NLGI
Serving
the grease
industry
since 1933

India Chapter
ISSN : 0972-2742

GREASETECH INDIA

A Quarterly Journal of NLGI-India Chapter

Vol. XXV, No. 2, Oct - Dec 22

GREASETECH INDIA

A Quartely Journal of NLGI-India Chapter

Vol. XXV, No. 2, Oct - Dec 22

In This Issue Page No

1. Effect of the presence of other additives on EP additive performance Lithium and Lithium Complex Greases 3-20
2. Low Temperature Fluidity of Polymer-Modified Greases 21-43
3. Evaluation of EP Components for Gear Oil Packages 44-52
4. Impact of Friction Modifiers and Viscosity Modifiers in the formulation of Energy Efficient Automotive Gear Oils 53-69

Effect of the presence of other additives on EP additive performance -Lithium and Lithium Complex Greases

Vennampalli M., Kumar V., Yadav K.N., Pokhriyal N. K., Harinarain A. K., and Saxena D.
Indian Oil Corporation Limited, R&D Centre

Abstract-

Extreme pressure (EP) performance is an important property of lubricating greases which is required to avoid scuffing and seizure of mating surfaces under high load. Number of different additive types such as antioxidants, corrosion inhibitors, antiwear, solid additives etc are used in combination with EP additives to meet the desired application requirements. The additive-additive interactions play vital role in determining final performance of the grease. These interactions can be synergic or antagonistic in nature. Antagonist interactions could lead to increase in friction, wear and eventually welding. Tuning of the combination is desired to make effective formulation.

In the present study we have studied effect of different corrosion inhibitors on different EP additives in Lithium and Lithium complex greases. Effects of the different combinations were evaluated with four ball EP and wear tests, Rheometry and dynamic and static corrosion tests. Effect processing temperature and addition sequence were also discussed.

Key words – Lithium Grease, Additive interactions, EP greases, antagonist effect.

Introduction

In lubrication formulations additives are generally incorporated to improve certain desired properties, suppress some undesired properties and add certain special properties of the lubricant[1]. In formulating lubricants optimization of the additive system plays a vital role. To achieve different requirements combined use of different additive types such as antioxidants, corrosion inhibitors, extreme pressure, antiwear, solid additives etc has been well known for many years [2].

Figure1: Soap based lubricating grease structure

As shown in Figure 1, in lubricating greases particularly soap based greases are postulated to have a three-dimensional network of thickener particles which is acts like a sponge and on shear stress releases oil to perform the lubrication. Unlike oil based lubricants in greases; additive molecules will be trapped inside the sponge like 3D network of thickener and may need higher dosages comparably to reach the metal surface. In grease some additives (Figure 2) work in bulk such as anti oxidants, dropping point enhancers and scavengers while many work at metal surface such as extreme pressure, anti wear, corrosion inhibitors, metal deactivators and friction modifiers etc[3,4].

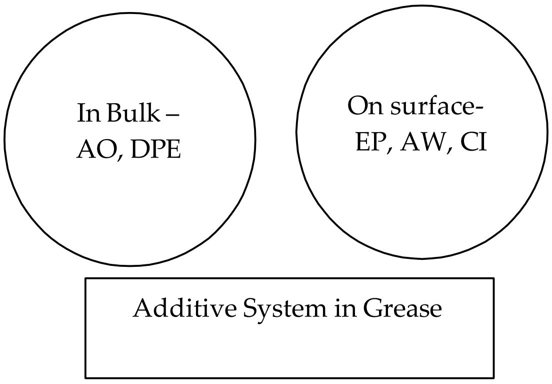


Figure2: Lubricant additive types functioning in grease

Unlike oil based systems where packages recommended by OEMs are mostly used, lubricating greases are generally formulated using different additive combinations to achieve desired formulations. The synergistic and antagonistic effects of various chemicals involved in system will decide final outcome of grease performance. The required performance depends on the application, dosage, temperature, effect of other components in the system. Additive suppliers suggest details on additives with dosages wrt application. Some additives are of multipurpose type such as ZDDP. Many times additives using for one purpose may show negative effect on other performance like effect of corrosion inhibitors (CI) on EP performance. Water resistance improvement by addition of polymers may affect low temperature properties and use of low viscosity and highly refined base oils may affect water resistance and thickener content etc. In another situation where EP and antiwear additives used, competition for forming layers on metal surface may cause domination of one additive over the other one resulting in suppression of weaker additive property[5, 6].

The final performance output of particular additive/s system depends on base oil and thickener system also. It is very crucial to consider all the components of the formulation that affect the grease performance in designing effective formulation. In development of high performance multipurpose greases tuning of multi component additives to optimize many properties such as extreme pressure, corrosion inhibition, low temperature and water resistance etc required. In industrial applications where high load and low speed situations exists greases required to have high load carrying capacity. Grease having good extreme pressure (EP) properties is required to avoid scuffing and seizure of mating surfaces under high load[6].

Mostly the EP required applications involve outdoor-use or exposure to humidity, water, moisture and marine exposure may risk deterioration of bearings from corrosion. In such applications greases should contain additives EP enhancers and corrosion inhibitors. Both the additive systems work at metal surface and at contact asperities leading to a competition in binding on the surface. Some of EP & antiwear additives affect structural stability of the grease also. Study of the interaction of corrosion inhibitors with EP additives is very crucial to understand and design formulations meeting lubricating greases withoptimized performance at both EP and corrosion properties. In this work to understand additive-additive integrations, we have studied EP and CI additives combinations in commonly used greases.

