased (compatibility decreased) with treat of PB at an accelerating rate.

The key parameter in the **Figure 4.3** plot was the increasing molar volume of higher MW PB. It is known that most petroleum-based oils range from 300-700 MW and that increasing viscosity (and MW) reduces the solubility of polymers.[20] [21] The corresponding molar volume is 400 – 900 cm^3/mol. The substitution of base oil for concentrated VII like polybutene rapidly increased overall oil molecular volume (cm^3/mol > 1,000).

Figure 4.4 demonstrates the effect of increasing solvent or oil size on polymer compatibility. Ideally, a 'proper' solvent for a polymer is only 50 – 200 cm^3/mol or no bigger than the molar volume of the polymer's monomer.[19] This requirement occurs because oil and solvent must diffuse into the polymer coil to dissolve it or expand with temperature.[5] As concentrated VII like PB or PMA was added to oil, the molar volume of the oil increased and reduced the solvency. Polymers and other large solvent components in the formulated oil are too large to fill the space inside the polymer coil.

Some instances of Case 3 behavior with non-PB VII, especially PMA, may also be due to Case 4 effects. Shear stable PMA VII must include higher amounts of polymer and less diluent oil to achieve acceptable thickening efficiencies comparable to OCP and other competing technologies. The lower solubility of the polymer causes the polymer coils to become smaller in solution and expand less at high temperature which may induce Case 3 (no change in VI) behavior.

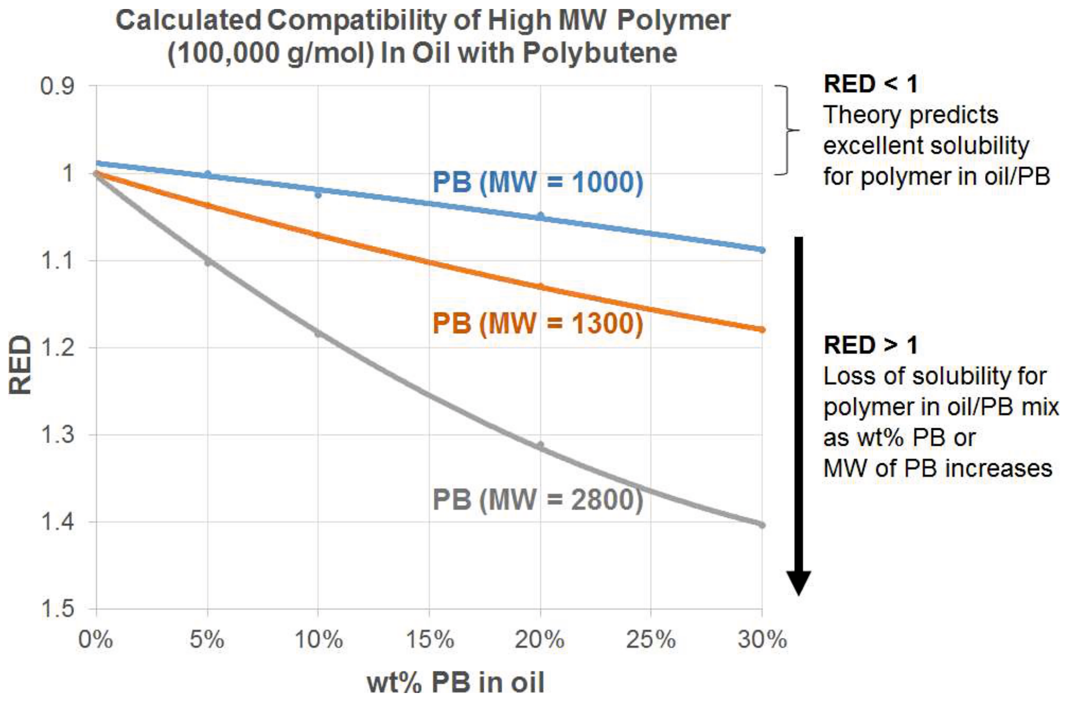


Figure 4.3: Hansen solubility theory calculates the compatibility of oil and polymer as an RED (relative energy difference) value: <1.0 predicts excellent solubility of the polymer while values above 1.0 indicate increasing solubility problems.[19] Calculated RED between a high MW OCP polymer and a mixture of oil with PB shows that increasing MW and/or wt% of the polybutene negatively affects the polymer's solubility. This is attributed to poor solvency of PB and the reduced solvency of the oil/PB mix.

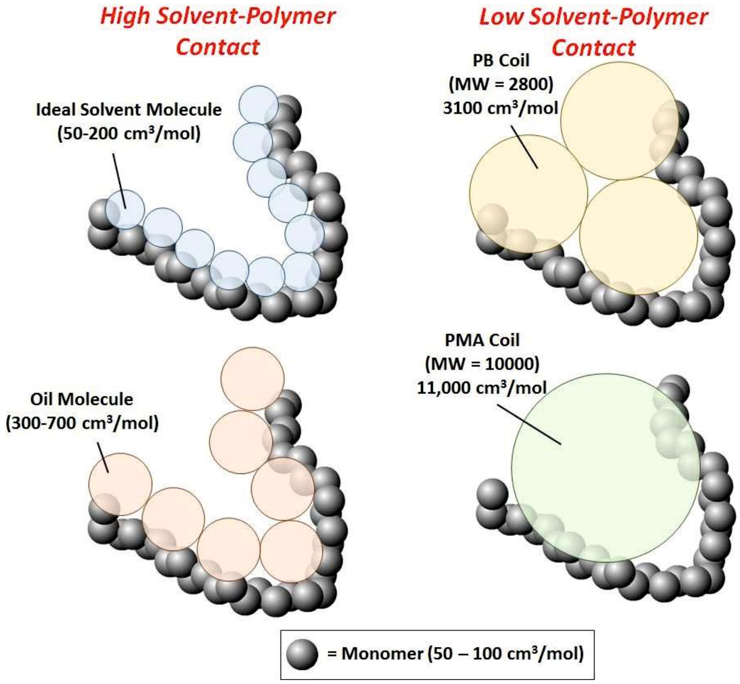


Figure 4.4: An example segment of a polymer coil is shown above with gray spheres representing individual monomers. The colored circles represent different components of an oil – solvent molecules or polymers – of increasing molar volume (MW/ρ). As the individual components of an oil become larger, the components cannot

fit inside the polymer coil and exhibit very low polymer- solvent contact. Low contact and interaction between polymer and solvent causes the polymer to become less soluble in the oil molecule and the coil size collapses. Low thickening or haze/drop-out occurs.

4.2 Trend in pour point with blending VII

Pour point of unmodified oil has been found to be a function of viscosity, density, and molecular weight.[22] The exact process of how oil forms a temporary gel at this temperature varies by oil. Paraffinic oil gel due to separation of long, waxy linear alkanes at low temperature to form a semi-solid gel. Highly branched synthetic fluids (PAO, ester) will crystallize.[23] The addition of extra components – VI improver, pour point depressants, friction modifiers, and other packages – will influence the pour point of a fully formulated lubricant by contributing waxy species and affecting both viscosity and molecular weight of the total mixture.

The mixed VII formulations in Group II, III, and PAO exhibited three separate cases (A to C, **Figure 3.3**) in pour point behavior with increasing treat of VII. All Group II and III oil formulations were treated with 0.2wt% of a base oil-specific PPD to inhibit oil-based wax. PPD level was not increased after adding VII to observe the effect of VII on p.p.

Figure 4.5 summarizes occurrence of cases A-C by oil and by VII for all data from Tables A-1 and A-2.

Figure 4.6 demonstrates the co-occurrence of Cases 1-4 (VI trends) and Cases A-C (p.p. trends). 50% of formulations with Case A pour point behavior (no change in p.p. with VII) exhibited Case 4 (VI continuously worsens with treat). 62% of formulations with Case C pour point behavior (p.p. continuously worsens with VII) exhibited Case 2 VI behavior (temporary increase in VI at low/medium treat with decrease in VI at high treat). Since Case A and Case 4 occurred together it can be assumed that their origin is related to collapse of the polymer coils as previously discussed. Case C occurred with Case 2 which was explained by the behavior of polymers at the semi-dilute concentration.

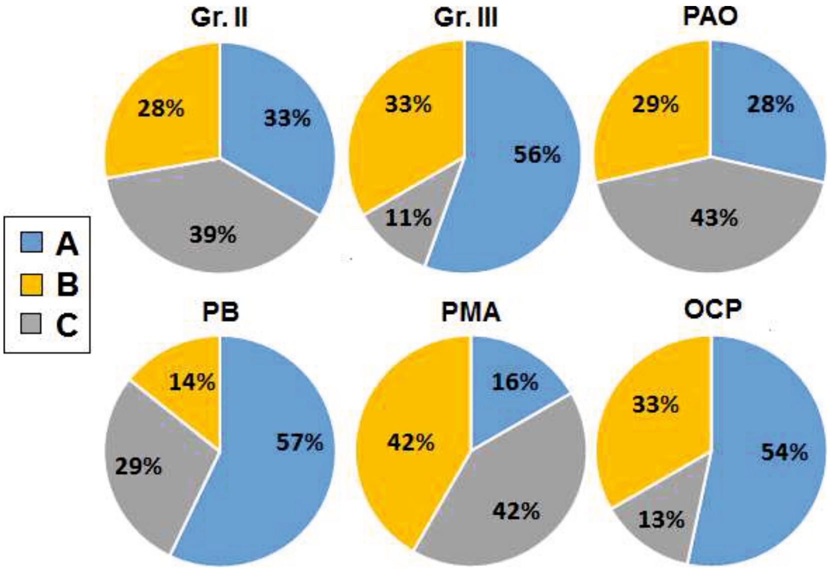
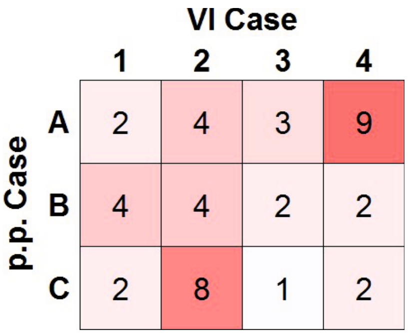


Figure 4.5: Comparison of p.p. trend cases (A-C) by base oil and varying VII to determine if specific base oils or polymers are responsible for different trends



p.p. Case \ VI Case	1	2	3	4
A	2	4	3	9
B	4	4	2	2
C	2	8	1	2

Figure 4.6: Grid comparing the occurrence of specific VI trends (Case 1-4) with specific p.p. trends (Case A-C) to determine if mechanisms for either behavior may be related. Case A occurred in 50% of formulations with Case 4 VI behavior and Case C occurred in 62% of formulations with Case 2 VI behavior. High co-occurrence of Case A+4 and C+2 suggest the trends occur under the same conditions and from the same causes.

