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In This Issue

Page No.

1. A study of friction modifies in grease 3
2. Solid lubrication – an examination of synergy of Graphite/MoS₂ and metallic sulphide 14
3. Biobased polymer additives for environmentally friendly lubricants – Tackfiers 25

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A Study of Friction Modifiers in Grease

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Abstract

Friction decreases efficiency. Wherever there is friction, heat is created indicating that some energy is lost. Efficiency, wear and friction reduction in greases are such important parameters that, in some cases, the minimum levels of certain friction modifiers are specified. Molybdenum disulfide is probably the most widely used solid lubricant friction modifier. Recently, due to competition from the steel industry, the cost of molybdenum-containing additives has risen, encouraging researchers and engineers to look for cheaper alternatives. In this effort, an evaluation of various friction modifiers has been completed. Results from bench tests to evaluate friction and wear are presented.

Introduction

Molybdenum disulfide's affinity for metal surfaces and its low shear strength have made it an effective choice in reducing friction between contacting surfaces that are moving relative to each other. It has been so widely recognized for its role as a friction modifier that several military and industrial specifications require a minimum amount of MoS₂ in their lubricating greases.(1,2)

The use of alternate friction modifiers has recently become of more interest to the grease community as the cost of molybdenum has risen. Although the use of MoS₂ in lubricant applications accounts for only 1.5% of the total molybdenum market(3), recent shortages in the that market have caused the price to rise to approximately 10 times what it was in 2002.(1)

Previous work has looked at a variety of different friction modifiers in grease applications including studies evaluating the effect of different solid lubricants on Timken, 4 ball wear and wear (1), polarized graphite (4) and synergism with graphite (2). Nanoparticles have also been investigated as replacements for MoS₂ including surface-capped molybdenum trisulphide particles, which showed good friction and scuffing protection (5)

Rohr has studied bismuth sulfide in lithium grease and found better 4 ball wear scars and high 4 ball wear points.(6) Faci included the use of SRV to examine friction coefficients in addition to wear scars and wear points (7). Landry used 4 ball wear, 4 ball wear and Timken to evaluate seven different sulfides of tungsten, bismuth, tin and zinc at various concentrations and found some synergies between molybdenum and tin.(8) Some authors have seen interactions with MoS₂ that are antagonistic in nature. These are generally thought to be due to surface competition between polar additives used for EP protection, rust inhibition, antioxidancy or antiwear and the molybdenum chemistry.(9,10,11,12,13)

Aswath and Suresh have looked at mixtures of organothiophosphate and fluoropolymers compared to MoS₂ using 4 ball wear and wear as well as examining tribofilms using SEM/EDX techniques.(12) Aswath also found synergies between ZDDP, PTFE and FeF₃ which gave much higher wear loads than 3 wt% MoS₂ by itself.(13)

Experimental Details

A study was undertaken to investigate a variety of different friction modifiers in grease. Molybdenum disulfide was included in the study to evaluate the effectiveness of the novel friction modifiers in comparison with different levels of MoS₂ which are often mandated by specifications. The initial study looked at the friction modifiers in the base grease alone while additional work focused on the same set of friction modifiers in a fully formulated grease in order to better understand the effect of interactions likely to be seen with surface-active polar componentry.

Initial screening was done using High Frequency Reciprocating Rig to determine the coefficient of friction. The fully formulated greases were then evaluated using 4 ball wear. A select few greases were then chosen for additional performance testing using 4 ball wear and Timken tests. Finally, a Scanning Electron Microscope (SEM) with Electron Dispersive X-Ray (EDX) attachment was used to examine the tribolayers formed on the metal surfaces of the balls used for wear testing. Standardized test methods were employed to examine the friction, wear and extreme pressure (EP) characteristics of these grease formulations.

Lubricating compositions:

The base grease used was an unadditized lithium 12-hydroxystearate base cut to an NLGI #2 grade. The finished grease had a worked (60X) penetration of 291 and a dropping point of 201 °C. The diluent oil used was a 600N Group I base oil with a kinematic viscosity at 40 °C of 114.5 cSt (**Table 1**).

Additives: Four different organo metal components and five different nanoparticles were evaluated in the lithium base grease alone (**Table 2**) and then in the lithium base grease with a proprietary zinc/sulfur/phosphorus additive package (**Table 3**). Each friction modifier was treated at 3 wt% to avoid dilution problems and to keep the levels of base grease and oil constant for the study. This means that the level of metals or active components may differ for

each formulation. Additionally, a fully formulated grease with 5 wt% MoS₂ was included in order to compare the effect of this additional amount of molybdenum disulfide that is specified in some greases.

Table 1: Composition of Base Grease

Thickener	Lithium 12-OH
NLGI Grade	2
Base Oil Viscosity, KV @ 40C, cSt	114.5
Viscosity Index	97
Penetration, worked 60x, mm ⁻¹ [ASTM D 1403]	291*
Dropping Point, C° [ASTM D 2265]	201*

*Base grease alone

Table 2: Base Grease + Additives: Formulations

<i>Test greases consist of Base Grease blended with different friction modifiers shown below:</i>		
Additive Type	Designation	Treat rate (wt%)
None	Base Grease	---
Moly Disulfide	MoS ₂	3.0
Organo metal – 1	OM-1	3.0
Organo metal – 2	OM-2	3.0
Organo metal – 3	OM-3	3.0
Organo metal – 4	OM-4	3.0
Nano particle – 1	NP-1	3.0
Nano particle – 2	NP-2	3.0
Nano particle – 3	NP-3	3.0
Nano particle – 4	NP-4	3.0
Nano particle – 5	NP-5	3.0

Table 3: Fully Formulated Grease + Additives: Formulations

<i>Test greases consist of Base Grease blended with 4 wt% proprietary grease additive package and with different friction modifiers shown below:</i>		
Additive Type	Designation	Treat rate (wt%)
None	Base Grease	---
Moly Disulfide	MoS ₂	3.0
Moly Disulfide	MoS ₂	5.0
Organo metal – 1	OM-1	3.0
Organo metal – 2	OM-2	3.0
Organo metal – 3	OM-3	3.0
Organo metal – 4	OM-4	3.0
Nano particle – 1	NP-1	3.0
Nano particle – 2	NP-2	3.0
Nano particle – 3	NP-3	3.0
Nano particle – 4	NP-4	3.0
Nano particle – 5	NP-5	3.0

Testing: Testing was carried out using the following standard methods for determining friction, wear and extreme pressure (EP) protection:

A High Frequency Reciprocating Rig (HFRR) was used to generate the Coefficient of Friction data. The HFRR test measures the ability of a lubricant to affect friction between the contacting parts and the wear of surfaces in sliding motion under load. A 6 mm diameter ANSI 52100 steel ball oscillates in contact with an ANSI 52100 steel flat under standard test conditions. A test load of 4 N with a frequency of 20 Hz and a stroke amplitude of 1.0 mm was used to measure the coefficient of friction at 70°C, 100°C and 130°C for each sample.

The Four Ball Wear testing was completed by rotating one ball against three fixed balls under standard conditions and measuring the average wear scar worn into the fixed balls. This testing was carried out using ASTM D 2266 “Standard Test Method for Wear Preventive Characteristics of Lubricating Grease (Four-Ball Method)”(14).

The Four Ball Weld testing was completed by rotating one ball against three fixed balls under standard conditions for 10 second intervals at each load level. This testing was carried out using ASTM D 2596 “Standard Test Method for Measurement of Extreme-Pressure Properties of Lubricating Grease (Four-Ball Method)” (15) with the modification of using test loads at 10 kg intervals to better monitor the performance of the greases under extreme pressure.

Timken testing was carried out using a rotating steel test cup under load against a steel test block according to ASTM D 2509 “Standard Test Method for Measurement of Load-Carrying Capacity of Lubricating Grease (Timken Method)”(16).

The tribolayer analysis was completed using a JEOL JSM-5800LV Scanning Electron Microscope (SEM). This microscope was also equipped with a ThermoElectron Nanotrace Detector for performing Energy Dispersive X-ray Spectroscopy (EDX) to allow chemical analysis of the tribofilm. SEM images and EDX spectra were recorded at 7 keV incident beam energy.

The methods’ repeatability and reproducibility data are summarized in **Table 4**. The 95% confidence limits shown on the charts are calculated from the repeatability statements of the appropriate ASTM methods, unless otherwise noted.

Table 4: Method Repeatability

Method	Designation	r	R
HFRR Coefficient of Friction		0.006**	---
4 Ball Wear	ASTM D 2266	0.2 mm	0.37 mm
4 Ball EP	ASTM D 2596	1 increment	1 increment
Timken	ASTM D 2509	0.23 x mean	0.59 x mean

**Standard error calculated from internal data set

Results and Discussion

The initial friction evaluation was completed using the HFRR on the set of individual friction modifiers blended with the base grease alone. Testing was done to determine the coefficient of friction at three different temperatures for each sample: 70°C, 100°C and 130°C. The complete data set is shown in **Table 5**.

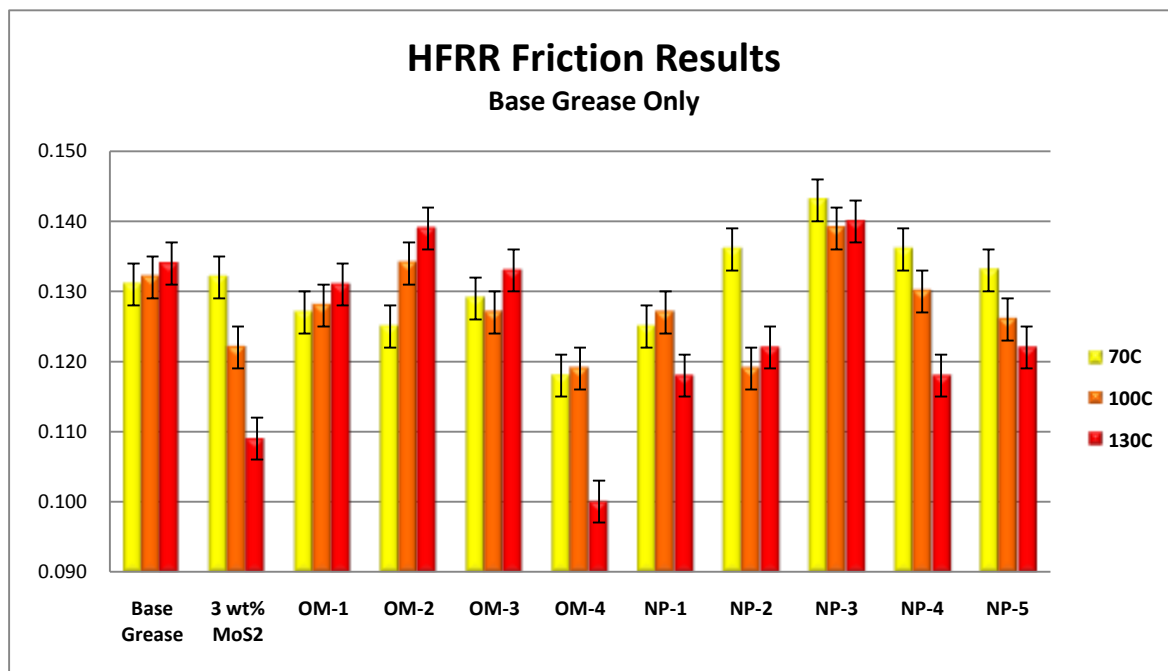
Table 5: HFRR Coefficient of Friction Data: Base Grease + FM

Friction (1mm, 20 Hz, 4 N)	Base Grease	MoS ₂	OM-1	OM-2	OM-3	OM-4	NP-1	NP-2	NP-3	NP-4	NP-5
70C	0.131	0.132	0.127	0.125	0.129	0.118	0.125	0.136	0.143	0.136	0.133
100C	0.132	0.122	0.128	0.134	0.127	0.119	0.127	0.119	0.139	0.130	0.126
130C	0.134	0.109	0.131	0.139	0.133	0.100	0.118	0.122	0.140	0.118	0.122

As seen graphically in **Figure 1**, the base grease containing MoS₂ showed significantly better friction reduction only at the higher temperatures. In fact, there seemed to be a direct correlation with higher temperatures giving lower coefficients of friction. This same response was noted in several other instances with OM-4, NP-4 and NP-5 all showing similar trends. One notable exception was OM-2 which showed the opposite trend and had the highest coefficient of friction at 130°C.