The most popular soap based greases are lithium and lithium complex prepared in API group-I mineral base oils. In the present study we have studied effect of different corrosion inhibitors on different EP additives in Lithium and Lithium complex greases with API group-I mineral base oils of ISO VG 150 viscosity. Effects of the different combinations were evaluated with four ball EP, dynamic, static corrosion tests and rheological studies.

EP additives are of different types such as fatty acids, chloride, sulfur and phosphorous based. Activation of the EP additives depends on the temperature as shown in the Figure 3[7]. Most of these EP additives are in liquid state and sometimes solid additives also used. As mentioned by Dr. Fish choice of liquid/oil soluble and solid additive is determined mostly by application requirement[8]. For high-speed applications solid additives may be thrown out due to density differences which lead to grease leakage. In High speed applications use of liquid additives is recommended, while in low speed, high load applications where mostly boundary lubricant condition prevails, solid lubricant such as molybdenum disulfide would work better.

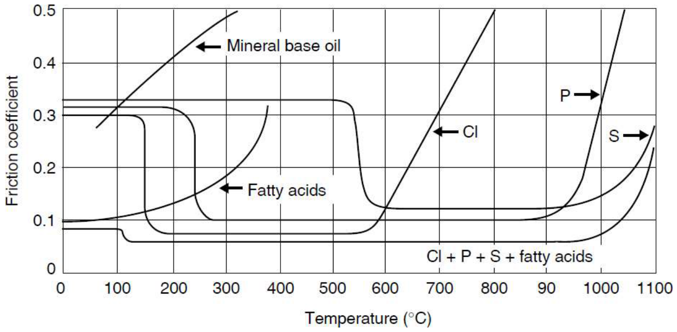


Figure 3: Activation profile of different EP additives with temperature

There are many types of EP and corrosion inhibitors, multipurpose additives. Several groups, additive manufacturers published literature on their chemistries and applications. As described by K. Mistry *et al* in their study on corrosion inhibitor interacting extreme pressure or anti-wear additives on steel surface, the effectiveness of EP additives depends mainly on corrosive wear[9]. Corrosion is a well known an electrochemical reaction between anodic metal surface and the lubricant which work as cathode. In presence of oxygen and water on metal surface, cathodic and anodic electrochemical reactions will initiate resulting in corrosion(Figure 4). Corrosion inhibitor due to their affinity to the metal approach the surface and form metal deactivating film, a passive film that chemically insulate the metallic anode from the cathode on the contact surface which can control the reaction rate by separate the metal surfaces from oxygen and water thus prevent the reactions, preventing corrosion [1, 10 & 11].

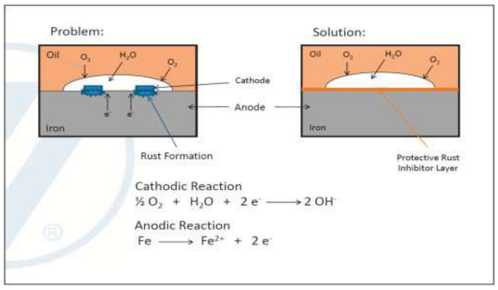


Figure 4: Schematic representation of corrosion and protective CI layer formation.

Since both EP and CI additives work on metal surface competition for binding space will arise. The competition between EP additive and CI additive for metal surface is very crucial in determining final performance the system. As mentioned by J Kaperick corrosion problems are complicated and mostly dependent on the application and but additive combination that work synergistic may required[3].

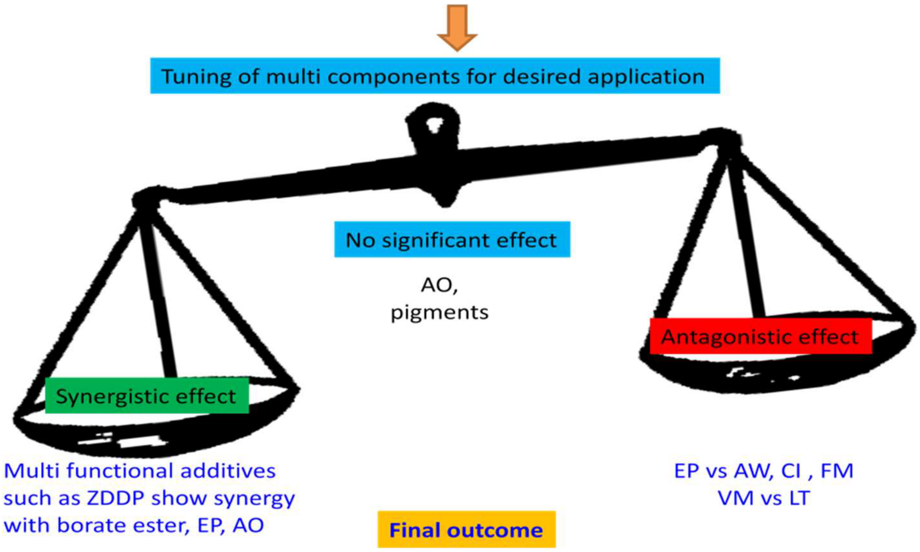


Figure 5: General additive-additive interactions

Materials

Lithium and Lithium complex greases were processed using ISO VG 150 grade mineral oil. Lithium greases made with lithum hydroxide mono hydrate and 12-hydroxy stearic acid(12-HSA) while in lithium complex greases azelaic acid was used as complexing acid. Regular commercial EP, corrosion inhibitors were used for making different combinations.