Case A – pour point unaffected by VII – occurred most often for two types of formulations: a) Group III with varying treat of PB or OCP; and b) blends containing PMA and PB VII. PB is common to most Case A formulations. Polybutenes are highly branched or 'isomerized' structures unlike the linear C20 to C30+ alkanes attributed to wax in oil.[24] [11] Linear alkanes gel oil due to crystallization of long -CH_2- repeat units which coordinate into orderly structures at low temperature. The short and random branching of methyl, ethyl, and propyl side groups from the polybutene chain prevent orderly packing of –CH_2- groups and improves low temperature flow of polybutenes.[25] Polybutenes up to 100,000 g/mol will flow spontaneously, albeit slowly, at room temperature while polyethylene and polypropylene form rigid waxes at very low MW (< 1,000 g/mol) due to crystallinity. Highly isomerized and wax-free polybutene at high treat will dilute the wax content of oil and help prevent a critical mass of wax crystals from forming.[11]

The relation between Case A p.p. behavior (no change in p.p. with VII) and Case 4 VI behavior (VI worsens continually with VII) was demonstrated in **Figure 4.6** and occurred in PMA and PB blends. Calculated polymer solubility versus PB content in oil in **Figure 4.3** suggests that PB reduces the solubility of PMA. This caused collapse of the PMA polymer coil and poor VI (Case 4 behavior) but also prevented the worsening of p.p. with VII (Case A). Smaller polymer coils appeared to be related to better low temperature properties while the connection between Case C p.p. behavior (p.p. worsens continuously with VII) and Case 2 (VI improves at low/medium treat, worsens at high treat; semi-dilute effect). Comparing the two situations suggests that the network-like interaction between coils in the semi-dilute concentration range (**Figure 4.1**) accelerates wax formation at low temperature while collapsing the coils with solvent effects will prevent the polymers from aiding wax formation.

Case B – pour point worsens at high treat – also occurred frequently with PMA and OCP blends. Most instances of Case C in PAO occurred from blending OCP. No VI improver case (1 – 4) was observed greatly favoring Case B p.p. behavior in **Figure 4.6**.
However, Case B occurred 67% as either Case 1 or Case 2. Case B was also significantly less common in PB formulations as shown in **Figure 4.5**. These findings suggest that Case B behavior is related to Case A but is due to an effect that is lacking in PB. One key difference is that PB is used in pure form (100wt% polymer) while PMA and OCP VII were diluted in a Group II paraffinic oil (see **Table 2.1**). It is reasonable to conclude

that the loss of low temperature performance at high treat in Case B is due to the accumulation of wax from the diluent oil.

Case C – pour point worsens continuously – was common in blends of PMA with OCP. Case C likely originates from the same cause as Case 2 VI behavior since both Case C and Case 2 trends occurred together frequently (**Figure 4.6**). This behavior is due to a high concentration of large polymer coils in oil which begin to overlap in solution and form a network. PMA and OCP both achieve semi-dilute concentration at < 20wt% in oil as demonstrated in **Figure 4.1** with a change in slope of the log-log plot. Wax formation similarly relies on the formation of a network throughout the oil.[11] The pour point data suggests that contact between polymers (semi-dilute condition) tend to help the formation of the wax crystal network and worsen the pour point temperature.

No pour point improvement was observed using the PMA VII among the tested formulations. Low temperature properties of the tested PMA were less than expected for polymethacrylates. Polymethacrylates are commonly used as pour point depressants and their effectiveness is highly dependent on the selection of monomers.[26] PMA did improve pour point behavior relative to OCP. Formulations with Case B or C p.p. behavior with OCP often improved to Case A or B, respectively. However, PPDs for mineral oil are limited in effectiveness to very low (0.1 – 0.5wt%) treat with less effect at higher treat. The 5 – 20wt% treat of PMA used in this study exceeds the useful range for observing PPD behavior with polymethacrylate chemistry.

4.3. Recommendations for starting point formulations

Several general recommendations for formulators can be summarized from Sections 4.1 (VI behavior) and 4.2 (p.p. behavior) for designing low temperature, high VI products.

Negative VI and p.p. performance occurred with at the semi-dilute polymer concentration where polymer coils were of sufficient number and size to contact in solution. This prevented the expansion of the coils at high temperature to offset the thinning of the oil (bad VI improvement) and reinforced the formation of a wax network (pour point greatly reduced). The dilute/semi-dilute transition may be easily measured with simple viscosity equipment following the plot in **Figure 4.1** for a given VII product. The treat rate of the VII for high VI and low p.p. lubricants should not exceed the critical concentration. High MW polymers should be avoided and may only be allowed at a few wt% but can provide substantial thickening to meet target viscosities.

Formulations with the highest rated VI and p.p. behavior (Case 1 + Case A, Case 1 + Case B, or Case 2 + Case A) were found with low treat (5wt%) of PB with PMA or OCP. Case 1 + Case A was only found with Group III oil. Due to solubility issues few useful PAO formulations were found in this study due to the need for esters to improve solubility. **Table 3.1** is a useful resource to observe which viscosity, VI, and p.p. ranges were possible in each base oil. **Table A-1** and **Table A-2** in Appendix A show the components, viscometrics, VI, p.p., and viscosity grade (based on KV40 or KV100) data for each formulation prepared.

Table 4.1 and **Table 4.2**, below, summarize the four VI and three p.p. behavior cases. By understanding the cause of each observed trend with VII it is possible to recommend several actions to improve VI and p.p.

Table 4.1: Summary of the four observed cases in VI behavior with blended VII

	Trend	Explanation	Suggested Improvements	Figure
Case 1	VI increases continuously from low to high treat	Polymer coils expand at high temperature to increase KV100; higher KV100 per KV40 means VI improves	N/A	Fig. 1.1
Case 2	VI increases at low/medium treat; VI decreases or remains constant at high treat	Polymer coil concentration is sufficient for coil-coil interference (semi-dilute behavior)	Replace some wt% of VII with higher viscosity base oil	Fig. 4.1
Case 3	VI unaffected by additive wt%	Polymer expansion is too small to compensate for base oil thinning at high temperature	Use higher MW VII and/or increase initial base oil VI	Fig. 4.2
Case 4	VI decreases continuousy	Polymer coils collapse due to high polymer content and/or low oil solvency	Replace some wt% of VII with higher viscosity base oil Increase base oil solvency with low viscosity ester/AN	Fig. 4.4

Table 4.3: Summary of the three observed trends in pour point with suggested improvements

	Trend	Explanation	Suggested Improvement
Case A	Pour point unaffected by VII treat level	PB + OCP - Dilution of waxes by PB and polymer wt% is in dilute concentration PB + PMA – collapse of polymer chains prevents polymer coils from accelerating wax formation	N/A
Case B	Pour point	Similar to Case A; wax from	

	worsens at high treat	diluent oil in VII at high treat increases total wax content of oil	Use VII with higher wt% polymer or more refined oil Reduce VII use by increasing base oil viscosity
Case C	Pour point continuously worsens from low to high treat	High MW polymer coils begin to form a network in oil (semi-dilute condition) which helps the wax network form at low temperature	Reduce wt% or MW of VII to avoid semi-dilute condition Replace some VII with high viscosity base oil

5. Conclusions

Polymeric VII products have complex effects on viscosity, VI, and pour point when blended at high concentration necessary for high shear stability lubricants using lower MW polymers. VI improvement is generally understood to involve the simple thermal expansion and contraction of the polymer coil in oil to counteract the effects of base oil thinning at high temperature. In practice, several non-ideal behaviors are observed. These non-ideal cases in the VI or p.p. with the blending low to high treat of VIIs in oil can be explained by fundamental principles in polymer science and polymer solution theory. This work provides a framework for rationalizing non-intuitive behavior of VI and p.p. and suggested several recommendations to correct for the fundamental concepts at work.

Future work is required to further develop the ideas presented in this study. The dilute/semi-dilute transition appears to be critical in determining if high treat of a polymer will cause loss of VI improvement or sudden loss of low temperature flow. Base oil solvency with the addition of components like PB or ester appear to be able to shift the dilute/semi-dilute transition by collapsing the polymer coils slightly. This would allow more polymer in solution before coil-coil contact (the semi-dilute condition) is reached.