In comparison to the base grease alone, only OM-4 showed significant improvement in reduction of friction at 70°C. At 100°C, MoS₂, OM-4 and NP-2 showed improvement over the base grease, while at the highest temperature (130°C), six different friction modifiers showed significantly lower coefficients of friction than the base grease alone. Only OM-4 showed an advantage over MoS₂ at each temperature, while none of the other friction modifiers were equal to or better than the molybdenum component in friction reduction at any of the temperatures studied.

Figure 1: HFRR Coefficient of Friction Data: Base Grease + FM



Next, the HFRR was used to evaluate, at the same three temperatures, the collection of friction modifiers in a fully formulated base grease. Included in this set was an extra grease containing 5 wt% of moly disulfide for comparison against the lower treat sample containing 3 wt%. Again, the coefficient of friction of each grease at each of the test temperatures was measured as shown in **Table 6**.

Table 6: HFRR Coefficient of Friction Data: Fully Formulated Grease + FM

Friction (1mm, 20 Hz, 4 N)	Fully Formulated	3 wt% MoS ₂	5 wt% MoS ₂	OM-1	OM-2	OM-3	OM-4	NP-1	NP-2	NP-3	NP-4	NP-5
70C	0.118	0.111	0.141	0.125	0.131	0.128	0.119	0.134	0.143	0.141	0.128	0.118
100C	0.131	0.134	0.153	0.132	0.148	0.145	0.115	0.138	0.137	0.154	0.144	0.135
130C	0.138	0.135	0.151	0.131	0.158	0.150	0.135	0.135	0.147	0.167	0.149	0.145

As can be seen from **Figure 2**, the friction coefficient of the base grease at 70°C was significantly reduced by the additive package and was again further reduced by the addition of 3 wt% MoS₂. None of the friction modifiers in the study had a statistically significant effect in lowering the coefficient of friction of the fully formulated grease at this temperature. Indeed, many had a negative impact on friction including the higher (5 wt%) MoS₂ level, three of the organo metals (OM-1, OM-2, OM-3) and four of the nano particles (NP-1, NP-2, NP-3, NP-4).

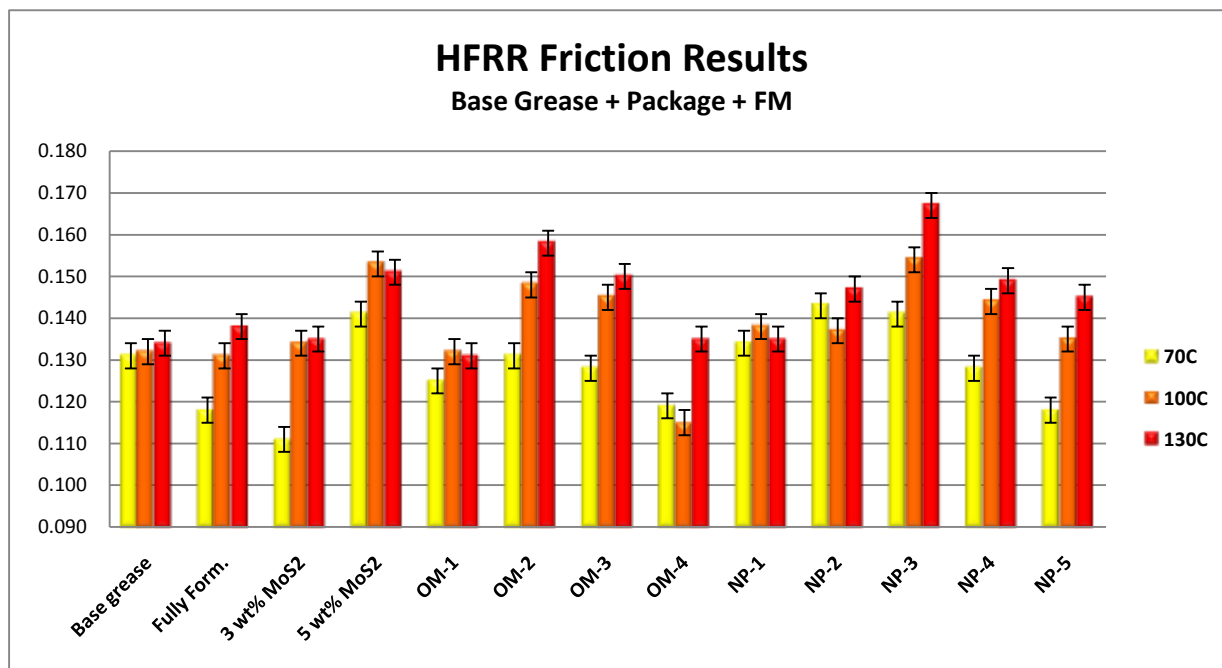
This same effect was noted at 100°C for most of the study group with 5 wt% MoS₂, OM-2, OM-3, NP-1, NP-2, NP-3, NP-4 all showing significantly higher friction levels than the fully formulated grease. The difference at this higher temperature was that the base grease, the additized grease and the 3 wt% MoS₂ grease showed no differentiation

in coefficient of friction. The only component to show an improvement in friction at this temperature was OM-4 which showed a drop of 0.016.

At the highest temperature studied (130°C), the same effect was noted with many of the same components showing antagonistic effects on friction (5 wt% MoS₂, OM-2, OM-3, NP-2, NP-3, NP-4, NP-5) and only OM-1 showing a slight, albeit statistically significant, reduction in friction. Again, the base grease, the additized grease and the 3 wt% MoS₂ grease showed no significant differences with regard to friction.

The overall trend that appeared to correlate increasing temperature with a reduction in friction in several of the base grease only formulations, was reversed in many of the fully additized grease formulations. This trend was particularly distinct in the fully formulated grease sample as well as the OM-2, OM-3, NP-3, NP-4 and NP-5 samples. It is possible that the competition for the surface between the polar performance additives in the fully formulated grease is exaggerated at the higher temperatures through greater activity at the molecular level. Additional studies examining component interaction as well as treat rate dependence would be needed to further investigate this theory.

Figure 2: HFRR Coefficient of Friction Data: Fully Formulated Grease + FM



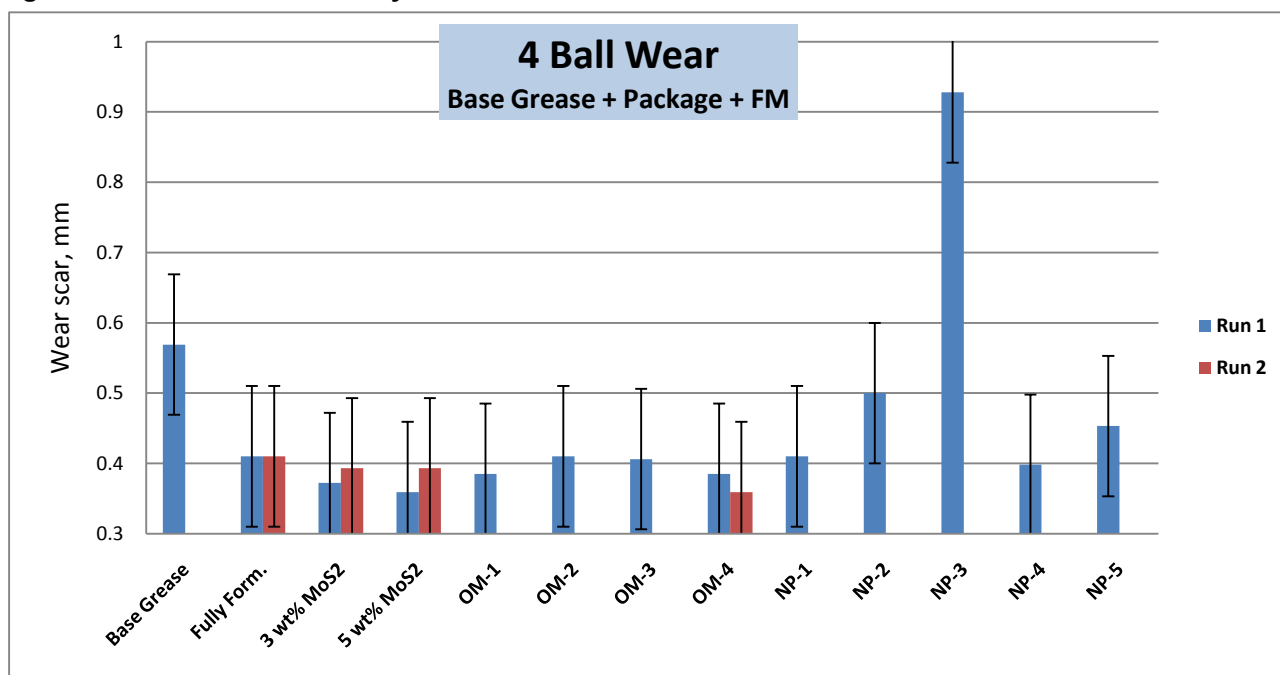
The negative impact of additional MoS₂ (3 wt% vs 5 wt%) in a fully formulated grease tends to confirm findings in other studies (9, 10, 11, 12, 13) and may be due to potential abrasiveness of the lamellar particles when not allowed to form smooth planes due to interaction and surface competition with other surface active additives.

This same set of fully formulated greases was tested using the four ball wear tester according to ASTM D 2266 and the results are shown in **Table 7** and graphed in **Figure 3**. Relative to the base grease, NP-3 was significantly worse with respect to wear protection, while NP-2 showed no statistical difference. All other greases showed an improvement in antiwear performance with reductions of at least 0.12 mm in the wear scar compared to the base grease alone. Relative to the fully formulated grease, only NP-3 showed a negative impact on wear performance. All of the other friction modifiers produced wear scars that were not statistically different from the control. However, the MoS₂ (3 wt% and 5 wt%) and the OM-4 appeared to trend lower in the order shown. Each was run in duplicate but further testing would be needed to prove a statistical difference between the four greases.

Table 7: 4 Ball Wear Data: Fully Formulated Grease + FM

	Fully Formulated	3 wt% MoS ₂	5 wt% MoS ₂	OM-1	OM-2	OM-3	OM-4	NP-1	NP-2	NP-3	NP-4	NP-5
4 ball wear scar, mm	0.410	0.372	0.359	0.385	0.410	0.406	0.385	0.410	0.500	0.928	0.398	0.453
	0.410	0.393	0.393				0.359					

Figure 3: 4 Ball Wear Data: Fully Formulated Grease + FM



A small subset was selected from the original greases tested for additional performance testing (see **Table 8**). This smaller group included the base grease, the fully formulated grease (as a control), 3 wt% MoS₂, 5wt% MoS₂ and OM-4, an organo tungsten additive which had showed promising results in both the friction and wear testing.