EP additives: EP-1: Sulfurised Olefin(SO), **EP-2**: Antimony dialkyl dithiocarbamate(SbDTC) and **EP-3**: Molybdenum disulfide (MoS_2)

Corrosion Inhibitors: CI-1: Amine Phosphate(AmPh) **CI-2**: Half Ester of Succinic Acid(HESA), and **CI-3**: Barium Sulfonate(BaSul).

Equipment

Standard equipment conforming to ASTM and IP test methods was used for evaluation of physical and chemical properties such as dropping point (ASTM D2265), penetration (ASTM D217), copper corrosion (ASTM D4048), static rust preventive properties (ASTM D1743), dynamic anti corrosion test (EMCOR, ASTM D6138), four ball weld load (IP 239), four ball wear scar diameter (ASTM D2266), and roll stability (D1831). Rheometry was performed using a 3-plate and ball geometry Tribocell attached to MCR 301 Anton Paar viscometer using upgraded Rheoplus software.

Procedure

Figure 6: General scheme for making EP and CI additive combination.

All greases were prepared by batch (4 kg) process in a pressure reactor. The processing temperature was increased by one degree per minute, and the final temperature for lithium greases was 200 °C while lithium complex greases 225 °C. Additives were blended in grease at 90 °C and mixed for 30 minutes and homogenized to get final grease. General schematic representation for making EP and CI additive combination is given in Figure 6.

Data, Observations, Results and Discussion

In the present study we have used two liquid EP additives namely Sulfurised olefin and Antimony dithiocarbamate and one solid additive MoS_2 which are very commonly used in grease formulations. The corrosion inhibitors selected are also very commonly used additives amine phosphate, half ester of succinic acid and barium sulfonate. As shown in Figure 6, Lithium12-HSA base grease was treated with EP additive and homogenized to get Li-EP-Gr, which was treated with CI additive to get final Li-Gr-EP- CI.

	SO	SbDTC	MoS_2	AmPh	HESA	BaSul
Li-Gr –EP-1	2.00					
Li-Gr –EP-1+CI-1	2.00			1.50		
Li-Gr –EP-1+CI-2	2.00				0.50	
Li-Gr –EP-1+CI-3	2.00					1.50
Li-Gr –EP-2		2.00				
Li-Gr –EP-2+CI-1		2.00		1.50		
Li-Gr –EP-2+CI-2		2.00			0.50	
Li-Gr –EP-2+CI-3		2.00				1.50
Li-Gr –EP-3			2.00			
Li-Gr –EP-3+CI-1			2.00	1.50		
Li-Gr –EP-3+CI-2			2.00		0.50	
Li-Gr –EP-3+CI-3			2.00			1.50

Table 1: EP and CI additive compositions in Lithium grease

As shown in Table 1 and Table 2 EP additive treated at 2wt% while CI additives amine phosphate and barium sulfonate at 1.5 wt% and half ester of succinic acid at 0.5wt%. The additive treat rates are chosen based on additive supplier recommended dosages. Based on the outcome further tuning of concentrations will be studied. Details of the evaluation and results will be discussed based on EP additive type.

	SO	SbDTC	MoS_2	AmPh	HESA	BaSul
Liplex-Gr –EP-1	2.00					
Liplex -Gr –EP-1+CI-1	2.00			1.50		
Liplex -Gr –EP-1+CI-2	2.00				0.50	
Liplex -Gr –EP-1+CI-3	2.00					1.50
Liplex -Gr –EP-2		2.00				
Liplex -Gr –EP-2+CI-1		2.00		1.50		
Liplex -Gr –EP-2+CI-2		2.00			0.50	
Liplex -Gr –EP-2+CI-3		2.00				1.50
Liplex -Gr –EP-3			2.00			
Liplex -Gr –EP-3+CI-1			2.00	1.50		
Liplex -Gr –EP-3+CI-2			2.00		0.50	
Liplex -Gr –EP-3+CI-3			2.00			1.50

Table 2: EP and CI additive compositions in Lithium complex grease of the present study

Sulfurised olefins: In combination with CI additives amine phosphate, Half ester of Succinic acid and Barium Sulfonate

Sulfurised olefins are regularly used as EP additives which contain sulfur that gives EP properties[12, 13]. Sulfur releases out through thermal decomposition mechanisms at high temperatures and load which forms iron sulfide intermediate that carries load and work as sacrificial layer to protect from seizure. Active sulfur in the SO additives results in copper as well as steel corrosion. To overcome the corrosion with SO additives it is required to add corrosion inhibitors and copper passivators. As discussed above both EP and CI additives work at metal contact surface they compete for positioning on the surface. This antagonistic effect obviously leads to suppression of properties of each other. It is very crucial to optimize additive CI additives which may not work antagonistic or minimal antagonistic effect.