Several recommendations for improving the low temperature or VI characteristics of a formulation involved the partial substitution of VII for a higher viscosity base oil. It was also stated that increasing viscosity or MW of base oil can further reduce solvency for high MW polymers in oil. The balance of reducing polymer treat by increasing oil viscosity versus the lower solvency of higher viscosity oil warrants further investigation.

In summary, the activity of polymeric VII in shear stable and low temperature lubricants requires anticipating the behavior of polymers in solution through established fundamental concepts. This study has provided an outline for troubleshooting non-intuitive results from formulating various VII combinations in multiple oils.

Appendix A – Formulation Data Table

Table A-1 shows all 81 samples prepared including formulation, viscometric, low temperature, and viscosity grade information. There are six ways to present the results for blending the single VII at constant wt% with a second VII at varying wt%. **Table A-1** shows three combinations. **Table A-2** shows the remaining three combinations by rearranging data from Table A-1. This allows each combination to be viewed together in one place by using two tables.

To determine which chart to reference for a given pair of VII, consult the following chart:

		Varying VII		
Constant VII		PB	PMA	OCP
	PB	---	Table A-1	Table A-1
	PMA	Table A-2	---	Table A-1
	OCP	Table A-2	Table A-2	---

The "Cases" column in each table refers to the four cases of VI and p.p. behavior described in Results sections 3.2-3.

5. Conclusions

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Future work is required to further develop the ideas presented in this study. The dilute/semi-dilute transition appears to be critical in determining if high treat of a polymer will cause loss of VI improvement or sudden loss of low temperature flow. Base oil solvency with the addition of components like PB or ester appear to be able to shift the dilute/semi-dilute transition by collapsing the polymer coils slightly. This would allow more polymer in solution before coil-coil contact (the semi-dilute condition) is reached.

Several recommendations for improving the low temperature or VI characteristics of a formulation involved the partial substitution of VII for a higher viscosity base oil. It was also stated that increasing viscosity or MW of base oil can further reduce solvency for high MW polymers in oil. The balance of reducing polymer treat by increasing oil viscosity versus the lower solvency of higher viscosity oil warrants further investigation.

In summary, the activity of polymeric VII in shear stable and low temperature lubricants requires anticipating the behavior of polymers in solution through established fundamental concepts. This study has provided an outline for troubleshooting non-intuitive results from formulating various VII combinations in multiple oils.

Appendix A – Formulation Data Table

Table A-1 shows all 81 samples prepared including formulation, viscometric, low temperature, and viscosity grade information. There are six ways to present the results for blending the single VII at constant wt% with a second VII at varying wt%. **Table A-1** shows three combinations. **Table A-2** shows the remaining three combinations by rearranging data from Table A-1. This allows each combination to be viewed together in one place by using two tables.

To determine which chart to reference for a given pair of VII, consult the following chart:

		Varying VII		
Constant VII		PB	PMA	OCP
	PB	---	Table A-1	Table A-1
	PMA	Table A-2	---	Table A-1
	OCP	Table A-2	Table A-2	---

The "Cases" column in each table refers to the four cases of VI and p.p. behavior described in Results sections 3.2-3.

Table A-1. Formulations, Constant PB or PMA with Varying OCP or PMA

	Formula					**Viscometrics**			**Low T**	**Cases**		**Appearance**			**Viscosity Grade**			
#	**Base Oil**	**PPD wt%**	**PB wt%**	**PMA wt%**	**OCP wt%**	**KV 40**	**KV 100**	**VI**	**p.p.**	**VI**	**p.p.**	**Haze**	**Separ-ation**	**Overall**	**ISO VG**	**AGMA VG**	**SAE**	**SAE Gear**
1	Gr. II	.2	5	5		64.0	10.0	141	-42	1	B	No	No	Good	68	2	30	80
2		.2	5	10		74.3	12.1	160	-45			No	No	Good	68	2	30	85
3		.2	5	20		127.5	19.6	176	-30			No	No	Good			50	110
4	Gr. II	.2	10	5		81.6	12.5	151	-42	3	B	No	No	Good			30	85
5		.2	10	10		101.6	14.7	150	-33			No	No	Good	100	3	40	90
6		.2	10	20		132.9	18.7	159	-30			No	No	Good			50	110
7	Gr. II	.2	20	5		176.4	21.5	145	-33	4	A	No	No	Good			50	110
8		.2	20	10		221.0	25.2	144	-33			No	No	Good	220	5	60	140
9		.2	20	20		262.3	26.3	130	-33			No	No	Good				140
10	Gr. II	.2	5		5	77.8	11.6	142	-36	2	A	No	No	Good			30	85
11		.2	5		10	176.4	21.5	174	-33			No	No	Good			50	110
12		.2	5		20	324.0	38.7	170	-36			No	No	Good	320	6		190
13	Gr. II	.2	10		5	110.6	15.3	145	-36	1	C	No	No	Good			40	90
14		.2	10		10	174.1	30.9	152	-33			No	No	Good				140
15		.2	10		20	436.9	50.1	177	-30			No	No	Good	460	7		250
16	Gr. II	.2	20		5	232.2	28.0	157	-33	1	C	No	No	Good	220	5		140
17		.2	20		10	325.6	38.0	167	-27			No	No	Good	320	6		190
18		.2	20		20	763.7	75.1	177	-24			No	No	Good				
19	Gr. II	.2		5	5	62.8	10.6	159	-45	2	A	No	No	Good	68	2	30	85
20		.2		5	10	92.6	15.0	171	-42			No	No	Good	100	3	40	90
21		.2		5	20	104.0	16.2	168	-42			No	No	Good	100	3	40	90
22	Gr. II	.2		10	5	66.5	11.7	173	-45	1	D	No	No	Good	68	2	30	85
23		.2		10	10	127.7	19.7	176	-42			No	No	Good			50	110
24		.2		10	20	317.3	39.9	179	-33			No	No	Good	320	6		190
25	Gr. II	.2		20	5	133.7	20.2	174	-30	3	A	No	No	Good			50	110
26		.2		20	10	223.5	29.8	174	-27			Yes	No	Poor	220	5		140
27		.2		20	20	525.4	54.8	169	-27			Yes	Yes	Bad				
28	Gr. III	.2	5	5		36.9	7.3	167	-36	2	A	No	No	Good			20	
29		.2	5	10		46.2	9.3	189	-36			No	No	Good	46	1	30	80
30		.2	5	20		89.4	15.2	180	-33			No	No	Good			40	90
31	Gr. III	.2	10	5		56.6	9.8	160	-39	2	C	No	No	Good			30	80
32		.2	10	10		72.3	12.4	171	-33			No	No	Good	68	2	30	85
33		.2	10	20		167.5	23.3	168	-24			No	No	Good			60	110

34	Gr. III	.2	20	5		124.7	16.7	145	-36	1	B	No	No	Good			50	90
35		.2	20	10		138.5	18.3	148	-36			No	No	Good	150	4	50	110
36		.2	20	20		193.4	24.9	160	-27			No	No	Good			60	140
37	Gr. III	.2	5		5	51.5	9.5	171	-39	1	A	No	No	Good			30	80
38		.2	5		10	92.8	15.7	181	-42			No	No	Good	100	3	40	90
39		.2	5		20	213.5	30.4	185	-39			No	No	Good	220	5		140
40	Gr. III	.2	10		5	74.5	12.8	173	-39	2	A	No	No	Good	68	2	40	85
41		.2	10		10	132.8	19.7	170	-39			No	No	Good			50	110
42		.2	10		20	302.2	38.8	180	-42			No	No	Good	320	6		190
43	Gr. III	.2	20		5	153.1	21.0	161	-36	1	A	No	No	Good	150	4	50	110
44		.2	20		10	236.4	29.9	167	-36			No	No	Good	220	5		140
45		.2	20		20	557.4	61.2	181	-39			No	No	Good				250
46	Gr. III	.2		5	5	40.6	8.3	186	-42	2	B	No	No	Good			20	80
47		.2		5	10	66.9	12.8	195	-42			No	No	Good	68	2	40	85
48		.2		5	20	182.7	28.4	195	-42			No	No	Good				140
49	Gr. III	.2		10	5	50.0	10.7	211	-39	4	A	No	No	Good	46	1	30	85
50		.2		10	10	80.0	15.4	205	-39			No	No	Good			40	90
51		.2		10	20	194.3	29.8	195	-39			No	No	Good				140
52	Gr. III	.2		20	5	82.0	15.8	206	-33	4	A	No	No	Good			40	90
53		.2		20	10	120.6	18.6	173	-33			Yes	Yes	Bad				
54		.2		20	20	216.2	28.8	172	-33			Yes	Yes	Bad				
55	PAO		5	5		51.9	9.0	155	N/A	--	--	Yes	Yes	Bad				
56			5	10		59.2	10.9	178	N/A			Yes	Yes	Bad				
57			5	20		N/A	18.6	N/A	N/A			Yes	Yes	Bad				
58	PAO		10	5		75.7	11.2	139	N/A	--	--	Yes	Yes	Bad				
59			10	10		82.0	12.7	154	N/A			Yes	Yes	Bad				
60			10	20		N/A	26.2	N/A	N/A			Yes	Yes	Bad				
61	PAO		20	5		154.8	20.2	151	N/A	--	--	Yes	Yes	Bad				
62			20	10		205.5	24.6	149	N/A			Yes	Yes	Bad				
63			20	20		224.7	26.7	153	N/A			Yes	Yes	Bad				
64	PAO		5		5	73.3	12.0	160	-51	1	C	No	No	Good	68	2	30	85
65			5		10	114.4	17.4	168	-50			No	No	Good			50	110
66			5		20	309.7	42.4	194	-38			No	No	Good	320	6		190
67	PAO		10		5	105.3	15.5	156	-50	1	C	No	No	Good	100	3	40	90
68			10		10	165.2	22.3	162	-46			No	No	Good			60	110
69			10		20	395.2	47.1	179	-42			No	No	Good				190
70	PAO		20		5	217.4	26.2	154	-46	2	B	No	No	Good	220	5		140
71			20		10	327.2	37.8	165	-48			No	No	Good	320	6		190
72			20		20	423.9	44.8	162	-40			No	No	Good	460	7		190
73	PAO			5	5	61.2	10.8	169	-52	1	B	Yes	No	Poor			30	85
74				5	10	91.5	15.1	174	-52			Yes	No	Poor	100	3	40	90
75				5	20	246.2	33.5	182	-44			Yes	No	Poor				190
76	PAO			10	5	77.1	13.3	176	-51	1	--	Yes	No	Poor			40	90
77				10	10	105.1	17.5	184	-50			Yes	No	Poor	100	3	50	110
78				10	20	N/A	33.9	N/A	N/A			Yes	Yes	Bad				
79	PAO			20	5	N/A	19.9	N/A	N/A	--	--	Yes	Yes	Bad				
80				20	10	412.7	29.8	101	N/A			Yes	Yes	Bad				
81				20	20	786.6	47.3	106	N/A			Yes	Yes	Bad				