Table 8: Selected Greases for Additional Study

	Base Grease	Fully Formulated	3 wt% MoS ₂	5 wt% MoS ₂	Organo tungsten
Zn/P/S additive package		4	4	4	4
Molydisulphide			3	5	
Organo Tungsten					3
Base grease/oil	100	96	93	91	93
Total	100	100	100	100	100

Extreme pressure (EP) protection of the greases was tested using the four ball weld tester according to the parameters of ASTM D 2596 with a slight modification. The test loads were increased in increments of 10 kg rather than the larger increments prescribed in the method. This was done to gain a better understanding of the differences between the EP protection provided by the various additive systems. Due to the use of the smaller increments, the ASTM repeatability statistics are not applicable to this data set.

The results for the testing (**Figure 4**) show a clear advantage for each of the test greases in comparison to the base grease with a minimum increase of 110 kg in the weld points of each. The fully formulated grease gave an average weld point of 285 kg based on two runs and the addition of MoS₂ showed no benefit. In fact, the higher level (5 wt%) appeared to have a negative impact on the EP protection of the grease. The organo tungsten friction modifier (OM-4), however, showed a significant increase in performance in raising the weld point by 75 kg to 360 kg. Using the ASTM increments, this would easily allow the level of a 400 kg weld point to be reached.

Another measure of load carrying ability is the Timken method. This testing was carried out using ASTM D 2509 and the results are shown in **Figure 5**. Again, each of the test greases showed a distinct improvement over the base grease with a gain of at least 60 lbs in the OK load of each. The fully formulated grease gave an 80 lb OK load on its own so it was difficult to differentiate improvements in this level. The same trend was seen as with the 4 ball weld testing in that the 3 wt% MoS₂ gave a slightly better result (90 lb OK load), while the additional MoS₂ of

Figure 4: 4 Ball Weld Data: Fully Formulated Grease + FM

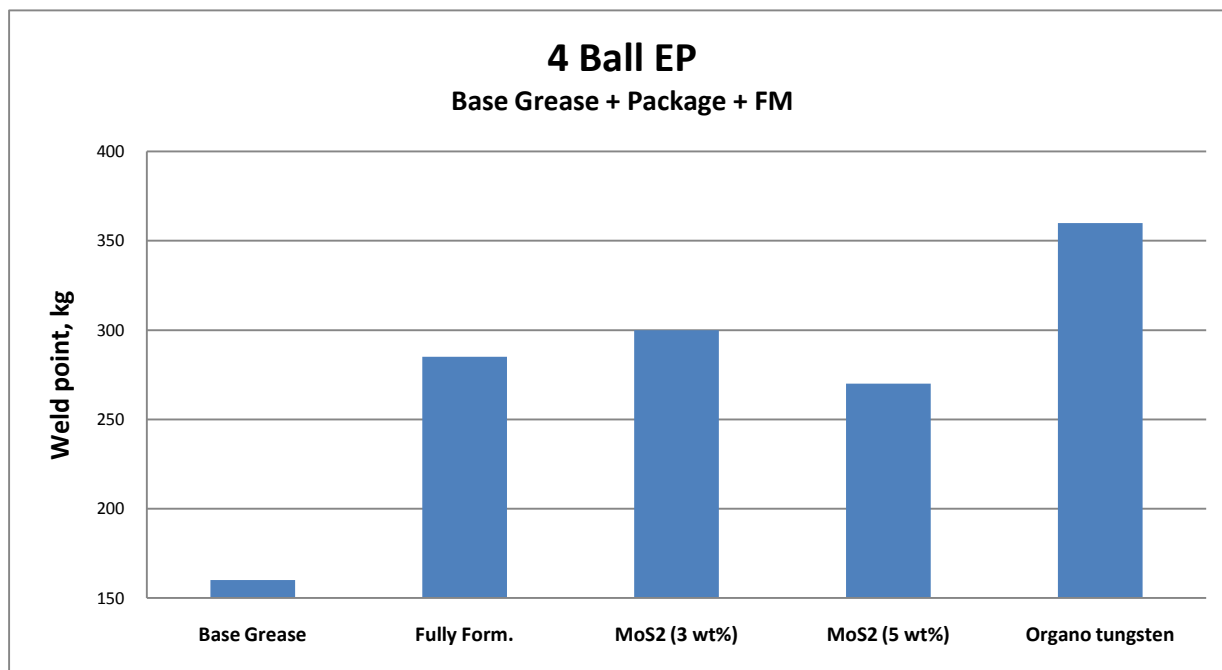
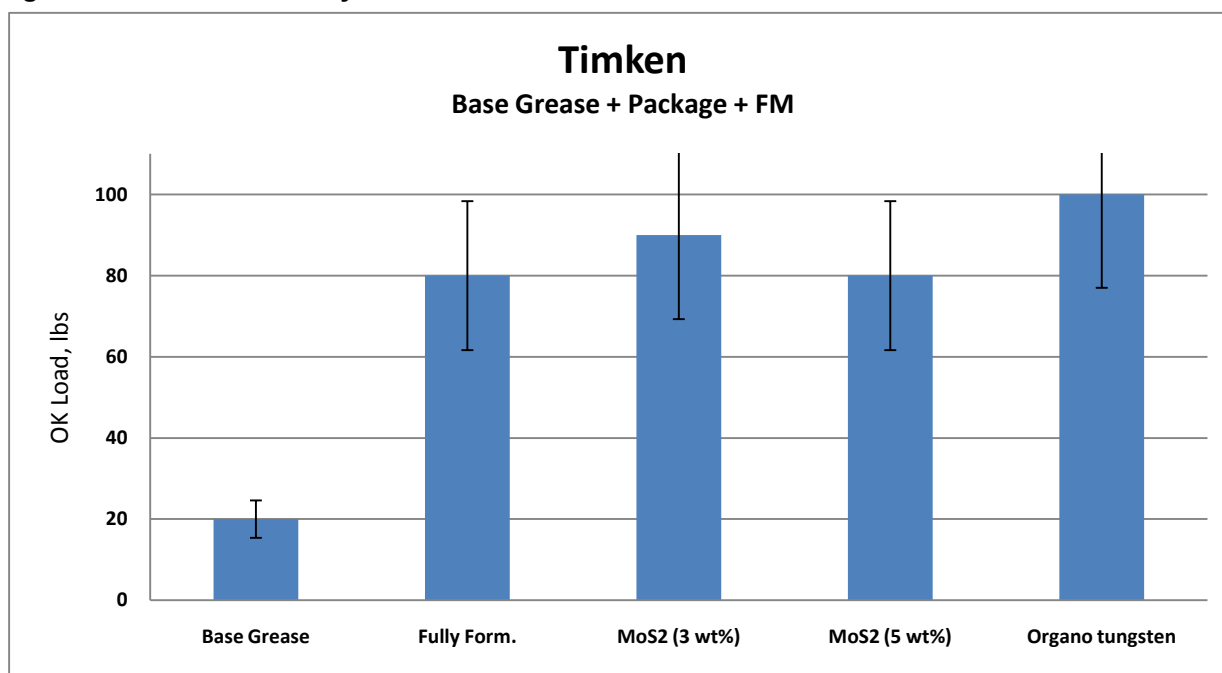


Figure 5: Timken Data: Fully Formulated Grease + FM



the 5 wt% level may have had a negative impact resulting in an 80 lb OK load. And again, the organo tungsten component gave the highest result with a 100 lb OK load. However, these differences are within the repeatability of the method and additional testing would be needed to confirm the possible impacts noted here. A package that gave OK loads in the range of 40 to 50 lbs would be desirable so that a better indication of positive (or negative) impacts could be obtained.

In addition to the performance testing carried out above, an analysis of the tribolayer formed by the different friction modifiers was attempted to better understand the elemental composition of the films formed on the surface. After selected four ball wear tests, the stainless steel balls were rinsed with heptane to remove any excess lubricating fluid. The contact area of the top rotating ball was then examined with a JEOL JSM-5800LV Scanning Electron Microscope (SEM). This microscope was also equipped with a ThermoElectron Nanotracer Detector for performing

Energy Dispersive X-ray Spectroscopy (EDX) to allow chemical analysis of the tribofilm. SEM images and EDX spectra were recorded at 7 keV incident beam energy.

Figure 6 shows the SEM images of the actual scars on each of the test balls while **Figure 6a** shows the tribolayers formed by each of the test greases on the ball during four ball wear testing.

Figure 6 – SEM image of 4 ball wear scar

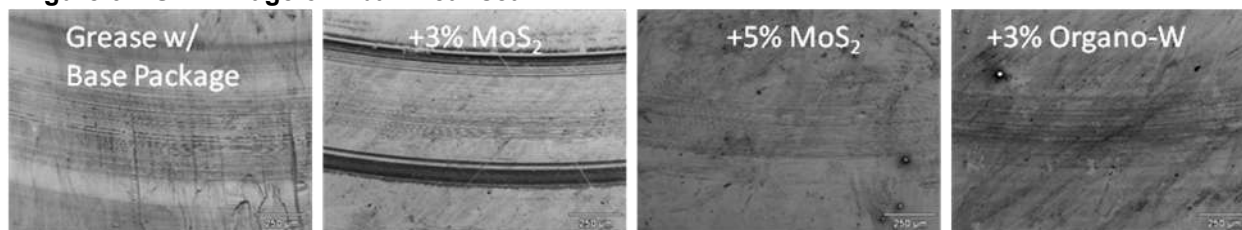


Figure 6a – Tribolayers formed on test balls

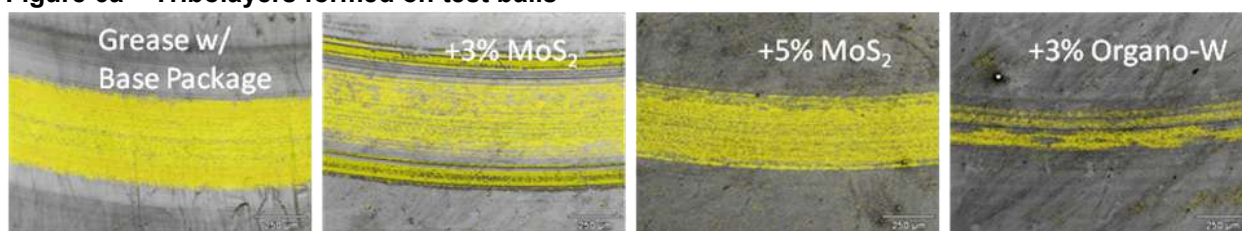
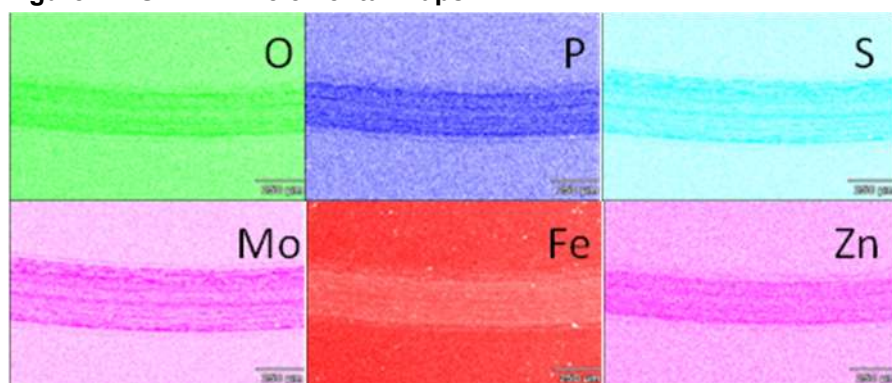


Figure 7 shows the SEM-EDX elemental maps for O, P, S, Mo, Fe and Zn on the ball from the test performed with 5 wt% MoS₂ in the fully formulated base grease. The darker coloration on each map shows the clear formation of a tribolayer containing each of the various elements. The less intense color in this same region on the Fe map shows the loss of Fe signal due to the formation of the tribolayer over the iron-rich steel surface.