As shown in Table-1 LiVG150 base grease is in harder side of NLGI grade 2 and weld load of 140 Kg and shows poor corrosion properties which is needed to be boosted with additives. The lithium base grease was treated with 2wt % of sulfurised olefin to get **Li-Gr –EP-1** and tested for general physical-chemical properties. **Li-Gr –EP-1** grease was found to be in grade 2 consistency with around 10 units increased consistency. Weld load found to be 280 Kg and corrosion properties become detrimental while other properties such as roll stability, oil separation, dropping point do not show significant variation. As shown in **Table -3** and **Figure 7**, **Li-Gr-EP-1** which contains 2wt% sulfurized olefin found to give 280 Kg weld load and the static and dynamic corrosion test showing severe corrosion. Li-Gr –EP-1+CI-1 where amine phosphate was used as CI additive, corrosion resistance to EMCOR in presence of distilled water and salt water got improved significantly. On the other hand the four ball weld load was found to down by two stages. The results indicate that the interaction between additives or competition for the surface may result in antagonistic effect to reduce the EP properties significantly. **Li-Gr –EP-1+CI-2** containing half ester succinic acid showed improved corrosion resistance but lowered weld load to 180 Kgs indicating competition for surface active layering as half ester of dioic acids being surface active are known to quickly bind surface to form protective layer. **Li-Gr –EP-1+CI-3** containing barium sulfonate as CI additives found to significantly lower the weld load by two stages and water resistance of the grease also became poor. This result indicating that sulfonate CI additive not only working on surface for competition with SO but also in bulk as absorbent of water to emulsify grease. The results are showing clearly that in presence of CI additives EP additives have shown lower performance. Other properties such as consistency, dropping point, mechanical stabilities of greases are not affected much.

Property	Method	**Li-VG150 Base Grease**	**Li-Gr – EP-1**	**Li-Gr – EP-1+CI-1**	**Li-Gr - EP1+CI-2**	**Li-Gr - EP1+CI-3**
Worked penetration, 0.1 mm	ASTM D217	268	277	271	280	285
Roll Stability, 16h, RT, % change in penetration from P60	ASTM D1831 (modified)	11.9	12.1	13.8	11.5	16.9
Dropping Point, °C	ASTM D566	196	196	193	194	194
Copper corrosion, rating	ASTM D4048	1b	2c	1a	1b	1a
Corrosion preventive properties, Distilled water, rating	ASTM D1743	Fail	Fail	Pass	Pass	Pass
Corrosion preventive properties, 3% NaCl solution, rating	ASTM D1743	Fail	Fail	Fail	Fail	Pass
Oil separation, %	ASTM D6184	1.6	1.3	1.1	1.6	1.3
Water washout	ASTM D1264	2.5	3.3	2.3	2.9	10.9
Weld Load, Kg	IP 239	**140**	**280**	**200**	**180**	**200**
Wear Scar Diameter, mm	ASTM D2266	0.70	0.60	0.55	0.55	0.60
EMCOR, Distilled water, rating	ASTM D6138	**2,2**	**3,3**	**0,0**	**0,0**	**0,0**
EMCOR, 3% NaCl solution, rating		**4,4**	**4,4**	**1,1**	**2,1**	**2,2**

Table-3: Evaluation of sulfurised olefin in combination with CI additives amine phosphate, half ester of succinic acid and barium sulfonate in lithium greases.

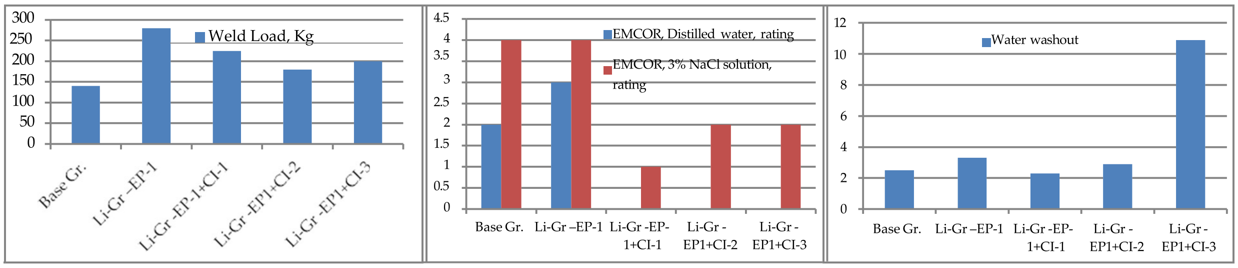


Figure 7: Weld load, EMCOR and water washout results with sulfurised olefin in combination with CI additives amine phosphate, half ester of succinic acid and barium sulfonate in lithium greases

In continuation of the same additive system in lithium complex grease, we have prepared blends as shown in Table 2 and evaluated. The weld load of **Liplex-Gr -EP1** found to be 315 kg while **Li-Gr -EP1** shown 250 Kg, which showing there is significant effect of complex thickener system over simple lithium 12HSA thickened grease. When the complex grease was treated with CI additives, weld load was reduced by 1-2 stages and corrosion resistance improved significantly. The study indicates that while using SO as EP additive CI additive optimization is required to get final performance of the grease. In salt water corrosion amine phosphate CI worked better compared to half ester of succinic acid while barium sulfonate grease corrosion resistance increased but water washout shown to be affected.