Table A-2: Reorganized Table A-1 to show ‘constant PMA or OCP/varying PB’ and ‘constant OCP/varying PMA’ trends

	Formula					Viscometrics			Low T	Cases		Appearance			Viscosity Grade			
#	Base Oil	PPD wt%	PB wt%	PMA wt%	OCP wt%	KV 40	KV 100	VI	p.p.	VI	p.p.	Haze	Separ-ation	Overall	ISO VG	AGMA VG	SAE	SAE Gear
1	Gr. II	.2	5	5		64.0	10.0	141	-42	2	B	No	No	Good	68	2	30	80
4		.2	10	5		81.6	12.5	151	-42			No	No	Good			30	85
7		.2	20	5		176.4	21.5	145	-33			No	No	Good			50	110
2	Gr. II	.2	5	10		74.3	12.1	160	-45	4	A	No	No	Good	68	2	30	85
5		.2	10	10		101.6	14.7	150	-33			No	No	Good	100	3	40	90
8		.2	20	10		221.0	25.2	144	-33			No	No	Good	220	5	60	140
3	Gr. II	.2	5	20		127.5	19.6	176	-30	4	A	No	No	Good			50	110
6		.2	10	20		132.9	18.7	159	-30			No	No	Good			50	110
9		.2	20	20		262.3	26.3	130	-33			No	No	Good				140
28	Gr. III	.2	5	5		36.9	7.3	167	-36	4	A	No	No	Good			20	
31		.2	10	5		56.6	9.8	160	-39			No	No	Good			30	80
34		.2	20	5		124.7	16.7	145	-36			No	No	Good			50	90
29	Gr. III	.2	5	10		46.2	9.3	189	-36	4	A	No	No	Good	46	1	30	80
32		.2	10	10		72.3	12.4	171	-33			No	No	Good	68	2	30	85
35		.2	20	10		138.5	18.3	148	-36			No	No	Good	150	4	50	110
30	Gr. III	.2	5	20		89.4	15.2	180	-33	4	C	No	No	Good			40	90
33		.2	10	20		167.5	23.3	168	-24			No	No	Good			60	110
36		.2	20	20		193.4	24.9	160	-27			No	No	Good			60	140
55	PAO		5	5		51.9	9.0	155	N/A	--	--	Yes	Yes	Bad				
58			10	5		75.7	11.2	139	N/A			Yes	Yes	Bad				
61			20	5		154.8	20.2	151	N/A			Yes	Yes	Bad				
56	PAO		5	10		59.2	10.9	178	N/A	--	--	Yes	Yes	Bad				
59			10	10		82.0	12.7	154	N/A			Yes	Yes	Bad				
62			20	10		205.5	24.6	149	N/A			Yes	Yes	Bad				
57	PAO		5	20		N/A	18.6	N/A	N/A	--	--	Yes	Yes	Bad				
60			10	20		N/A	26.2	N/A	N/A			Yes	Yes	Bad				
63			20	20		224.7	26.7	153	N/A			Yes	Yes	Bad				
10	Gr. II	.2	5		5	77.8	11.6	142	-36	1	B	No	No	Good			30	85
13		.2	10		5	110.6	15.3	145	-36			No	No	Good			40	90
16		.2	20		5	232.2	28.0	157	-33			No	No	Good	220	5		140
11	Gr. II	.2	5		10	176.4	21.5	174	-33	4	B	No	No	Good			50	110
14		.2	10		10	174.1	30.9	152	-33			No	No	Good				140
17		.2	20		10	325.6	38.0	167	-27			No	No	Good	320	6		190
12	Gr. II	.2	5		20	324.0	38.7	170	-36	2	C	No	No	Good	320	6		190
15		.2	10		20	436.9	50.1	177	-30			No	No	Good	460	7		250
18		.2	20		20	763.7	75.1	177	-24			No	No	Good				
37	Gr. III	.2	5		5	51.5	9.5	171	-39	4	A	No	No	Good			30	80
40		.2	10		5	74.5	12.8	173	-39			No	No	Good	68	2	40	85
43		.2	20		5	153.1	21.0	161	-36			No	No	Good	150	4	50	110
38	Gr. III	.2	5		10	92.8	15.7	181	-42	4	C	No	No	Good	100	3	40	90
41		.2	10		10	132.8	19.7	170	-39			No	No	Good			50	110
44		.2	20		10	236.4	29.9	167	-36			No	No	Good	220	5		140
39	Gr. III	.2	5		20	213.5	30.4	185	-39	3	A	No	No	Good	220	5		140
42		.2	10		20	302.2	38.8	180	-42			No	No	Good	320	6		190
45		.2	20		20	557.4	61.2	181	-39			No	No	Good				250
64	PAO		5		5	73.3	12.0	160	-51	4	B	No	No	Good	68	2	30	85
67			10		5	105.3	15.5	156	-50			No	No	Good	100	3	40	90
70			20		5	217.4	26.2	154	-46			No	No	Good	220	5		140
65	PAO		5		10	114.4	17.4	168	-50	3	A	No	No	Good			50	110
68			10		10	165.2	22.3	162	-46			No	No	Good			60	110
71			20		10	327.2	37.8	165	-48			No	No	Good	320	6		190
66	PAO		5		20	309.7	42.4	194	-38	4	A	No	No	Good	320	6		190
69			10		20	395.2	47.1	179	-42			No	No	Good				190
72			20		20	423.9	44.8	162	-40			No	No	Good	460	7		190
19	Gr. II	.2		5	5	62.8	10.6	159	-45	2	B	No	No	Good	68	2	30	85
22		.2		10	5	66.5	11.7	173	-45			No	No	Good	68	2	30	85

25		.2	20	5	133.7	20.2	174	-30			No	No	Good			50	110
20	Gr. II	.2	5	10	92.6	15.0	171	-42	3	B	No	No	Good	100	3	40	90
23		.2	10	10	127.7	19.7	176	-42			No	No	Good			50	110
26		.2	20	10	223.5	29.8	174	-27			Yes	No	Poor	220	5		140
21	Gr. II	.2	5	20	104.0	16.2	168	-42	2	C	No	No	Good	100	3	40	90
24		.2	10	20	317.3	39.9	179	-33			No	No	Good	320	6		190
27		.2	20	20	525.4	54.8	169	-27			Yes	Yes	Bad				
46	Gr. III	.2	5	5	40.6	8.3	186	-42	2	C	No	No	Good			20	80
49		.2	10	5	50.0	10.7	211	-39			No	No	Good	46	1	30	85
52		.2	20	5	82.0	15.8	206	-33			No	No	Good			40	90
47	Gr. III	.2	5	10	66.9	12.8	195	-42	2	C	No	No	Good	68	2	40	85
50		.2	10	10	80.0	15.4	205	-39			No	No	Good			40	90
53		.2	20	10	120.6	18.6	173	-33			Yes	Yes	Bad				
48	Gr. III	.2	5	20	182.7	28.4	195	-42	3	C	No	No	Good				140
51		.2	10	20	194.3	29.8	195	-39			No	No	Good				140
54		.2	20	20	216.2	28.8	172	-33			Yes	Yes	Bad				
73	PAO		5	5	61.2	10.8	169	-52	--	--	Yes	No	Poor			30	85
76			10	5	77.1	13.3	176	-51			Yes	No	Poor			40	90
79			20	5	N/A	19.9	N/A	N/A			Yes	Yes	Bad				
74	PAO		5	10	91.5	15.1	174	-52	--	--	Yes	No	Poor	100	3	40	90
77			10	10	105.1	17.5	184	-50			Yes	No	Poor	100	3	50	110
80			20	10	412.7	29.8	101	N/A			Yes	Yes	Bad				
75	PAO		5	20	246.2	33.5	182	-44	--	--	Yes	No	Poor				190
78			10	20	N/A	33.9	N/A	N/A			Yes	Yes	Bad				
81			20	20	786.6	47.3	106	N/A			Yes	Yes	Bad				

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Study on the application of DPU-B prefabricated biuret thickener

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Abstract:
In this paper, the prefabrication of biuret thickener was studied with isocyanate and organic amine as raw materials. The DPU-B type biuret thickener was prepared by the reaction of isocyanate and mixed amine in different solvents. The results of industrial amplification production show that polyurea grease produced by this thickener has good thermal stability, colloidal stability and water resistance, especially with outstanding mechanical stability and thickening ability. At the same time, the refining temperature is only 120 ℃. It can completely replace the traditional method to prepare polyurea grease.