Figure 7 – SEM/EDX elemental maps



To quantify the ratio of elements in the contact area, the SEM-EDX can be used to generate an EDX spectra at any given point on the surface. An example of such a spectra illustrates the elemental make up of one point in the tribolayer formed on the test ball (**Figure 8**). Finally, a composite ratio of the elements found in the contact area can be generated from these EDX spectra which averages the elemental compositions over the area inside the contact zone as shown in **Table 9**

From the SEM/EDX map, it was possible to separate the tribofilm from the steel background by looking for the elements known to be in tribofilms like P,O, S, and Zn. The tribofilm could then be mapped out on the surface (**Figure 6**) and the elements in the tribofilm quantified (one example in **Figure 8**), and a summary of the elementals can be found in **Table 9**.

Of interest for future work is 1) the ability to see tungsten in the tribolayer of that test grease, 2) the relative lack of molybdenum seen in any of the greases, as well as 3) the wide variation in the sulfur level seen in the various tribolayers. It is important to note that in EDX spectroscopy the Mo-L line overlaps the S-K line and this may provide some explanation for the low level of Mo seen in the tribolayers of the fully formulated grease and the organo tungsten-containing grease neither of which should have contained any molybdenum at all.

Figure 8 – EDX spectra from tribolayer (inset)

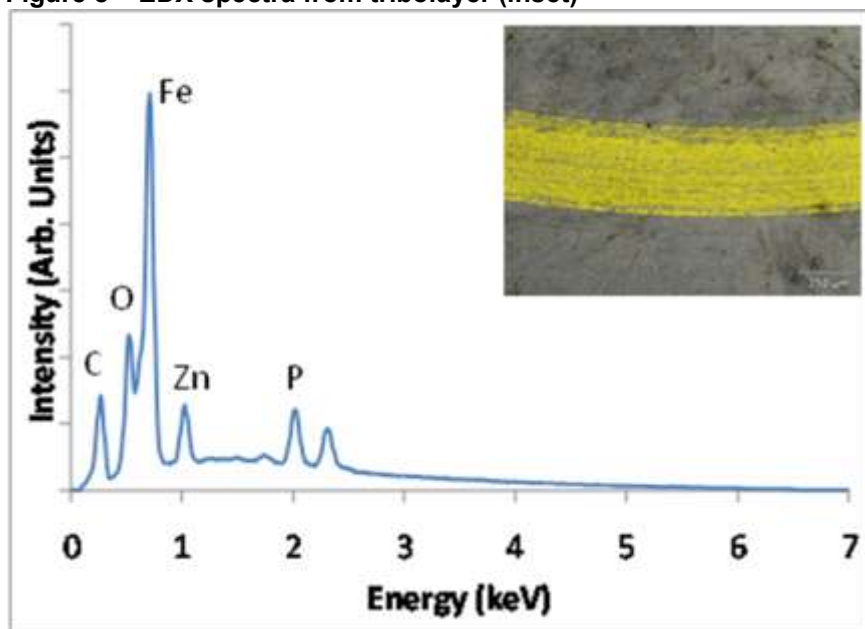


Table 9: Relative ratios of elements in the tribolayers found in the contact zone

	Fully Formulated Grease	+ 3 wt% MoS ₂	+ 5 wt% MoS ₂	+ Organo Tungsten
C K	44.3	41.6	42.9	45.8
O K	31.1	23.0	34.6	37.3
P K	6.7	4.6	8.1	5.6
S K	13.5	27.5	6.8	1.2
Zn L	3.3	1.8	5.5	3.5
Mo L	0.2	0.5	0.9	0.1
W M				5.8

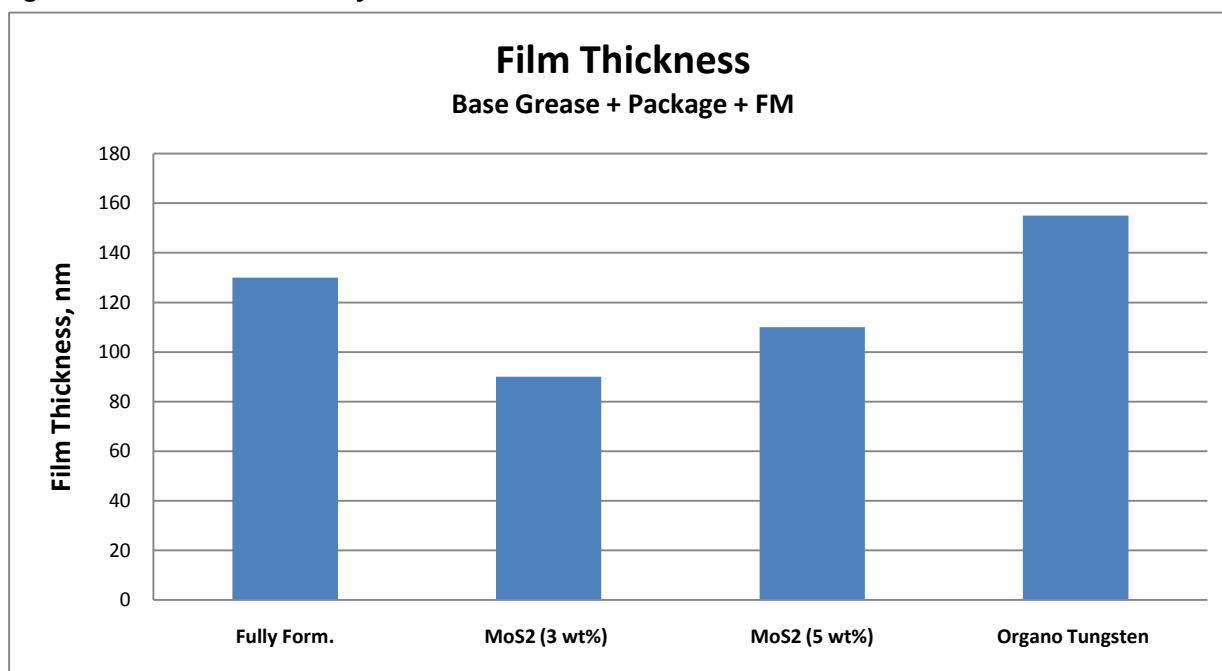
It is also possible to calculate the thickness of the tribolayer by examining the amount of Fe seen in the EDX of the tribolayer. The steel/Fe signal in the EDX is inversely proportional to the thickness of the tribofilm. Through this process the film thicknesses for the test grease tribolayers were calculated and are shown in **Figure 9**. The thickness of the tribolayer formed with the organo tungsten friction modifier may help to explain some of the performance benefits seen with this component in this study.

Future studies will include further examination of the temperature dependence of different friction modifiers especially in the context of their interaction with more polar additives found in fully formulated greases. Additional work will also be carried out to further understand the potential performance benefits of the organo tungsten and similar additives and to use the SEM/EDX to better understand their functionality. The ability to analyze tribolayers formed and identify elements found in the friction modifiers studied will certainly be a useful tool in better understanding the performance benefits of various componentry as well as possible mechanisms. Finally, it would be interesting to look more closely at the differences in performance between 3 wt% and 5 wt% of molybdenum disulfide especially in fully formulated greases and to further explore the findings of this study that seem to contradict the “more is better” cliché with respect to MoS₂ levels in grease.

Conclusions

- The organo tungsten friction modifier studied (OM-4) showed significant reduction of friction at various temperatures in both a base grease and a fully formulated grease, as well as indications of improved wear and extreme pressure protection as shown in 4 ball wear, 4 ball weld and Timken testing.

Figure 9 – Calculated tribolayer thickness



- Higher concentrations of molybdenum disulfide showed indications of poorer performance with a 5 wt% level having significantly worse friction control (HFRR) and EP protection (4 ball weld) than the 3 wt% level.
- The ability to form a tribolayer with test greases and use SEM/EDX analysis to quantify its elemental make up was demonstrated.

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Solid Lubricant – An Examination of Synergy of Graphite/MoS₂ and Metallic Sulfide

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Abstract

The mating surfaces of equipments operating in industrial application are separated by an oil film in hydrodynamic lubrication regime however in the boundary lubrication regimes the oil film become inefficient to keep the surfaces away from each other. This makes necessary the introduction of EP/AW additive to take care of such lubrication issue. In the heavily loaded application of bearing and gears, solid lubricants are preferred, which can take care of such extreme loads conditions.

Various types of solid lubricant are reported in literature, which can be used for satisfactory functioning of these highly loaded lubrication requirements. Some of the solid lubricants are: MoS₂, Sb₂S₃, potassium tri-sulfide, gilsonite, CaF₂, boron nitride, bentonite, zinc sulfide, talc and mica. However the most common solid lubricant that are being used in grease formulation, are MoS₂ and graphite whereas mica and talc are the reference of past.

The present lubrication technology suggests the use MoS₂, graphite and some other metallic sulfide alone or in combination with each others. Advantages have been described by some of the manufacturers of metallic sulphide such as MoS₂, ZnS etc. for meeting high temperature / high load requirements.

In the present paper, some of the studies conducted at author's laboratory to study the influence of some of these product along with graphite and MoS₂ separately and in combination of these metallic sulphides, in grease formulations and has been extrapolated to find the synergy.

Introduction

The international grease market as per NLGI Production survey has been reported in 2011 as 1.08 MMT based on the average response of 71% received from companies across the globe. However for 100 % response and multiplying the average figure 5812 ton per plant it comes out to be 1.5 MMT. Similarly the India and Sub continent figure comes out to be 86.7 TMT and 105 TMT, respectively based on the 83% response and average production of each plant as 3941 tons per year. The data on base oils used in these grease formulations as approx. 78% globally and 76% for India and sub continent indicates 22 % and 24% of thickener and additives in the greases produced. This quantity of thickener and additive appears to be higher and may contribute to higher cost in grease formulations. This may also be concluded that this quantity of thickener may be needed to achieve the high performance in the products as per the application requirement. The EP greases requiring higher weld load and lower wear scar dia need higher quantity of additives and some time solid lubricants to achieve target properties for load bearing.

Solid lubricant is used in lubricant formulations to achieve high load and anti-seizure properties under extreme load conditions. There are products reported to contain from about 0.5% to more than 50% of solid lubricants in grease formulations in specific products. The high cost of MoS₂ and super fine quality of graphite, give scope to look for alternatives as cost effective solutions. The present paper consists, studies conducted to find the synergy of graphite, MoS₂, ZnS and SnS₂ in lithium complex and sulphonate complex greases.

Typical Applications of Solid Lubricants

Solid Lubricants are useful in the conditions where conventional liquid/semisolid lubricants fail to perform adequately. These conditions include reciprocating motion that requires lubrication to minimize wear, for example in gears and chains. Due to heavy loads the liquid film squeezes out whereas the solids remain between the mating surfaces and prevent wear, fretting corrosion and galling.

These products also take care of higher operating temperatures and oxidizing environments where liquid lubricant will not survive. Fasteners are the typical example of such applications.

Solid lubricants are also suitable for applications where the surfaces are made up of polymers, ceramics etc as high reactive products may react with surface and ultimately may damage it.

In addition most applications where plastic deformation is carried out, solid lubricants are used such as wire drawing applications.