Property	Method	**Liplex-Gr - EP1**	**Liplex-Gr - EP1+CI-1**	**Liplex-Gr - EP1+CI-2**	**Liplex-Gr - EP1+CI-3**
Worked penetration, 0.1 mm	ASTM D217	268	272	277	280
Roll Stability, 16h, RT, % change in penetration fromP60	ASM D1831 (modified)	17.2	16.9	21.0	18.8
Dropping Point, °C	ASTM D566	271	274	267	272
Copper corrosion, rating	ASTM D4048	1b	1a	1a	1a
Corrosion preventive properties, Distilled water, rating	ASM D1743	Fail	Pass	Pass	Pass
Corrosion preventive properties, 3% NaCl solution, rating	ASTM D1743	Fail	Pass	Fail	Pass
Oil separation, %	ASTM D6184	1.1	0.9	1.2	1.0
Weld Load, Kg	IP 239	315	280	250	280
Wear Scar Diameter, mm	ASTM D2266	0.65	0.55	0.60	0.55
EMCOR, Distilled water, rating	ASTM D6138	2,2	0,0	0,0	0,0
EMCOR, 3% NaCl solution, rating		4,4	1,1	1,2	0,1

Table-4: Evaluation of Sulfurised olefin in combination with CI additives amine phosphate, Half ester of Succinic acid and Barium Sulfonate in lithium complex greases.

The results indicating that when treated with only EP booster additive weld load increased to at the highest level of the EP additive capacity, but resulted in corrosion test failure. On the addition of CI additives competition for surface binding resulted in compromising of some EP efficiency. Amine phosphate worked better in corrosion inhibition and minimum effect on sulfurised olefin EP performance. This finding will be useful in selecting EP+CI combination for further study with other additive combinations.

Antimony dithiocarbamate with CI additives:

Dithiocarbamates are used as mutifucntional additives and particularly as EP and AW additives[14]. Antimony dithiocarbamates are special class of EP additives which having certain advantages over sulfurized olefins wrt lack of pungent smell and low corrosion issues.[ref] Mixed metal dithiocarbamates are also used as better multifunctional additives but in this study we have used antimony dialkyl dithiocarbamate only as EP additive. In the present study, as shown in Table 1 **Li-Gr –EP2** prepared by addition of 2wt% of SbDTC, as expected the weld load of the grease increased to 315 Kg but severe corrosion occurred in static and dynamic corrosion tests. With introducing CI additives corrosion resistance increased. It is found that SbDTC working better with half ester of succinic acid both corrosion resistance and EP properties.

S. No.	Method	**Li-Gr –EP2**	**Li-Gr –EP2+CI-1**	**Li-Gr –EP2+CI-2**	**Li-Gr –EP2+CI-3**
Worked penetration, 0.1 mm	ASTM D217	281	285	288	282
Roll Stability, 16h, RT, % change in penetration from P60	ASTM D1831 (modified)	12.6	14.1	15.1	13.9
Dropping Point, °C	ASTM D566	202	198	200	202
Copper corrosion, rating	ASTM D4048	1c	1a	1a	1a
Corrosion preventive properties, Distilled water, rating	ASTM D1743	Fail	Pass	Pass	Pass
Corrosion preventive properties, 3% NaCl solution, rating	ASTM D1743	Fail	Pass	Fail	Fail
Oil separation, %	ASTM D6184	1.5	1.9	2.5	2.6
Water washout	ASTM D1264	2.1	2.7	2.2	7.5
Weld Load, Kg	IP 239	225	200	200	180
Wear Scar Diameter, mm	ASTM D2266	0.60	0.55	0.60	0.60
EMCOR, Distilled water,rating	ASTM D6138	3,3	0,0	0,0	1,0
EMCOR, 3% NaCl solution, rating		4,4	1,1	0,0	2,2

Table-4: Evaluation of SbDTC in combination with CI additives amine phosphate, Half ester of Succinic acid and Barium Sulfonate in lithium greases.

In lithium complex greases as shown in Table 5 similar trend was observed as with lithium grease.

S. No.	Method	**Liplex-Gr – EP2**	**Liplex-Gr – EP2+CI-1**	**Liplex-Gr – EP2+CI-2**	**Liplex-Gr – EP2+CI-3**
Worked penetration, 0.1 mm	ASTM D217	277	271	280	285
Roll Stability, 16h, RT, % change in penetration from P60	ASTM D1831 (modified)	17.1	15.6	14.9	16.7
Dropping Point, °C	ASTM D566	280	278	277	272
Copper corrosion, rating	ASTM D4048	1c	1a	1a	1a
Corrosion preventive properties, Distilled water, rating	ASTM D1743	Fail	Pass	Pass	Pass
Corrosion preventive properties, 3% NaCl solution, rating	ASTM D1743	Fail	Pass	Fail	Fail

Oil separation, %	ASTM D6184	1.5	1.9	2.5	2.6
Weld Load, Kg	IP 239	280	225	250	225
Wear Scar Diameter, mm	ASTM D2266	0.60	0.55	0.60	0.60
EMCOR, Distilled water,rating	ASTM D6138	1,1	0,0	0,1	0,0
EMCOR, 3% NaCl solution, rating		3,3	0,1	1,1	1,2

Table-5: Evaluation of SbDTC in combination with CI additives amine phosphate, Half ester of Succinic acid and Barium Sulfonate in lithium complex greases.