Keyword: Prefabrication; Biuret; Thickener; Grease.

1. Introduction

As a kind of high dropping point grease, polyurea grease has good oxidation stability because of no metal ions, as well as good thermal stability and long bearing life. It has been widely used in industrial fields such as electrical, metallurgy, food, papermaking, automobile and aircraft.

It is noteworthy that the vigorous development of new energy vehicles in recent years led to a sharp rise in the price of lithium hydroxide, limiting the promotion and application of lithium-based grease especially lithium complex grease. As a result, the polyurea grease has attracted more and more attention to the manufacturers and users.

The main materials for preparing polyurea greases are base oil, isocyanate and organic amine. Different types of organic amines and isocyanates can be used to synthesize different polyurea greases. According to different structures, polyurea grease can be divided into biuret grease and tetraurea grease. The common production methods of biuret grease include one-step method and prefabrication method. One-step method refers to the preparation of biuret grease by the reaction of isocyanates and amines in base oil. Prefabrication is a method that the biuret thickening agent is prepared in advance, then the prefabricated thickener is expanded in the base oil to prepare the biuret grease.

Because of the strong toxicity, volatility and corrosiveness of isocyanates and some organic amines, the safety and protection requirements in the production of polyurea grease are very strict. The transport and storage of isocyanates and organic amines are also regulated by the relevant laws and regulations of various countries. And the polymerization of some isocyanates requires that they must be stored at lowtemperature. Therefore, if the production of polyurea grease is not up to a certain scale, the cost of environmental protection and safety will be very high. Meanwhile, the control of hazardous chemicals and the increasing demand for environmental protection in many countries restrict the production of polyurea grease in some enterprises. As an alternative, the prefabrication method to produce biuret grease is not only convenient and fast, but also does not involve the use, transportation and storage of toxic chemicals. And it is more safe and environmentally friendly.

At present, commercially available polyurea greases thickened by prefabricated biuret thickeners present some problems such as high thickener dosage, poor mechanical stability, high swelling temperature and high selling prices. In this paper, formula-based adjustment, solvent screening and process improvement have been adopted to prepare urea-based prefabricated thickener, named DPU-B prefabricated polyurea thickener (abbreviated as DPU-B),with excellent performance and to solve the existing problems. This paper also studies the effect of different base oils on the performance of DPU-B greases.

2. The preparation of DPU-B

2.1 Raw materials

There are many varieties of raw materials to be chosen for preparation of prefabricated biuret thickener. The thickener is usually prepared by the reaction of two molecule monoamine and one molecular diisocyanate. The raw materials of DPU-B are diphenylmethane-4, 4'-diisocyanate (MDI) and mixed amine of aliphatic amine A and aromatic amine B. And the solvent is a complex organic solvent C.

2.2 Preparation process of DPU-B

The brief flow chart of preparation process of DPU-B is shown in Figure 1.

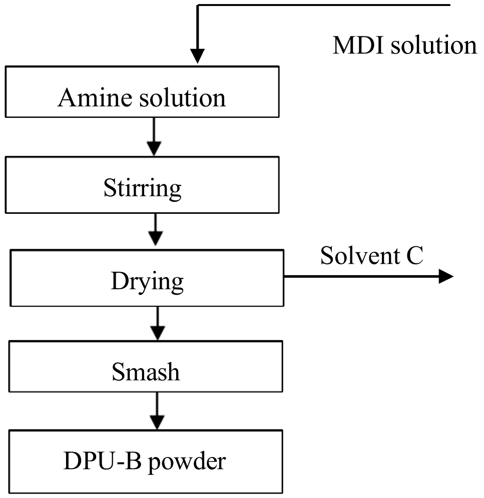

Figure 1 Flow chart of preparation process of DPU-B

3.Experiment

The greases were prepared with DPU-B as thickener and several selected base oils. And the consistency, thermal stability, colloidal stability, mechanical stability and water resistance of the prepared greases were studied.

3.1 Materials

3.1.1 DPU-B

DPU-B is white powder prepared by drying and smash process after the reaction of MDI and mixed amines of aliphatic amine A and aromatic amine B.

3.1.2 Base oils

In order to investigate the application performance of DPU-B, we choose several common types of base oils, including mineral oil, ester oil and polyalphaolefin. The main physicochemical indexes of base oils are shown in Table 1.

Table1 The main physicochemical indexes of base oils

Item	500N	KN401 0	150BS	PA010	PA040	Tridecyl trimellitate	Dipentaerythritol ester	Test method
Kinematic viscosity (100℃)/$(mm^2 \cdot s^{-1})$	10.42	9.927	32.09	10.29	40.26	9.536	18.81	GB/T 265
Kinematic viscosity (40℃)/$(mm^2 \cdot s^{-1})$	90.64	132.7	553.3	62.49	405．8	75.25	212.4	GB/T 265
Viscosity index	96	21	87	153	149	104	93	GB/T 2541
Flash point(opening)/℃	255	220	281	259	289	279	286	GB/T 3536
Condensation point/℃	-25	-25	-20	-48	-45	-35	-30	GB/T 510

3.1.3 Preparation process of biuret grease

The preparation process of biuret grease thickened by DPU-B(abbreviated as DPU-B grease) is as follow: Firstly, 8wt% DPU-B and 92wt% base oil were added into a beaker (or stirred tank). Then the mixture were stirred and heated to 120 ℃ and keep the temperature for 3 hours. After cooling to room temperature, the above product was ground twice with a three-roll mill. Preparation process was shown in Figure 2.

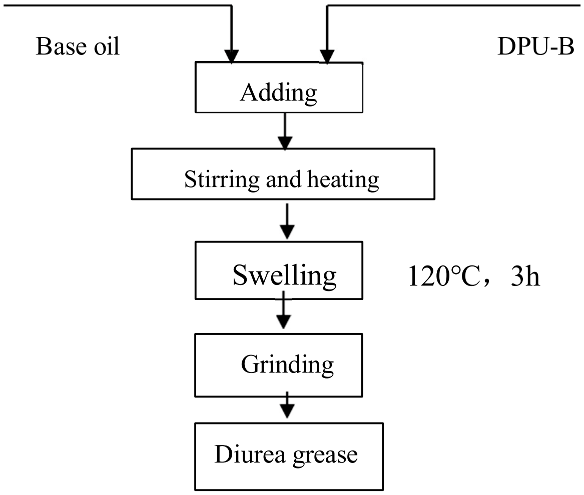

Figure 2 Preparation process of DPU-B grease

3.2 Test methods

3.2.1 Consistency

The consistency is tested according to the ASTM D217 method.

3.2.2 Thermal stability

The dropping point is tested according to the ASTM D2265 method. The evaporation loss is tested according to the ASTM D2595 method.

3.2.3 Colloidal stability

The oil separation (conical sieve method) is tested according to the ASTM D6184 method.

3.2.4 Mechanical stability

The rate of cone penetration change is tested according to the ASTM D217 method. The roll stability is tested according to the ASTM D1831 method. The leakage tendencies of greases are tested according to the ASTM D1263 method.

3.2.5 Water resistance

The water washout is tested according to the ASTM D1264 method. The roll stability with water is tested according to the ASTM D1831 method.

4.Results and discussion

4.1 Consistency

The worked cone penetrations of greases thickened by 8wt% DPU-B with different base oils are shown in Figure 2. It can be seen that the thickening ability of DPU-B to different base oils is in turn: mineral oil >PAO> ester oil.

Figure 2 The worked cone penetration of greases

Item	500N	KN4010	150BS	PA010	PA040	Tridecyl trimellitate	Dipentaerythritol ester
Worked cone penetration，0.1mm	288	235	231	300	292	337	321

4.2 Thermal stability

Figure 3 shows the dropping point and evaporation loss of DPU-B greases with different base oils. The DPU-B greases show good thermal stability with the dropping point above 270 ℃ and evaporation loss less than 0.5wt% at 180 ℃. When the base oil is PAO or ester oil, the evaporation loss of the greases can be less than 0.1wt%.