Types of Solid Lubricants

There are many types of solid lubricants such as graphite, MoS₂, Boron nitride, PTFE, WS₂, Sb₂S₃, Bi₂S₃, ZnS, SnS₂ etc that are being used in typical applications however most commonly used are graphite and MoS₂. Some details selected in this study is given as under.

Graphite

Graphite is structurally composed of planes of polycyclic carbon atoms that are in hexagonal orientation. The distance of carbon atoms is longer and therefore bonding is weaker. The lamellar structure of graphite is best suited for regular atmosphere. Water vapour is necessary component for graphite lubrication as it reduces bond energy between planes and thus planes can move smoothly. Due to this property graphite lubrication is not effective in vacuum. In oxidizing atmosphere it withstands a temperature of 450 deg C continuously and intermittently it can take care of higher temperature peaks. Graphite also shows electrical conductivity whereas thermal conductivity is generally low.

Graphite is available in natural and synthetic grades. Natural graphite is obtained from mines and contain carbon (96-98 %), SiO₂, Sulphur and ash whereas synthetic graphite contains carbon (99.5-99.9 %). Table 1 summarizes typical properties of graphite used in this study.

Molybdenum Di Sulphide

MoS₂ is also mineral metal highly refined to lubricant grade. It has hexagonal lamellar structure with intrinsic property of easy shear. It lubricates efficiently up to 400 deg C and oxidizes at higher temperatures of more than 400 deg C. The particle size of about 5 microns is most suitable for lubrication as lesser particle show more prone to oxidation and higher size result in higher wear. Table 2 summarizes typical properties of MoS₂.

Zinc sulphide (ZnS)

This is an inorganic compound found in nature as occurring mineral sphalerite. Pure ZnS is crystalline powder with tetrahedral to hexagonal skeleton. At high temperature this hexagonal structure performs as good lubricant by separating the two mating surfaces. The sulphur atom released behaves similarly as other sulphides on the surface. Typical properties of ZnS are given in table 3.

Tin Di Sulphide (SnS₂)

Tin Di Sulphide is solid product with mosaic gold colour having prototype crystalline structure. The product contains 35% sulphur and 64.9 % Sn. It decomposes at 600 deg C. This product demonstrates excellent anti friction properties in applications such as clutch and brake liners. Typical properties are given in table 4.

Experimental

Lithium complex and sulphonate complex greases with NLGI no 2 consistency with drop point of more than 290 deg C were prepared using usual grease making technique. A total of eleven blends each with lithium complex and sulphonate complex greases using graphite, MoS₂, ZnS and SnS₂ and their combinations as given in table 5 and 6. Total 24 samples were prepared and evaluated for penetration – D217, dropping point – D2265, weld load – D2596 and wear scar diameter- D2266. The results are included in table 5 and 6 respectively.

Results and Discussion

1.0 Lithium complex grease (LCG) was prepared using azelaic acid as complexing agent and fortified with EP additives. The grease has a penetration of 285, drop point (DP) deg C of 305, weld load (WL) of 250 kgf and Wear scar diameter (WSD) of 0.263 mm (table 5).

1.2 Penetration:

Addition of 3% graphite, MoS₂, ZnS and SnS₂ alone in LCG led to softening in penetration by 10-12 units. This change occurs due to some degree of degelling in the oil and thickener interaction. Similar trend has been observed in the combinations of solid lubricants except graphite - MoS₂ and MoS₂-ZnS combination (sno.5, 9 of table5).

1.3 Drop Point:

Drop point of the grease and other grease blends with the solid lubricants alone or in combination with LCG have been observed to be in repeatability limits. Thus it can be concluded that solid lubricants or their combination do not have any effect on LCG drop point.

1.4 Weld load (WL):

Weld load of samples 1 to 5 of table 5 i.e. LCG and its combination with graphite, MoS₂, ZnS and SnS₂ indicate no change ascertaining similar load bearing capability. Sample 6 of table 5 (LCG +3% graphite + 2% SnS₂) resulted increase in weld load by one stage falling in repeatability indicating no effect in EP properties. Sample 7 of table 5 showed synergy as weld load increases from 250 to 400 kgf. This shows that combination of graphite and MoS₂ is a synergetic mixture. Similar synergy has been observed in combination of MoS₂ - ZnS, Graphite – MoS₂- ZnS and SnS₂ – ZnS. However MoS₂ - SnS₂ has not been observed to show synergy alone or in combination with graphite.

Interpretation of data concludes synergy of graphite – MoS₂, SnS₂ – ZnS, graphite – MoS₂ – ZnS observed whereas MoS₂ – SnS₂ does not, in LCG. However no antagonism has been observed.

1.5 Wear Scar Diameter (WSDD):

Addition of 3% graphite and MoS₂ marginally increased WSD (Table 5) whereas ZnS and SnS₂ decreased WSD indicating synergetic AW performance in LCG. Different combinations of solid lubricant undertaken in the study designated as S No 5-12 reduced WSD indicating synergy with LCG. However MoS₂ – ZnS combination showed an excellent synergy by reducing WSD to 0.063 mm from 0.263 of LCG.

The studies conclude that ZnS alone or in combination with MoS₂ gives the best synergy in anti-wear characteristic.

2.0 Sulphonate complex grease:

2.1 Slphonate complex grease (SCG) was prepared from usual raw materials and usual manufacturing process and solid lubricants and their combinations were added in it at room temperature and milled in a colloid mill. Base grease and different blends were tested for penetration, drop point, WL and WSD. The results are tabulated in table -6. The base grease has the characteristics as: penetration – 281, Drop point - >310, WL- 400 kgf and WSD – 0.233 mm.

2.2 Penetration:

Addition of graphite, MoS₂, ZnS and SnS₂ and their combinations in SCG did not change the consistency of the grease as penetration figures obtained, remained in repeatability limits. This concludes that Solid lubricants do not change the consistency of SCG.

2.3 Drop Point:

Similar observations emerged for drop point as all the blends gave >310 deg C drop point. This also indicates that solid lubricants taken in the study do not result any adverse effect on drop point.

2.4 Weld Load:

SCG has weld load of 400kgf and addition of 3% graphite increased to 500 kgf whereas addition of 3% MoS₂, ZnS and SnS₂ increased to 620 kgf indicating

synergistic effect of these products. The weld load figures of SNo. 6,9 and 12 show excellent synergy of ZnS with MoS₂ whereas SnS₂ shows synergy with graphite. The synergy of the products and mixtures of combinations with SCG observed is given as under:

- | | | |
|---------------------------------------|-----------|--------------|
| • MoS ₂ – graphite | WL – 800 | - Synergy |
| • MoS ₂ – ZnS | WL – 800+ | - Synergy |
| • Graphite- SnS ₂ | WL – 800+ | - Synergy |
| • ZnS - SnS ₂ | WL- 800 | - Synergy |
| • MoS ₂ – SnS ₂ | WL – 800 | - Synergy |
| • Graphite – ZnS- MoS ₂ | WL 620 | - No synergy |

The results show excellent synergy of the above combinations with SCG.

2.5 Wear Scar diameter:

SCG alone has a WSD of 0.263 mm and addition of graphite, MoS₂, ZnS and SnS₂ reduced the same 0.233. The figures of these WSD are included in table-6. Based on the results following observations can be made.

- | | | |
|---|----------------|-------------------|
| • MoS ₂ ,SnS ₂ , graphite and ZnS marginally reduce WSD | | |
| • MoS ₂ - graphite | wsd – 0.087 mm | - synergy |
| • MoS ₂ - SnS ₂ | wsd – 0.037 | - Synergy |
| • MoS ₂ – ZnS | wsd – 0.080 | - Synergy |
| • ZnS - SnS ₂ | wsd – 0.093 | - Synergy |
| • Graphite – MoS ₂ - ZnS | wsd – 0.063 | - Synergy |
| • Graphite – MoS ₂ - SnS ₂ | wsd – 0.183 | -Moderate Synergy |

The studies indicate that products with SCG and above combinations can result in excellent anti-wear characteristics.

3.0 Conclusion:

- The studies conducted are limited to graphite, MoS₂, ZnS and SnS₂ and their combinations when blended in different concentration in LCG and

SCG. The blends were characterized for properties viz penetration, drop point, weld load and WSD.

- In general no change has been observed in penetration and drop point of LCG and SCG by addition of solid lubricants and their combinations.
- The solid lubricant and their combination in general show synergistic effect in WL and WSD with LCG and SCG.
- Greater synergy, have been observed in MoS₂-ZnS, MoS₂-graphite, Graphite-SnS₂ in WL and WSD in both LCG and SCG.
- MoS₂-SnS₂ showed limited synergy.
- More studies are needed for optimization of solid lubricant and their combination's concentrations.

4.0 References:

- Molybdenum disulphide : Wikipedia
- Zinc Sulphide: Wikipedia
- Solid Lubricants : www.tribology-abc.com

Table 1

Characteristics of Graphite

1. Type	Natural/Synthetic
2. Colour	Black
3. Structure	Crystalline, hexagonal, Lamellar
4. Particle size	about 6-8 micron
5. Ash % wt	0.5
6. Moisture content %wt	0.1

Table 2

Characteristics of MoS₂

1. Type	Natural
2. Colour	Greyish Black
3. Structure	Crystalline, hexagonal, Lamellar
4. Particle size	about 6-8 micron
5. Moisture content %wt	0.1
6. Acidity %wt	0.3
7. Molecular formula	MoS ₂

Table 3

Characteristics of ZnS

1. Type	Natural/Synthetic
2. Appearance	Powder
3. Colour	White
4. Structure	Crystalline, tetrahedral/hexagonal,
5. Particle size	about 0.5 to 1.0micron

Table 4

Characteristics of SnS₂

1. Appearance	Crystalline solid
2. Colour	Gold Yellow
3. Structure	Crystalline Powder
4. Particle size	about 3-9 micron
5. Density	4.5 gm/cm ³

Table 5

Influence of Solid Lubricant / their mixtures on Lithium Complex Grease

S No.	Composition	Penetration D 217	Drop Point , deg C D2265	Weld Load , Kgf D2596	WSD , mm D2266
1	Lithium Complex grease	285	305	250	0.263
2	Sno 1 + 3% graphite	295	305	250	0.285
3	Sno 1 + 3% MoS ₂	297	300	250	0.308
4	Sno 1 + 3% Zns	301	307	250	0.08
5	Sno 1 + 3% SnS ₂	297	305	250	0.21
6	Sno 1 + 3%graphite +2% Sns ₂	294	306	315	0.162
7	Sno 1 + 5% graphite + 2% MoS ₂	285	310	400	0.237
8	Sno 1 + 3% MoS ₂ + 2% SnS ₂	293	310	315	0.237
9	Sno 1 + 5% MoS ₂ +2 % Zns	287	310	400	0.063
10	Sno 1 + 3% MoS ₂ + 3% graphite +2% SnS ₂	291	307	400	0.183
11	Sno 1 + 3% MoS ₂ + 3% graphite + 2% ZnS	293	308	500	0.26
12	Sno 1 + 3% ZnS + 3% SnS ₂	303	308	400	0.168