MoS_2 with CI additives:

Unlike oils solid additives can be incorporated in greases which will remain in network and work in bulk. Solid additives in greases are mostly used for EP and anti seize purpose. In high speed automotive applications solid additives may be centrifuged out due to density variations. But in low speed and high load applications solid additives are better choice to enhance load-carrying performance for preventing wear and seizure by forming thick physical EP layer. Molybdenum disulfide is well known solid additive use in greases designed for low speed high load applications[15].

In the present study we have treated Lithium and lithium complex greases with MoS_2 at 2wt% and checked for EP and CI performances along with other regular physical tests. As shown in Table 6, **Li-Gr – EP3** found to show 250 Kg weld load though the wear scar diameter is high, while corrosion of copper and dynamic, static corrosion test show mild corrosion. Upon addition of corrosion inhibitors, improved corrosion resistance and weld load was not affected much. MoS_2 work in on surface as sacrificial load carrying layer have more load carrying capacity which is required at slow moving situations.

S. No.	Method	**Li-Gr –EP3**	**Li-Gr –EP3+CI-1**	**Li-Gr –EP3+CI-2**	**Li-Gr –EP3+CI-3**
Worked penetration, 0.1 mm	ASTM D217	286	287	283	277
Roll Stability, 16h, RT, % change in penetration from P60	ASTM D1831 (modified)	11.6	9.7	11.1	10.8
Dropping Point, °C	ASTM D566	199	195	197	199
Copper corrosion, rating	ASTM D4048	2c	1b	1a	1a
Corrosion preventive properties, Distilled water, rating	ASTM D1743	Pass	Pass	Pass	Pass
Corrosion preventive properties, 3% NaCl solution, rating	ASTM D1743	Fail	Pass	Pass	Fail
Oil separation, %	ASTM D6184	1.5	1.9	2.5	2.6
Water washout, % loss	ASTM D1264	2.1	2.7	2.2	7.5
Weld Load, Kg	IP 239	250	225	225	225
Wear Scar Diameter, mm	ASTM D2266	0.85	0.75	0.80	0.80
EMCOR, Distilled water, rating	ASTM D6138	2,2	0,0	0,0	0,0
EMCOR, 3% NaCl solution, rating		3,2	0,0	1,1	1,0

Table-6: Evaluation of MoS_2 in combination with CI additives amine phosphate, Half ester of Succinic acid and Barium Sulfonate in lithum greases.

In lithium complex grease MoS_2 found to show similar results.

S. No.	Method	**Liplex-Gr –EP3**	**Liplex-Gr – EP3+CI-1**	**Liplex-Gr – EP3+CI-2**	**Liplex-Gr – EP3+CI-3**
Worked penetration, 0.1 mm	ASTM D217	279	278	284	281
Roll Stability, 16h, RT, % change in penetration from P60	ASTM D1831 (modified)	19.6	16.3	18.1	15.9

Dropping Point, °C	ASTM D566	271	268	274	272
Copper corrosion, rating	ASTM D4048	1c	1a	1a	1a
Corrosion preventive properties, Distilled water, rating	ASTM D1743	Fail	Pass	Pass	Pass
Corrosion preventive properties, 3% NaCl solution, rating	ASTM D1743	Fail	Pass	Pass	Fail
Oil separation, %	ASTM D6184	1.9	2.4	2.1	2.7
Weld Load, Kg	IP 239	250	225	220	250
Wear Scar Diameter, mm	ASTM D2266	0.80	0.75	0.75	0.70
EMCOR, Distilled water, rating	ASTM D6138	2,2	0,0	0,0	0,0
EMCOR, 3% NaCl solution, rating		3,3	0,0	1,1	1,0

Table-7: Evaluation of MoS_2 in combination with CI additives amine phosphate, Half ester of Succinic acid and Barium Sulfonate in lithium complex greases.

From above study it is evident that EP additives and CI additives compete on surface.
ZDDP is known to be a versatile multifunctional additive used as antiwear, anti oxidant, corrosion inhibitor and EP booster. In further study, sulfurized olefin with amine phosphate system was treated with 0.60wt% of ZDDP. As shown in Table 8 grease **Li-Gr -EP1+CI-1+ZDDP** shown elevated dropping point by around 15 units in ASTM D566 which is well established synergistic effect between EP and ZDDP. Oxidation stability of the grease as per ASTM D942 also got significantly improved as ZDDP acts as secondary anti oxidant and rapid small scale oxidation as per ASTM D8206 also show significant improvement in oxidation time to achieve 10% pressure drop. Wear scar diameter also reduced to 0.45 mm and weld load of the grease improved a step to 250 kg showing synergetic effect of ZDDP.