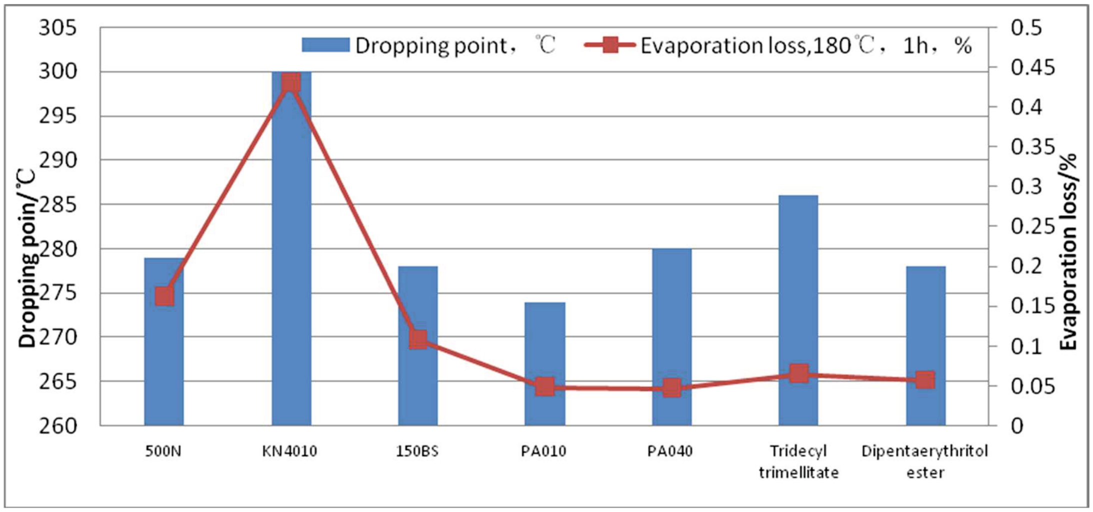

Figure 3 The dropping point and evaporation loss of DPU-B greases

3.3 Colloidal stability

As shown in Figure 4, the oil separation (conical sieve method) of DPU-B greases are within 5wt% which indicated the good colloidal stability of DPU-B greases. There is a significant correlation between oil separation and consistency of the DPU-B grease. And the smaller the penetration is, the smaller the oil separation is.

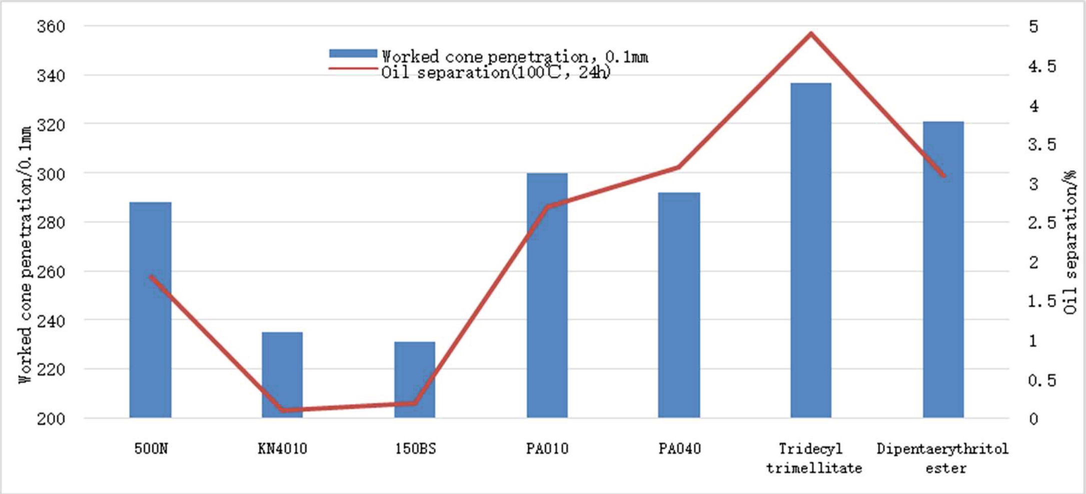

Figure 4 The worked cone penetration and oil separation of DPU-B greases

3.4 Mechanical stability

It can be seen from the rate of cone penetration change, roll stability and leakage tendency of DPU-B greases shown in table 3 that the DPU-B greases have excellent mechanical stability. The rate of cone penetration change of DPU-B greases are less than 20% except the grease with 150BS as base oil. And the rate of roll stability change of DPU-B greases are less than 10% while the leakage of DPU-B greases are all less than 2g.

Table 3 Mechanical stability of DPU-B greases

Item	500N	KN4010	150BS	PA010	PA040	Tridecyl trimellitate	Dipentaerythritol ester
Rate of cone penetration change，%	9.03	1.70	23.81	19.00	16.44	16.32	19.00
Roll stability,%	3.82	5.11	7.79	7.00	7.19	8.01	6.54
Leakage tendency，g	0.8	0.3	0.5	1.7	0.9	1.8	1.6

3.5 Water resistance

Water resistance is quantified by the amount of water washout and the chang rate of roll stability with water . It can be seen from the table 4 that water washout of DPU-B greases are within 1wt%. The rate of roll stability change indicates that the greases still maintain stable colloidal structure with addition of 20wt% water. The rate of cone penetration change does not exceed 10% before and after shearing. The above experiments show that the DPU-B greases have good water resistance.

Table 4 The water resistance of DPU-B greases

Item	500N	KN4010	150BS	PA010	PA040	Tridecyl trimellitate	Dipentaerythritol ester
Water washout (38°C ， 1h)	0.52	0.35	0.13	0.48	0.39	0.5	0.75
Roll stability with water,%	5.90	6.81	9.09	8.33	8.56	9.50	8.41

5.Conclusion

(1) Preparation of polyurea greases with prefabricated thickeners can effectively avoid the use, storage and transportation of toxic chemicals. Therefore, it is safe, environmentally friendly and convenient.

(2) The DPU-B prefabricated biuret thickener which prepared by special design and process makes the refining temperature reduce from traditional 160°C～180°C to 120°C, saving time and energy consumption.

(3) A variety of base oils, such as mineral oil, PAO and ester oil can be successfully thickened by relatively low content DPU-B prefabricated biuret thickener for the preparation of biuret greases. And the DPU-B greases have good thermal stability, colloidal stability, mechanical stability and water resistance.

Micronized PTFE powders - Role in High temperature and High load applications of FoodGrade lubricants.

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ABSTRACT

Poly urea greases are known for their unusual high temperature industrial grease application areas. Also current trends of availability issues, of Lithium hydroxide also makes poly urea greases in demand as an alternate source of thickener for future. On other hand, poly urea greases were associated with some disadvantages like poor shear stability, storage hardening, pump ability, limited rust and extreme pressure-anti wear characteristics. Poly urea grease with PTFE combination tends to have high temperature performance, inherent anti oxidative properties and can offer high load-bearing capacity. A study on poly urea grease with micronized PTFE powder combinations revealed that the combination suitable for high temperature and high load applications. Further the combination proved improvement in rust preventive and anti wear characteristics highly suitable for food grade high temperature and high load applications.

Keywords- Polyurea grease, PTFE, food grade grease, high temperature.

1. INTRODUCTION

The invention and development of Polyurea thickened greases is one of the most important advances in grease technology since the end of the Second World War. The first reported poly urea grease was made with aryl substituted urea during 1954. The technology was developed in Japan. Attempt at that time was made to develop fibrous poly urea grease primarily as a replacement for the barium greases which have disposal problems related to barium toxicity. These poly urea based greases are non-soap based where thickener moieties do not contain any metallic elements rendering the grease ash less [1]. Poly urea thickened greases were developed around same time as lithium complex greases, but owing predominantly to poor stability, they had not penetrated the market to the same degree. Further development of technology then lead to a new series of poly urea that were susceptible to age hardening. Modern polyurea grease has overcome both of these problems and are now gaining market share.

Another distinction of these greases over soap based greases is that the molecular structure of these greases is potentially dominated by hydrogen bonding whereas in the case of soap base greases bonding is primarily dominated by weaker Vander Waal forces. This provides poly urea greases better structural stability at elevated temperatures and a preferred choice for fill for life applications over metallic based counterparts. In Japan, urea greases were re-evaluated in 1980s where it still occupies maximum percentage of the grease market share. [2, 3]

Poly urea greases are at present produced in situ by reaction of amines with isocyanates in the base oil. Handling isocyanates causes considerable industrial problems to the grease producers. Reaction of isocyanates with amines to form urea is shown in figure-1. In spite of the industrial advantages in relation to lubricating greases based on metal soaps; this state of affairs has an adverse effect on more widespread use of polyurea greases. However, recently grease manufacturers have simplified the process by use of commercially available poly urea which is prepared separately, pulverized and dispersed in the lubricating oil to produce the grease. [4]

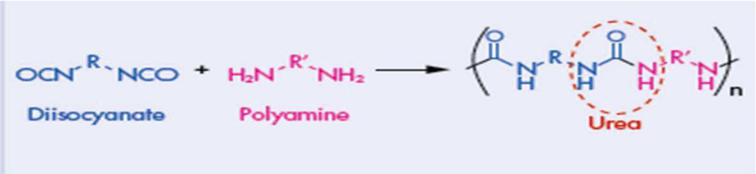

Figure-1: Poly Urea formation

The current trend of availability issues of Lithium hydroxide now makes poly urea to come in demand as an alternate source of thickener for future. NLGI- grease market survey indicates thatpoly urea greases constitute about 4 % of the total worldwide grease volumes whereas in North America it is about 5.7 %. Poly urea greases are most favoured in Japan, constituting about 25 %of the volume and their market share is growing [5]. Industrial application is expected to play a key role in fuelling the growth of the overall high temperature grease market owing to the rapid industrialization in the Asia-Pacific region. With the growth and advancement in technology, the demand for such greases has been increased. This relates to the development of compact, high speed, high load, high operating temperature and low maintenance operations. In modern practice, it has become increasingly important that grease compositions are able to provide adequate lubrication at high temperatures, eg 175-235°C, or higher. It is also essential that the thickener impart a high degree of mechanical stability to the grease formulation operating at such high temperatures. [4]. Distribution of end use application of polyurea grease is shown in figure- 2.