Table 6

Influence of Solid Lubricant / their mixtures on Sulphonate complex grease

S No.	Composition	Penetration D 217	Drop Point , deg C D2265	Weld Load , Kgf D2596	WSD , mm D2266
1	Sulphonate complex grease	281	>310	400	0.233
2	Sno 1 + 3% graphite	280	>310	500	0.223
3	Sno 1 + 3% MoS ₂	285	>310	620	0.117
4	Sno 1 + 3% ZnS	278	>310	620	0.24
5	Sno 1 + 3% SnS ₂	279	>310	620	0.165
6	Sno 1 + 3%graphite +2% Sns ₂	281	>310	>800	0.162
7	Sno 1 + 5% graphite + 2% MoS ₂	275	>310	800	0.087
8	Sno 1 + 5% MoS ₂ + 2% SnS ₂	279	>310	800	0.037
9	Sno 1 + 5% MoS ₂ +2 % ZnS	281	>310	>800	0.080
10	Sno 1 + 3% MoS ₂ + 3% graphite +2% SnS ₂	278	>310	>800	0.263
11	Sno 1 + 3% MoS ₂ + 3% graphite + 2% ZnS	277	>310	620	0.213
12	Sno 1 + 3% ZnS + 3% SnS ₂	278	>310	>800	0.093

Biobased Polymer Additives for Environmentally Friendly lubricants – Tackifiers

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Introduction

For the past 60 years, tackifiers have been used in petroleum – based oils for applications that include chain conveyor lubricants, saw oils, way lubricants, and greases. Tackifiers are typically polymeric additives that impart tack or stringiness to a lubricant. It may be used to provide adherence in Way oils and chain lubricants, added stringiness in greases, and anti-mist properties to metalworking fluids. This anti-mist feature is becoming more important as the laws concerning workplace safety have become more stringent. The molecule of choice is polyisobutylene which is made by the polymerization of isobutylene. Other mineral oil soluble polymers such as olefin copolymers (OCP's) can also be used. The degree of tackiness is determined primarily by controlling the molecular weight of the polymer, the concentration of the polymer, and the diluent oil selected. With the focus currently on renewable resources, the shift has been to vegetable base oils. Vegetable oils offer unique advantages to a lubricant formulator but they also have their disadvantages. For instance, polyisobutylene is not soluble in vegetable oils, therefore new polymers needed to be evaluated. The initial discussion of this paper will focus mineral oil tackifiers and then on vegetable based tackifiers. It is well known that the NSF has approved high molecular weight polyisobutylene as a polymer that is safe for incidental food contact, however it is also well understood that environmentally, polyisobutylene does not readily degrade [1].

Closely related to tackifiers are viscosity index improvers or VI improvers (sometimes called thickeners). These polymers increase the viscosity or thickness of a fluid. Both tackifiers and viscosity index improvers, if compatible with the base oil, thicken the oil (tackifiers less so), but under shear conditions the tackifier usually breaks down. Tackifiers and viscosity modifiers have differing viscoelastic properties. .

A discussion of the mechanistic theory on polyisobutylene based tackifiers for mineral oil based systems will be presented first, and will be extended to vegetable based systems using the same mechanistic framework. The bio-based polymers studied are polyisoprene (PIP) and polybutadiene (PB). Because of their unsaturation these polymers possess both biodegradability and solubility in vegetable oils [2].

Discussion

The viscoelastic properties under shearing conditions differ for tackifiers and viscosity modifiers. The cohesive energy within the polymer, adhesive energy in polymer compatibility with the base oil concentration and molecular weight of the polymer all affect tackiness. This can be practically achieved by increasing the cohesive energy or cohesion of the lubricant while not substantially increasing its viscosity. As it is well known, adhesion is the attraction shared between several dissimilar molecules. It is then the joining (gluing) of different forms of matter together (see Figure 1). In other words, adhesion is the force that holds substrates together in opposition to stresses exerted to pull the substrates apart. Cohesion, on the contrary, is the force of attraction between similar molecules. It is simply the force that holds all molecules of one type of matter or object together (see Figure 2). Cohesion (or cohesive energy) is the attraction of particles within the tackifier molecules themselves that holds the tackifier mass together. This cohesive energy gives the tackifier its elasticity and stringiness property.

Fig. 1 – Adhesion (Courtesy [3M](#))

Attractive force between dissimilar surfaces

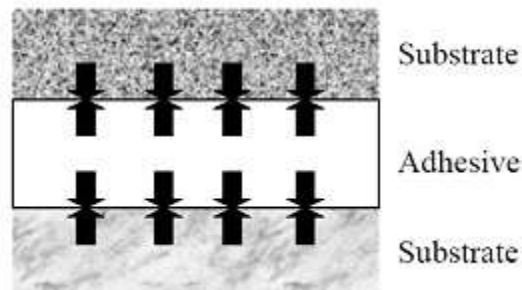
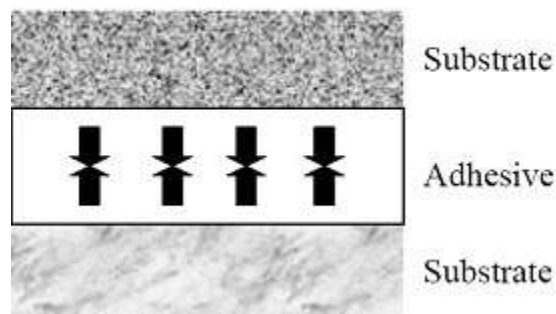


Fig. 2 – Cohesion (Courtesy [3M](#))

Internal strength of material

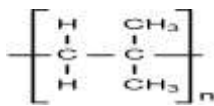
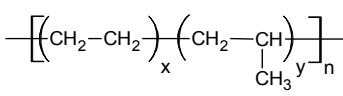
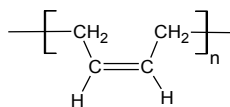
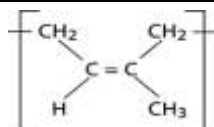


For polymer solutions to be tacky, the polymer chains should have the capacity to extend and to be of a high molecular weight. The cohesive energy then should be high allowing the molecules to extend and also, the base oil must be a good solvent for the polymer this allows the polymer chains to uncoil. For reasons that will be explained more fully below, the greater the degree of polymer uncoiling, the greater the tackiness for a given molecular weight.

The present article investigates the tackiness of very dilute solutions of polymer containing lubricants using the measurement technique of the open siphon method. The open siphon method [3] vertically withdraws tacky fluids from a graduated cylinder through a capillary tube which is connected to a vacuum pump. The capillary tube is placed just below the surface of the liquid in the cylinder. Vacuum is applied and the tacky liquid is pulled upward into the capillary and exhausted into a recovery flask. As the liquid surface in the cylinder drops below the end of the capillary a free jet (or string) is formed. More tacky fluids draw a longer string than less tacky ones, whereas non-tacky fluids are not drawn upwards into the capillary and no string is formed. The point at which the string breaks correlates with the Weissenberg number, where the shear forces overcome the cohesive energy of the polymer.

The following polymers have been selected for evaluation of tackiness using the open siphon method. These polymers below are compatible with their respective base oils, which will be discussed below.

Table 1. Polymer types

Polymers	Chemical structure	Oil Compatibility
Polyisobutylene (PIB)		Mineral Oil
Ethylene/ propylene copolymer (OCP) (saturated hydrocarbon)		Mineral Oil
Polybutadiene (PB) (unsaturated hydrocarbon)		Vegetable Oil
Polyisoprene (PIP)		Vegetable Oil

Experimental set up and procedure

The experimental device used in the open siphon method for testing tackiness of lubricating fluids is similar to those described in Refs. [4, 5, 11]. The setup is explained in Fig. 3 where the glass tube (capillary) with inner diameter of 1.58 mm and length 120 mm is connected to the common vacuum equipment. We use in the experiment vacuum pressures equal to 84 KPa. The graduated glass cylinder filled with the test fluid was of inner diameter 28mm and height 190mm. The maximum length of the free jet supported by the vacuum is recorded as the “string length”. in this experiment, we used an 0.025% (weight) PIB solution with a viscosity average molecular weight $M_{\eta} = 2.1 \times 10^6$ [6] in ISO 68 oil, which has viscosities $\eta_s \approx 0.138$, 0.0585, and 0.0073 Pa · s at 20, 40 and 100°C, respectively. Viscosities were measured by using capillary ASTM D 445 method. The density ρ_s of this oil at 25°C is equal 0.86 g/cm³. Surface tension γ_s at 20° is equal to 2.7 Pa · cm [7].

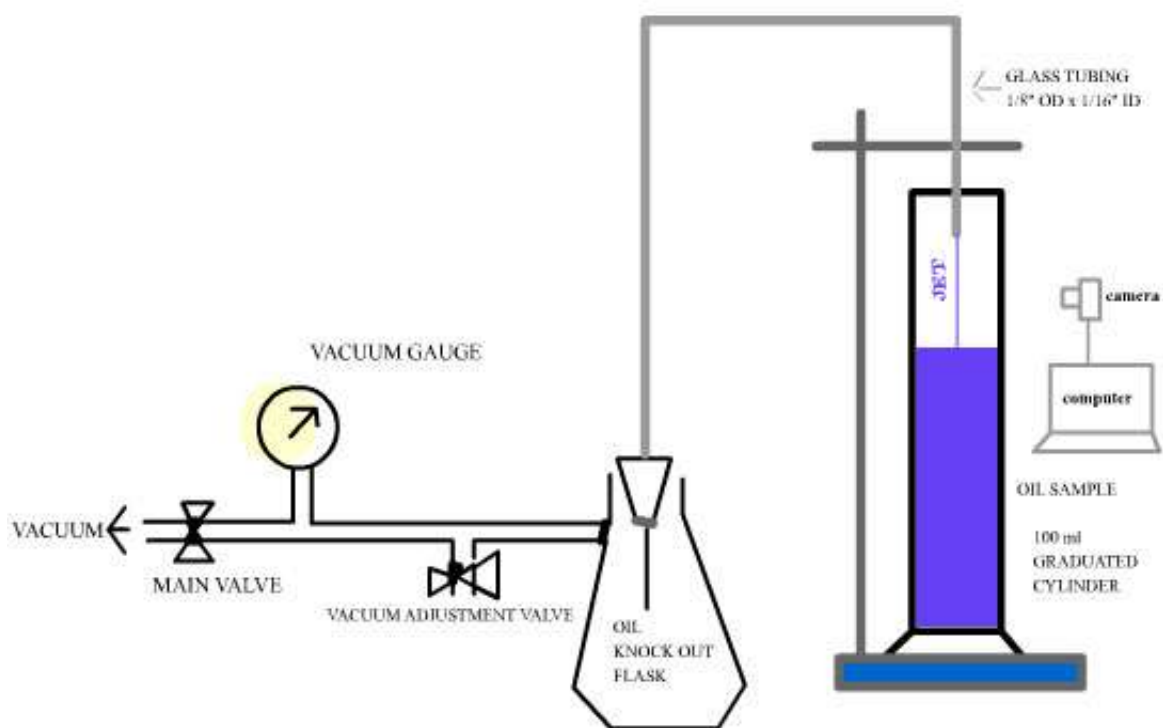
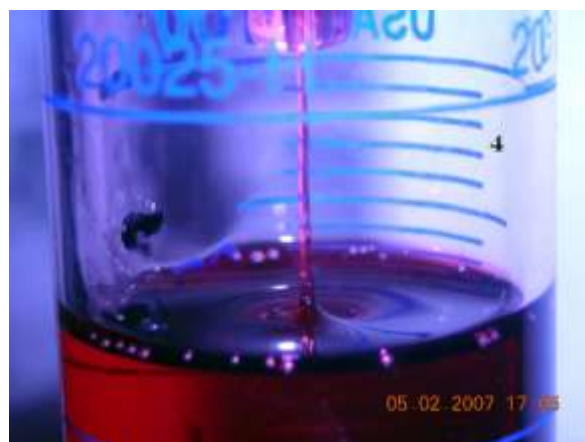


FIGURE 1

Figure 3 Experimental set up for testing and measuring tackiness.