Property	Method	**Base Gr.**	**Li-Gr –EP-1**	**Li-Gr - EP- 1+CI-1**	**Li-Gr - EP1+CI-1+ZDDP**
Worked penetration, 0.1 mm	ASTM D217	268	277	271	283
Roll Stability, 16h, RT, % change in penetration from P60	ASTM D1831 (modified)	11.9	12.1	13.8	12.5
Dropping Point, °C	ASTM D566	196	196	193	218
Copper corrosion, rating	ASTM D4048	1b	1c	1a	1a
Corrosion preventive properties, Distilled water, rating	ASTM D1743	Fail	Fail	Pass	Pass
Oxidation Stability	ASTM D942				
RSSOT	ASTM D				
Water washout	ASTM D1264	3.1	3.3	3.1	2.4
Weld Load, Kg	IP 239	**140**	**280**	**225**	**250**
Wear Scar Diameter, mm	ASTM D2266	0.70	0.60	0.55	0.45
EMCOR, Distilled water, rating	ASTM D6138	2,2	3,3	0,0	0,0
EMCOR, 3% NaCl solution, rating	ASTM D6138	4,4	4,4	1,1	1,1

Table-8: Lithium grease Li-Gr -EP-1+CI-1 with ZDDP as multi functional additive

Rheological evaluation of Li-greases to study effect of EP and CI additive combinations:
The synergistic or antagonistic effects of additive combinations should also be obvious in friction studies. To evaluate this point in detail, a friction study was planned using a tribocell fitted to rheometer. The experiments on rheological properties were carried out using a Physica MCR301 rotational rheometer (manufactured by Anton Paar), equipped with tribocell with three-plate-ball geometry(Figure 8). Plates and balls were made up of steel and were supplied by M/s Anton Paar Austria. Rheoplus software is used to control and measurement of Stribeck curve generation[16].

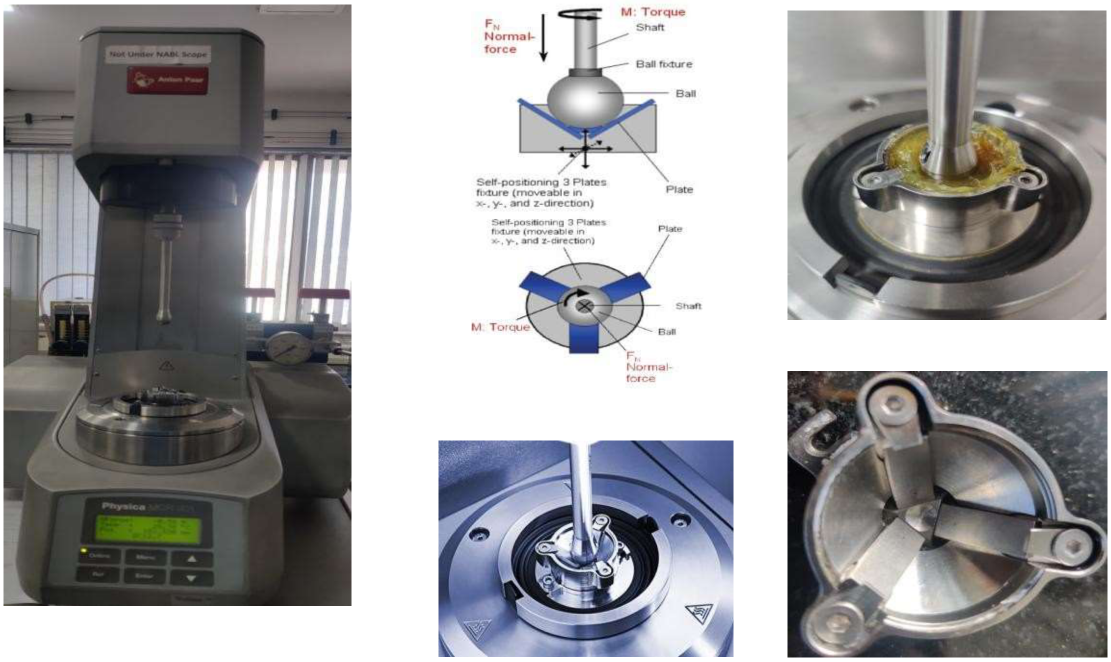


Figure 8: Tribocell attached to MCR 301 Anton Paar viscometer

One of the lubricant's primary jobs is to prevent wear between surfaces. To perform this job, different formulations are developed based on specific applications and the "lubrication regimes" associated with them. There are three major lubrication regimes -1. Boundary 2. Mixed and 3. Hydrodynamic (Figure 9). In **boundary lubrication**, opposing surfaces are in full contact with each other under slow movement and high loads. To prevent wear within this regime, lubricants are specifically formulated to form a low- friction, protective layer on the wear surface. The base oil of the lubricant acts as a carrier to effectively deposit the additives where they are needed.

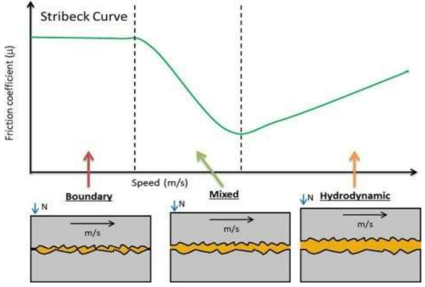


Figure 9: Stribeck Curve- Lubrication Regimes[17]

Mixed lubrication is a transitional regime situated between boundary and hydrodynamic lubrication, sharing characteristics of both. Typically, mixed lubrication can occur during the startup of rotational equipment, as the shafts gain rotational speed from a full stop. It also can occur between surfaces where low loads and high speeds are encountered, such as when reciprocating pistons slide against piston walls. With this transitional regime, wear protection depends on both the lubricant viscosity as well as the additives within the formulation. In **hydrodynamic lubrication**, two moving surfaces are completely separated from each other. For example - when a shaft rotates within a journal bearing, it carries lubricant. As the rotational speed of the shaft increases, the rate at which oil is carried around the shaft increases. This pumping action creates an "oil wedge" beneath the shaft leading to complete separation of the two surfaces, preventing any contact and, thus, preventing friction and wear between them. A proper viscosity is critical for effective oil-wedge development, efficient operation and long bearing life.