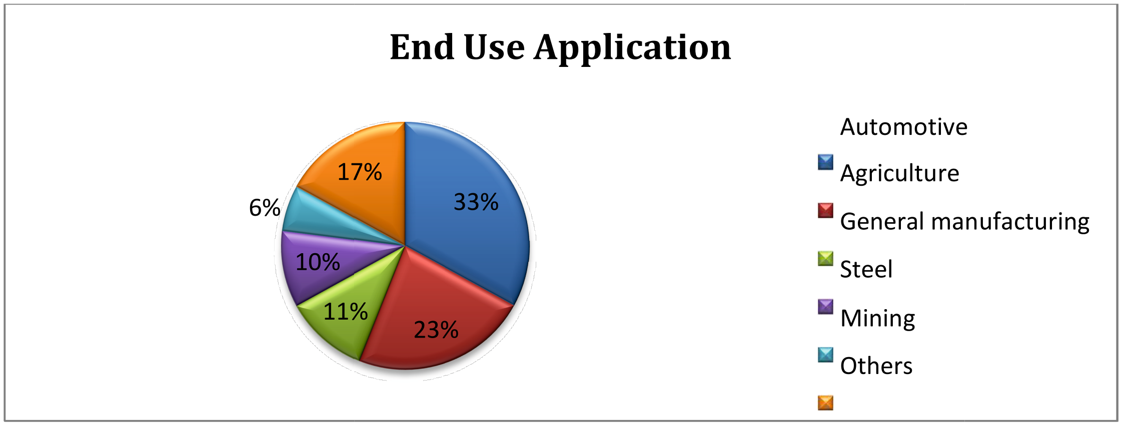

Figure-2: Poly urea grease end application distribution

With advancement in formulation technology to make them user friendly, polyurea greases gained importance in steel plants, automotive wheel bearings, constant velocity joints, electrical instrumentation and auxiliary equipment bearings and also as food grade greases etc. Because of wide range of applications and significant amount of research in this area, the volumes of these greases are steadily growing [4].

In steel mills, by the process of continuous casting (CC), the refined molten steel from blast furnace is solidified into an intermediate product called the slab. This slab proceeds to rolling mill for finishing. The bearings which support the slab are under high load and are exposed to elevated temperatures with low rotational speed. For such application grease with high viscosity base oil must be selected to resist corrosion and aid in sealing as a result of continuous exposure to secondary cooling water spray and hard debris contamination. For continuous casters, themost widely used lubrication method is the centralized grease distribution system. These systems pump a relatively small amount of grease at frequent intervals to the bearing. This frequent cycle keeps the bearing full with fresh grease while also purging old grease and contaminants. Good flow properties are essential for grease to be used in steel plant applications and polyurea grease possess excellent pumpability characteristics. The thixotropic nature of urea based greases provides an excellent sealing barrier to prevent water and abrasive foreign particles from entering the bearings. In addition, the high dropping point (>260°C) and excellent oxidative stability offered by urea thickened greases provide extended high temperature capability, greatly enhancing high temperature bearing life [2].

Figure-3: Continuous casting process

The food processing industry in India has been identified as a priority sector for growth in coming years. In fact, the Government of India has adopted a major policy decision for commercializing agriculture and developing food processing, preservation and packaging sectors, according to a 2010 report by TEDO (Technology Exports Development Organization). As the food processing industry is dynamic and fast -paced, the equipment sector is also gaining its importance. The need for high volumes, high productivity and high quality has led to increasing demand for automation in the food industry [7]. Food-grade greases are used in various food-processing equipment and other industrial equipment applications. These include plain and rolling element bearings, joints, linkages and slides, centralized lubrication systems and enclosed gearboxes. Food grade greases play role in following functions:

- Resisting degradation from food products, chemicals, water and steam.
- Exhibiting a neutral behaviour when in contact with elastomers and plastics.
- Being physiologically inert, odour less, tasteless, nontoxic and harmless.

Poly urea grease acts as multi-purpose and high temperature food grade grease designed specifically for wide range of applications within the food industry. Food grade greases.

Figure-4: Food processing industry

Figure-5: Corn crop cutter

Polyureas grease shows, poor high load bearing property. Thus, addition of extreme pressure additive is important to improve its overall performance. More productive, long run and zero maintenance equipments need is growing requiring demanding upgraded performances in greases.

Extreme Pressure Additives:

To upgrade the base grease performance Extreme pressure (EP) additives are addedto lubricants with an need to improve the load bearing capacity of greases. EP additive typically functions by adsorbing on the metal surface to form a film that will reduce metal-to-metal contact. Some of the EP additives are Inactive sulfurized fat (1-2%), Active sulfurized fat(0.6-1%), Active sulfur hydrocarbon (0.4-0.6%), Zinc dialkyl dithiophosphates (2-4%), Poly-sulphides(2-4%), Molybdenum compounds(3-5%), Poly tetra fluoro ethylene (PTFE) (4-5%) etc The durability and performance of the grease depends upon the additives added. The additive package used here includes PTFE (Poly Tetra-flouro ethylene) for performing under extreme pressure conditions PTFE acts a food grade additive as it is highly inert and non-reactive with all chemicals. PTFE micronized powders are approved as Food grade EP additives in such applications.

PTFE micronized powder

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 electro-negativity of fluorine. PTFE has very lowest coefficients of friction..

Micronized Poly tetra fluoro ethylene (PTFE), also known as PTFE micro powder, is used where higher surface lubrication and anti-blocking properties are required. Micronized PTFE is prepared by the utilization of virgin PTFE resin or recycled PTFE.

Fluoro additives, 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 fluoro additives is by electron beam treatment.. Both methods allow the consumption of sintered and un sintered PTFE, which are produced during the various stages of processing. After the irradiation, the PTFE resin is ground into micro powders.

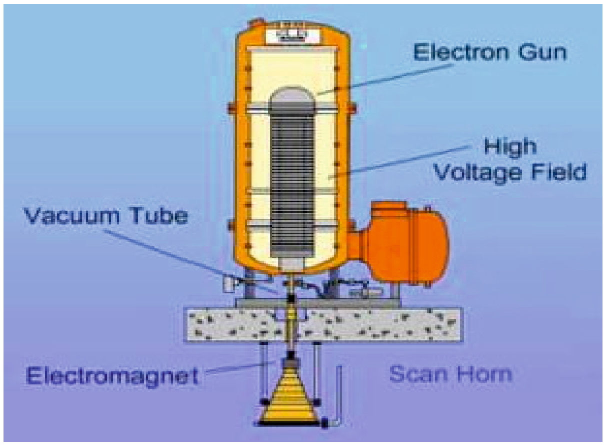

Figure-6: EBM Treatment setup

Figure-7: Apar PTFE powder210 grade

PTFE Micro powder of APAR 210 grade is manufactured by radiation degradation. APAR 210 PTFE micronized powder have uniform particle size distribution with average particle size of 5-10 microns [6].

2.MATERIAL AND METHODS

2.1 Material

An NLGI grade- 2, synthetic oil based Polyurea grease is used as the starting material.

The PTFE powder used is developed by advanced processing technology. Micronized PTFE is prepared by the utilization of high molecular weight PTFE components. PTFE Micro powder of APAR grade is manufactured by radiation degradation. PTFE powder of 10-6 µm (Grade 210) is used for experimentation.

To attain high load properties of grease we have selected the EP additives like

- Sulphur phosphorus based EP additives
- Molybdenum disulphide
- Micronized PTFE powder.

Plain Polyurea grease has been compared with the grease samples made by addition of different performance additives in sample Experiments. Product performance attributes like oil-separation at 100°C and at 40°C, leakage tendency, its wear Scar and extreme pressure characteristics where measured to attain the best combination. The additives were blended with grease using Mechanical Grease Worker. 200 strokes were given so as to ensure uniform mixing.

Table-1: plain Polyurea Grease attributes

TEST	TEST METHOD	TYPICAL VALUE
NLGI Grade	-	2
Appearance	Visual	Smooth, Homogeneous
Color	Visual	Pale Yellow
Penetration, 60 strokes	ASTM D-217	290
After 100,000 strokes (difference in units)	ASTM D-217	20
Drop point, deg C	ASTM D-2265	265
Copper Strip Corrosion	ASTM D-4048	1b
Water washout @ 80 deg C, % loss	ASTM D-1264	3.2%
Four ball Weld Load, Kgs.	IP 239	200

: List of samples poly urea grease with EP Additives is presented in Table 2..

Table 2: Samples used in the current study : Base poly greases and with EP Additives

SAMPLE NAME	SAMPLE	APPEARANCE
SAMPLE 1	Plain Polyurea grease	
SAMPLE 1+ 4.5% PTFE	Polyurea grease+4.5%PTFE	
SAMPLE 1+ Sulphur phosphorous additive 3%	Plain Poly urea grease	
SAMPLE 1 + 4.5% Moly	Polyurea grease+4.5%Molybdenum Disulphide	

In the current study, the effect of EP additive concentration on Weld load characteristics as per IP 239 with a target of 500 Kg minimum was optimized. . Further the optimized formulations were evaluated for various performance parameters such as Oil separation, heat stability, wear scar and weld load properties. The details are given in the following:

2.2 EXPERIMENTAL METHODS

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

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

2.2.2 Oil Separation ASTM D-1742 (Storage Stability)

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

2.2.3 Wear preventive and extreme pressure characteristics: Fourball tribo-tester

The purpose of the four ball tribo-tester is to measure the anti-wear (AW) and extreme pressure (EP) properties of lubricant oil and grease. The test was conducted using a common ball bearing with a diameter of 12.7 mm. A rotating ball bearing with a point of contact interface against three stationary ball bearings was immersed in the lubricant under a certain load. The parameters, such as normal load, speed of rotation, and temperature, were adjusted according to ASTM standards for the machine.