Photographs of free tacky jets for 0.025% PIB solution in oil. (See Fig 7 b below)

Viscoelastic effects

What are viscoelastic fluids?

While the cohesive energy helps explain the polymer's thickening efficiency and tackiness, the viscoelastic properties help explain the limits to the polymer's tackiness and provide a technique to measure tackiness. Viscoelastic materials comprise a wide variety of materials which will snap back or revert back to their original shape after being stressed but lose a rather significant amount of energy along the way. During this period of energy loss, the time lag between when the stress is released and when the material fully snaps back is defined as the *relaxation time* (λ) in the material. This relaxation time is an important parameter because it defines a boundary between a solid-like response (like tearing or cracking) and a fluid like response (like pouring or flowing).

When the viscoelastic polymer is solubilized in dilute solutions, the tacky lubricant liquids can be characterized by three basic parameters, solvent viscosity η_s , the polymer volume concentration C , and relaxation time θ . It is well known that at the very small concentrations of polymer additives, the viscosities η of polymer solutions practically coincided with those η_s for the mineral oil solvents. Nevertheless, it is important to note that adding very small concentrations of PIB into the mineral oil dramatically increases the relaxation time θ of the solutions.

Elastic liquids are in an intermediate position between viscous liquids and elastic solids. They behave as viscous liquids at low applied external forces and as elastic solids when these forces are high. A well-known example is the child's toy- Silly Putty. It has the ability to be shaped and molded being quite pliable by hand. Like a viscous liquid it flows slowly and takes the shape of its container. If the Silly Putty is molded by hand into a ball shape and thrown onto the floor it will bounce like a ball or if the ball is hit with a hammer the ball will shatter like glass, being an example of an elastic solid. This type of behavior of an elastic liquid is commonly estimated by the non-dimensional Weissenberg number We . In extensional flows, including the problem of liquid withdrawal from a cylinder by a capillary tube, the Weissenberg formula is presented as [8]:

$$We = \theta \cdot \dot{\epsilon}$$

The Weissenberg number is a measure of the strength of the shear rate or the force required to cause the shearing [9]. Here $\dot{\epsilon}$ is the elongation rate or the velocity gradient in the direction of extension (withdrawal). When extensional rate is low $We \ll 1$ a viscoelastic liquid behaves as a viscous one. In the opposite case when $We \gg 1$, the solid-like properties of viscoelastic liquids dominate and they behave as elastic solids. Along with well-known basic facts, many elastic liquids display a fast transition from the liquid-like to the solid-like behavior when passing through a certain threshold We_c in the Weissenberg number. This phenomenon called the fluidity loss, has been well documented for narrowly distributed polymers and treated as a relaxation transition [8]. The underlying physics of this transition as discussed in reference [8] is that the highly oriented polymer molecules in certain flows create physical cross-links which cause effective gelation of the polymer. In case of withdrawal of dilute polymer solutions the fluidity loss effect assumed in Refs. [8, 9] could also be caused by an increase in the polymer concentration in intense extensional flows near the axis of extension. This might happen because the fluid trajectories in extensional flows cause the polymer macromolecules to closely approach each other.

To develop a formal model of the dynamics involved in the withdrawal of a tackifier in an oil solution using the open siphon technique, we introduce the vertical coordinate z , which coincides with the jet centerline and is counted off the moving free surface (Fig.7B). The X coordinate is a centerline parallel to the surface of the liquid. The Y coordinate is in the same plane as the X , but perpendicular to it. So the origin $z = 0$ is located at the free surface, and the upper coordinate $z = l(t)$ at the capillary entrance indicates the length of visible jet at time t . It is convenient for theoretical treatment to roughly separate the whole domain of the liquid flow in the three regions: region 3 $\{z < 0\}$ located under the free surface, meniscus region 2 $\{0 \leq z \leq R(t)\}$ located from the free surface up to the end of meniscus, and the region 1 of free jet motion $\{R(t) \leq z \leq l(t)\}$. Here the functions $R(t)$ and $l(t)$ are unknown and have to be determined. Basic flow effects which occur in the three regions of flow could be qualitatively described as follows [8-10].

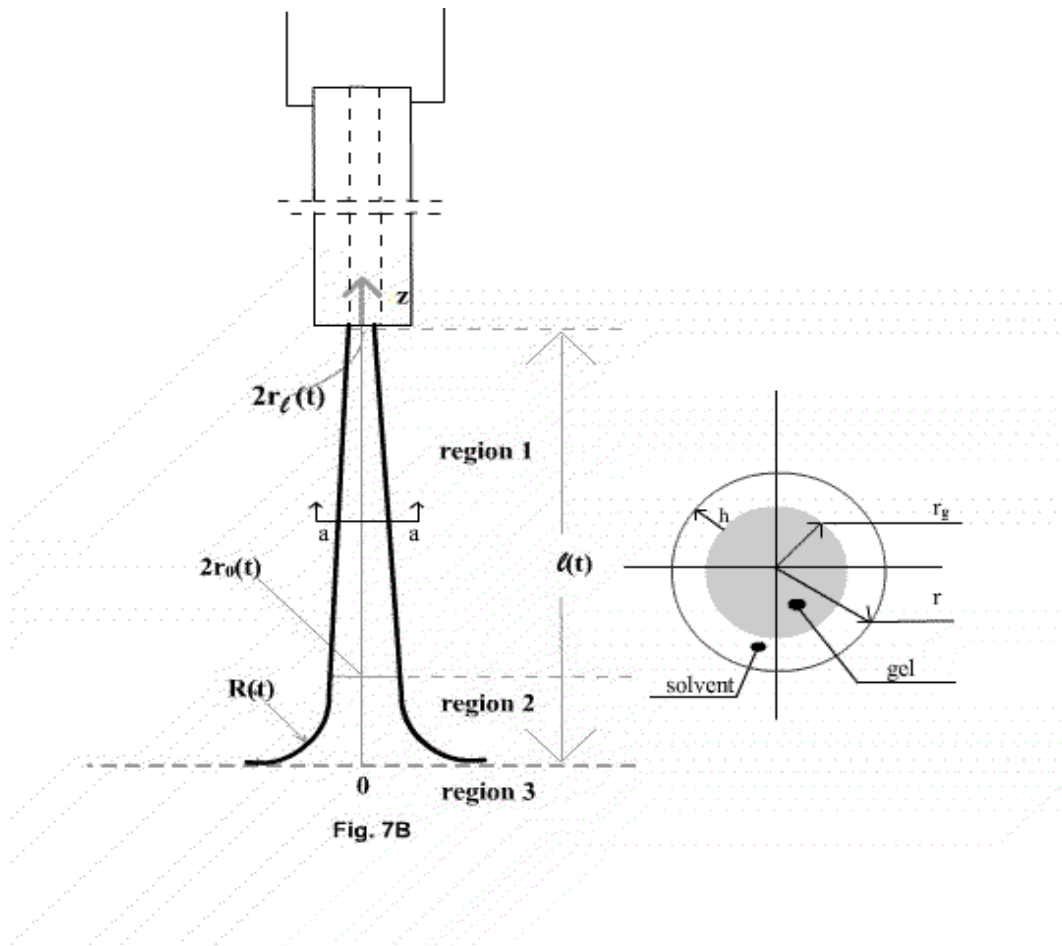


Fig. 7B

In region 3, the withdrawal of liquid by vacuum through the capillary causes a specific extensional flow under the surface of the liquid at the vortex. This flow, slowly changing in time, looks like an effective undersurface jet which narrows from the bottom to the surface. Therefore the vertical velocity of jet and the characteristic extensional velocity gradient $\dot{\epsilon} \approx dV/dz$ are increased when approaching the surface from below. Substituting this value of $\dot{\epsilon}$ into the Weissenberg equation

explains the increase in the Weissenberg number, which might cause the relaxation of the fluid-solid transition. It was speculated in Refs. [6,8] that the complete relaxation transition happens in the region 2, where still viscoelastic polymer solution forms a free jet which is squeezed under additional action of surface tension. In region 1 the free jet can be treated as an elastic gel swollen in solvent, which has a string-like shape, and is under the action of extensional force, gravity and surface tension [10, 11].

In this case of withdrawal of dilute polymer solutions, an additional effect of strain induced exudation of solvent should also be taken into account. Although the kinetics of this process is unknown, the flow of a thin film of solvent covering the gelled jet, swollen in the solvent, is guessed to be much the same as in case of thin film withdrawn from a vessel by a vertically moving plate moving upwards, i.e. controlled by the vertical drag speed, viscosity, gravity and surface tension [10].

Using open siphon method for evaluation of tackiness of lubricating fluids

As mentioned before, the tackiness (as measured by the jet length) strongly depends on the viscosity of oil, molecular weight of dissolved polymer and its concentration in solution. Fig.4 shows the dependence of jet length l on the concentration of PIB with $M_{\eta} \approx 2,000,000$ in two paraffinic oils with respective viscosities 0.068 and 0.022 Pa · sec at 40°C.

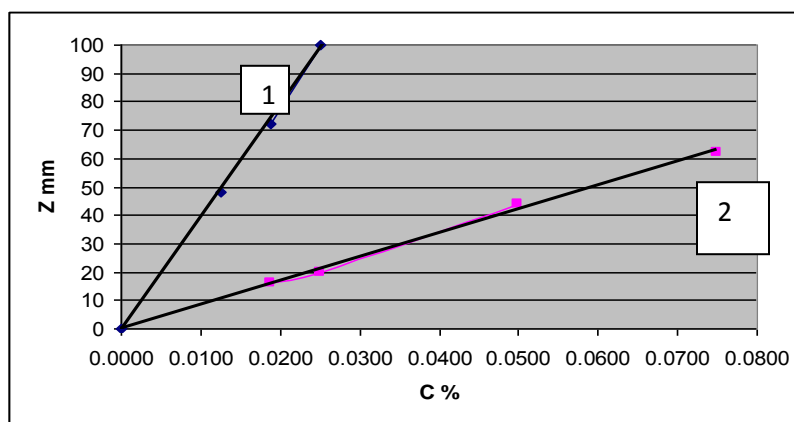


Fig.4. Ultimate jet length, l (Z mm) versus the concentration, C%, of PIB with $M_{\eta} \approx 2,100,000$ in two paraffin oils with respective viscosities 0.068 and 0.022 Pa · sec at 40°C.

One can see, the relationship between tackiness and polymer concentration in differing oils are linear, regardless of molecular weight. It is clear from Fig.4 that a lower viscosity oil s with the same concentration of polymers accompanied by a large decrease in tackiness. For example at a concentration 0.025% of PIB the jet length in oil with viscosity 0.068 Pa · sec is equal to 100 mm, whereas in oil with a viscosity 0.022 Pa · sec it is equal to 20 mm, i.e. 5 times less than in the first case.

Data presented in Fig.5 demonstrates what the concentration of PIB with different molecular weights in oil with a viscosity of 0.068 Pa · sec should be to reach a jet length of 100 mm. It is seen that by simply increasing the molecular weight it is possible to substantially increase the tackiness. It is known that, increasing the molecular weight causes, however, a decrease in both thermal/oxidative stability and shear stability [13].

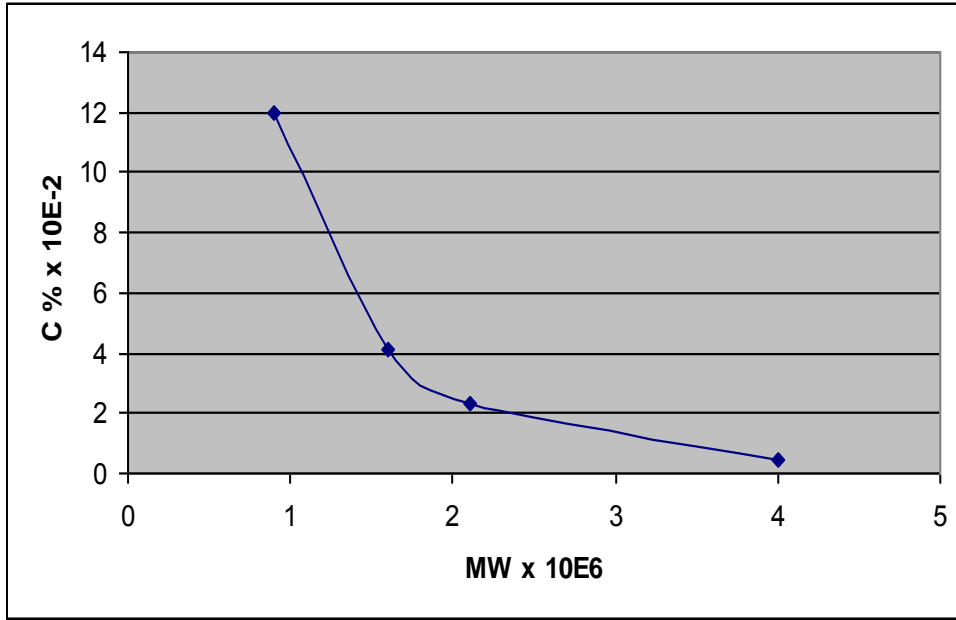


Fig.5. Concentration $C\%$ of PIB in oil with viscosity $0.068 \text{ Pa} \cdot \text{sec}$ corresponding to the jet length $l = 100 \text{ mm}$ versus viscosity average molecular weight M_η of polymer.

Combining the data presented on Figs. 4 and 5 it is possible to evaluate the jet length or tackiness for PIB solutions with different molecular weights and at different polymer concentrations. The chart above holds the string length of the jet constant. Fig 5 indicates that a greater molecular weight polymer at a low concentration imparts the same amount of tack as a low mw polymer at a high concentration.

In our studies, a curious attribute was learned. Unlike PIB's commonly used as tackifiers, the ethylene/propylene copolymers usually do not display tackiness. Nevertheless we obtained some unusual data for the blend of PIB with $M_\eta \approx 2,000,000$ with very small additive of ethylene/propylene copolymer. Fig. 6 demonstrates that adding 0.01% of the copolymer to the PIB solution increases the jet length by about 30%. It should also be mentioned that addition of 0.01% of copolymer to the solution of 0.025% of PIB practically does not change viscosity of the solution. As seen from Fig. 6, at higher concentration of the copolymer in PIB solutions the tackiness decreases.

This effect might be explained as follows. Solutions which have 0.01% of copolymer could be considered as very dilute, with macromolecules well separated. During flow induced orientation of long flexible PIB chains, much shorter and more rigid molecules of copolymer are involved in a process of orientation and this supports and oriented PIB macromolecules, causing an increase in tackiness. With an increase in the concentration of copolymer, macromolecules form ensembles, which could not be

involved in the orientation process and this could restrict the orientation of PIB macromolecules and therefore decrease tackiness.

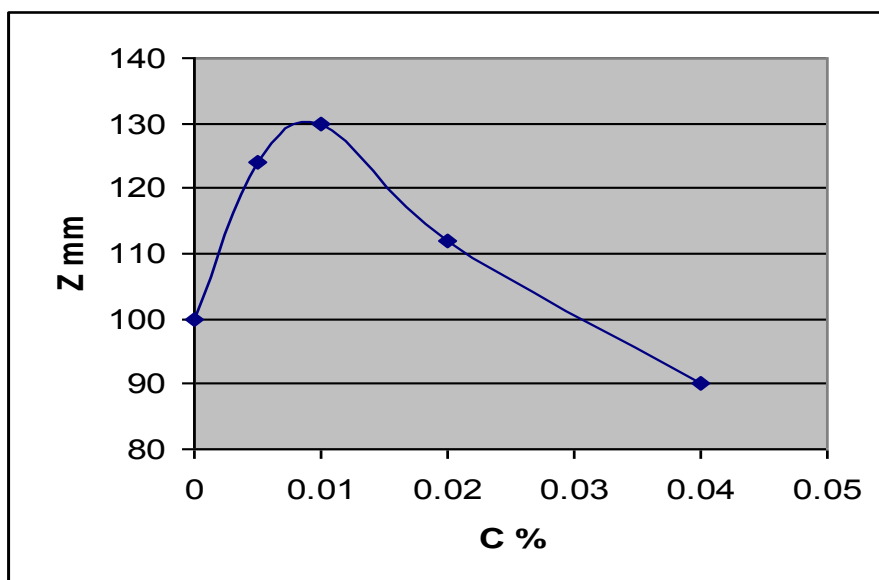


Fig.6. Tackiness effect versus concentration of ethylene/propylene copolymer added to the 0.025% PIB solution in lubricant oil.

String length data for Polyisobutylene / Mineral Oil solutions

Product	Diluent	Polymer	Viscosity, cSt at 100°C	Shear Stability	Stringiness
V-162	Paraffinic	PIB	1800	Good	Good
V-172	Paraffinic	PIB	4000	Very Good	Good
V-172E	Paraffinic	PIB	2800	Very Good	Good
V-174	Paraffinic	PIB	800	Good	Good
V-176	Paraffinic	PIB	2900	Good	Good
V-177	Paraffinic	PIB	10500	Good	Good
V-177L	Paraffinic	PIB	6800	Good	Good
V-178	Paraffinic	PIB	4000	Good	Good
V-178E	Paraffinic	PIB	2100	Good	Good
V-184	Naphthenic	PIB/OCP	4000	Very Good	Good
V-188	Paraffinic	OCP	4000	Excellent	Fair
V-189A	Paraffinic	OCP	1300	Excellent	Fair
V-198A	Paraffinic	PIB	4000	Poor	Excellent

Table 2. Industrial Lubricant Tackifiers in Petroleum Oils

Application to Bio-Based tackifiers

The same mechanistic theory developed for polyisobutylene polymers in petroleum oil (where we considered the polymer's molecular weight, relaxation transition, cohesive energy, the polymer concentration, and base oil compatibility) can be applied to bio-based tackifiers. Therefore the mechanistic theory will not be discussed again. The basic necessities are polymer solubility and a sufficiently high molecular weight.

Polymer compatibility in biobased oils

The mechanism of the mode of thickening of viscosity modifiers is associated with the hydrodynamic volume that the polymer chain occupies in the oil [13]. Polymers typically consist of a long molecular chain and a high molecular weight compared to the base oil. The base oil is the solvent for the polymer. The polymer chain forms a coil in the solvent. The polymer coil size depends on the solubility of the polymer in the solvent. Solubility is governed by many factors including Van der Waals forces, i.e., fluctuations in the polarizations of nearby molecules, chemical affinity for other polar atoms present in the polymer and the base oil. Also, steric effects, temperature and pressure affect the solubility of polymers. Polymer molecular chains can be nearly fully extended in a good solvent and form a large coil or not extended and form a small coil as in a poor solvent. The large coil not only occupies more hydrodynamic volume but also has the tendency to entangle with each other and generate more friction between molecules during the flow, as a result, it gives a fluid with a high viscosity. For most polymers, the solubility between polymer and base oil is increased at higher temperatures as illustrated in Figure 8. Higher temperatures favor a more fully extended polymer hence a larger hydrodynamic volume.

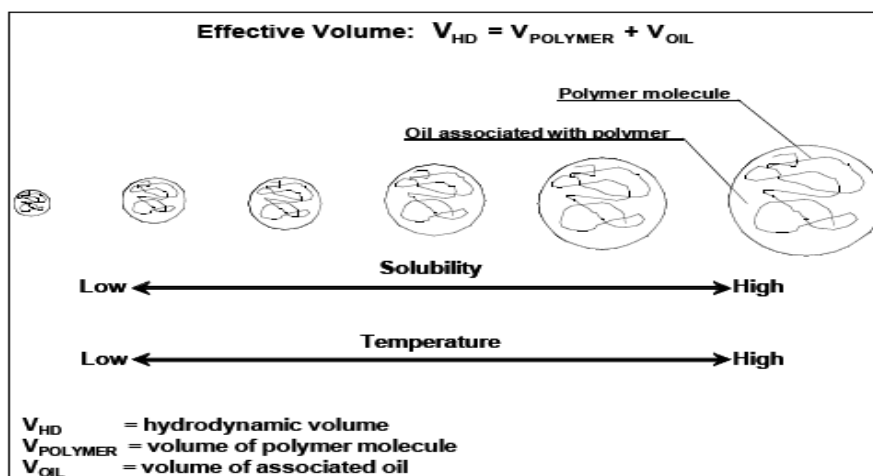


Fig.8. Illustration of the solubility of polymers in oil at different temperatures

Another aspect of polymer solubility is association of like structures. In particular for PB and vegetable oil one can describe the orientation of groups around the double bonds. (Figure 9) The Latin prefixes *Cis* and *Trans* describe the orientation of the hydrogen atoms with respect to the double bond. *Cis* means "on the same side" and *Trans* means "across" or "on the other side". Naturally occurring fatty acids generally have the *Cis* configuration. For example, the natural form of 9-octadecenoic acid (oleic acid) found in olive oil has a "V" shape due to the *Cis* configuration at position 9. The *Trans* configuration (elaidic acid) looks more like a straight line. PB has a minimum of 40% *Cis* and vegetable oil is around 97% *Cis*. (Figure 9) Similarity of conformations allows for more efficient packing and alignment of like structures in molecules thus better solubility.

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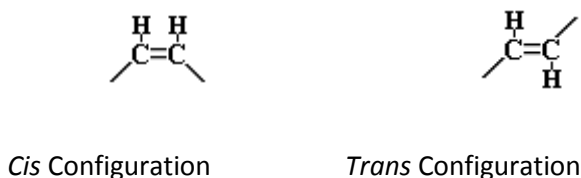


Fig 9. Cis/Trans configuration of double bonds

String length data for Bio-based polymer/Base oil solutions

This test data was created in the same manner as testing polymers in mineral oil, using the ductless siphon method to determine the point where the cohesive energy fails.

Product	Diluent	Viscosity, cSt at 100°C	Shear Stability	Stringiness
V-570	Vegetable	8000	Good	Fair
V-572	Vegetable	7500	Fair	Good
V-584	Vegetable	2500	Poor	Excellent

Table 3. Industrial Lubricant Tackifiers in Vegetable Oils

Conclusions

This article applies the open siphon method for evaluations of tackiness of several lubricant oils. In these experiments, a capillary tube assisted by vacuum withdraws a vertical free jet of liquid from a graduated cylinder. Dilute solutions of polyisobutylene (PIB) of different molecular weights and polymer concentrations in a lubricating oil, as well as the blends of PIB with ethylene-propylene copolymer were used in these experiments. The tackiness of lubricant fluids was quantified by the ultimate length of free jet (string) just before the string breaks. Several specific phenomena were observed in the experiments, such as solvent exudation out of extended jet and a maximum for the tackiness for solutions of blends with polyisobutylene as the tackifier and with OCP polymers as the non-tackifier. Also, it was shown that different base oil viscosities can affect the ultimate string length of a tackifier. It has also been shown that polymer structure and molecular weight is very important in determining the tackiness or the string length of bio-based polymers.

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