Wear preventive characteristics ASTM D 2266
The test measures the ability of grease to resist wear in sliding steel on steel contact and measures the Wear scar diameter.

Extreme Pressure characteristics IP 239

3. EXPERIMENTAL RESULTS

3.1 Oil separation Results (Storage and heat stability)

Table-3: Storage Stability results (ASTM D1742)

Sr. No.	SAMPLE	Storage Stability ASTM D 1742 (% of oil separated)	% Reduction in oil separation
1.	Sample 1	1.04	-
2.	Sample 1 + 4.5% PTFE	0.64	38
3.	Sample 1 + 3% S-P additive	0.88	15
4.	Sample 1 + 4.5% Moly	0.80	23

Table-4: Heat Stability results (ASTM D6184)

Sr. No.	SAMPLE	Heat stability test ASTM D -6184 (% of oil separated)	% Reduction in oil separation
1.	Sample 1	3.37	-
2.	Sample 1 + 4.5% PTFE	2.36	24
3.	Sample 1 + 3% S-P based additive	2.8	17
4.	Sample 1 + 4.5% Moly	2.76	18

Remarks: Addition of PTFE to poly urea grease showed improvement in preventing oil separation in storage condition as well as under elevated temperature condition.

3.2 Extreme pressure and Anti wear results.

Table-5: Extreme pressure and anti wear results by ASTM methods.

Sr. No.	SAMPLE	Wear Scar ASTM D 2266(mm)	Weld Load IP 239 (kg-Pass)
1.	Sample 1	0.6027	200
2.	Sample 1 +4.5% PTFE	0.5880	620
3.	Sample 1 + 3 % S-P based additive	0.6011	420
4.	Sample 1 + 4.5% Moly	0.6027	500

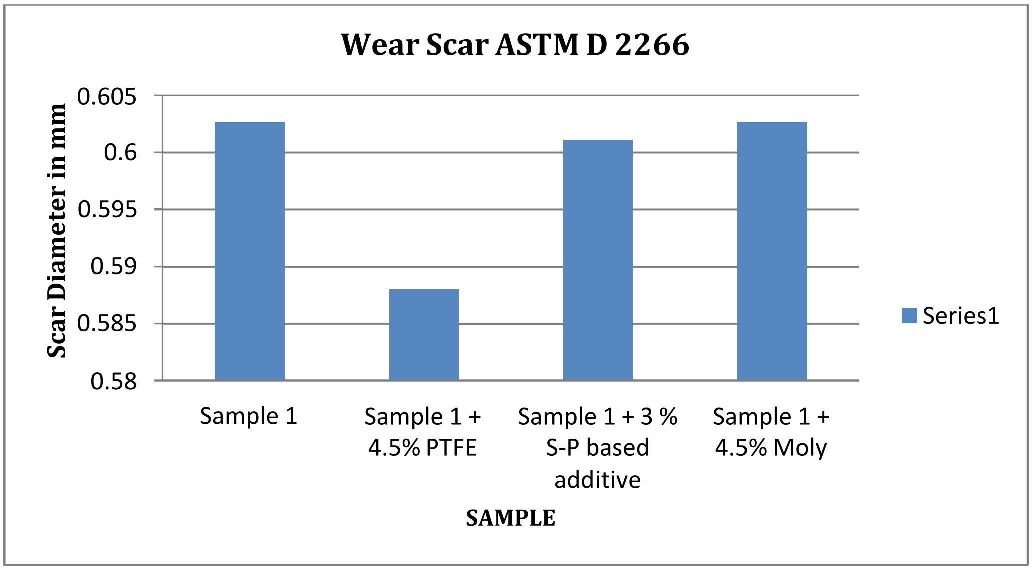

Figure-6: Graph showing wear scar diameters (ASTM D2266) of base grease sample and with added EP additive

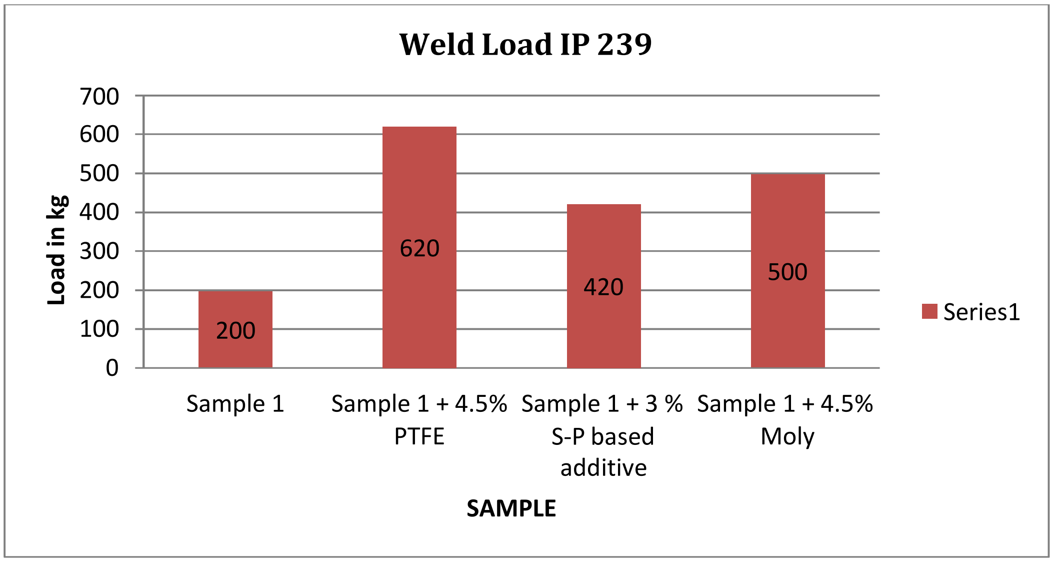

Figure-7: Graph showing weld load passing weight of base grease sample and with added EP additives

Remarks: Addition of PTFE alone to polyurea grease showed high weld load capacity and lower scar seizure as compared to molybdenum disulphide and SP added grease.

3.3 Effect of high temperature on grease

All the grease samples mentioned in Table-6 were exposed to 200^{0}C temperature in a muffle furnace for 2 hours. These samples were then tested for extreme pressure characteristics (IP 239).

Table-6: Weld load results (IP 239) before and after grease exposure to heat

Sr. No.	SAMPLE	Weld Load IP 239 (kg-Pass)- Before exposing to 200^0C	Weld Load IP 239 (kg-Pass)- After exposing to 200^0C
1.	Sample 1	200	200
2.	Sample 1 + 4.5% PTFE	620	620
3.	Sample 1 + 3 % S-P based additive	420	400
4.	Sample 1 + 4.5% Moly	500	500

Remarks: No remarkable change in weld load parameter noticed exposed to high temperature.

4. RESULTS AND DISCUSSION:

Table-7: Final result showing parameters of base poly urea grease and poly urea grease with added PTFE

Sr. No.	**Parameters**	**Test Method**	**Sample 1**	**Sample 1 + 4.5 % PTFE**
1	Appearance	Visual	Shiny and Smooth uniform layer	Smooth uniform layer
2	Color	Visual	Pale Yellow	Pale Yellow
3	Cone Penetration	ASTM D217 (Unworked)	290	282
4	After 100,000 strokes (difference in units)	ASTM D-217	20	18
5	NLGI Grade	-	2	2
6	Drop point, °C	ASTM D566	265	265
7	Heat stability, @ 100°C for 30Hrs, % of oil separated	ASTM D6148	3.37	2.56
8	Storage stability, @40°C for 42Hrs, % of oil separated	ASTM D1742	1.04	0.64
9	Weld load, Kg	IP 239	200(pass)	620(pass)
10	Wear Scare, mm	ASTM D2266	0.6027 mm	0.5880 mm
11	Salt spray test- 320 HOURS	ASTM B 117	NO STAINS	NO STAINS

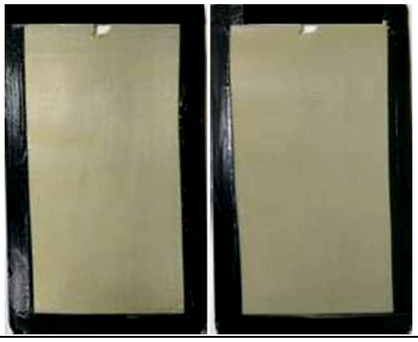

Figure-8: Initial Images: 0 Hours (Left: Sample 1; Right: Sample 1 + 4.5% PTFE)

Figure-9: Final Images: 240 Hours (Left: Sample 1; Right: Sample 1 + 4.5% PTFE)

4.1 : PTFE micronized waxes as EP additives in Polyurea grease improves the EP properties substantially to meet the heavy duty/high load applications of grease and gives better performance than Moly based grease under similar treat rates.
4.2 : PTFE as EP additive also improves the structural stability of the grease thus enhancing the storage and heat stability properties of Grease.
4.3 : Thermal stability of the PTFE added grease also is good similar to other EP additives. However the advantage could be the inert nature of the PTFE under high temperature conditions.
4.4 As PTFE micronized waxes can be registered as food grade additives for incidental/direct contact, thus with the improved high temperature and high load characteristics, will make an important ingredient for food grade applications..

5. CONCLUSION:

As from the above results it can be concluded that addition of PTFE leads to improvement in performance parameters of the base polyurea grease. PTFE micronized powders are best choice in food grade to enhance load as well the retention of oil in the grease. Also with the current scenario of non availability/escalating costs Lithium hydroxide, polyurea based greases with PTFE type EP additives will be Suitable alternative, in place of Lithium complex greases.

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