Using the rheometer tribocell set up experiments were done by increasing the sliding speed logarithmically, normal load 10N was applied and friction coefficient was measured as a function of the sliding speed at 100 °C.

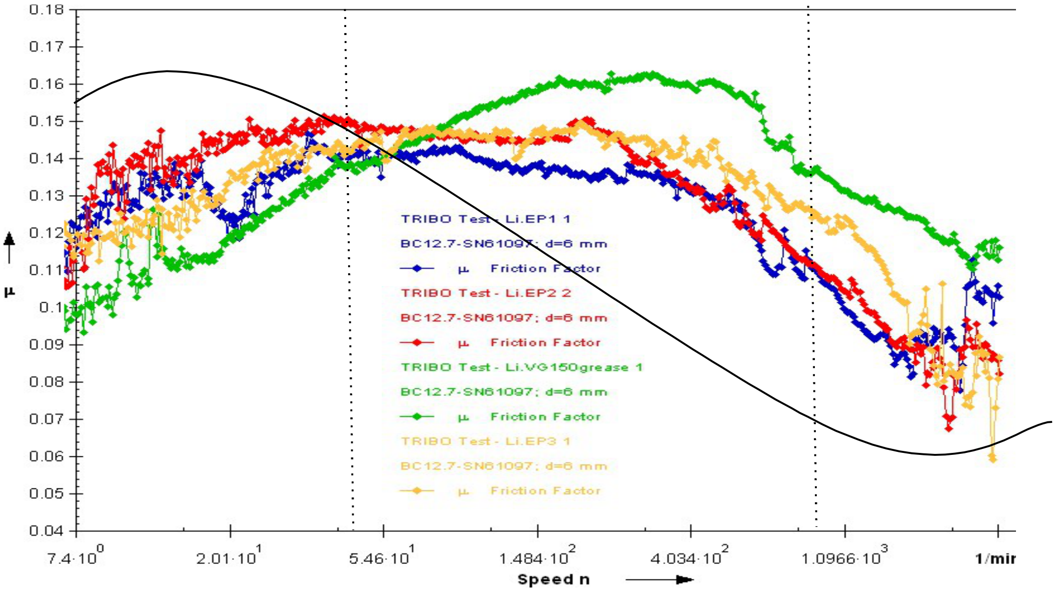


Figure 10: Stribeck Curve with lithium base grease and greases with EP additives

As shown in Figure 10 the green color graph of lithium base grease show oil/thickener based lubrication at low speeds and since no EP additive is present, friction increased with increasing speed. Other three curves containing EP additives found to form protective later resulting in low friction. Among the three, **Li-EP-1** with 2wt% sulfurized olefin found to show good protective layer formation resulting in low friction. In Figure 11, Stibeck curve obtained with Li-Gr-EP-1 SO without CI additives and Li-Gr-EP-1 with amine phosphate, half ester and barium sulfonate CI additives respectively. CI additives found to lower friction coefficient comparatively and half ester of succinic acid found to show lower friction among the four.

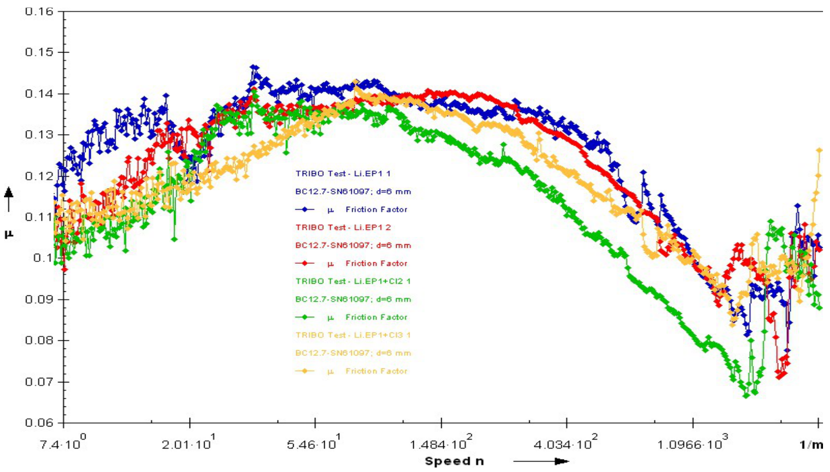


Figure 11: Stribeck Curve lithium base grease with sulfurized olefin and CI additives.

Under same experimental conditions as shown in Figure 12, tribotest of Li-Gr-EP2 having SbDTC provided lower friction coefficient at low speed whereas at higher speeds Li-Gr-EP2+CI2 having half ester of succinic acid found to give lower friction indicating formation of good tribo film at higher speeds. The results showing good agreement with the results obtained in weld load tests.

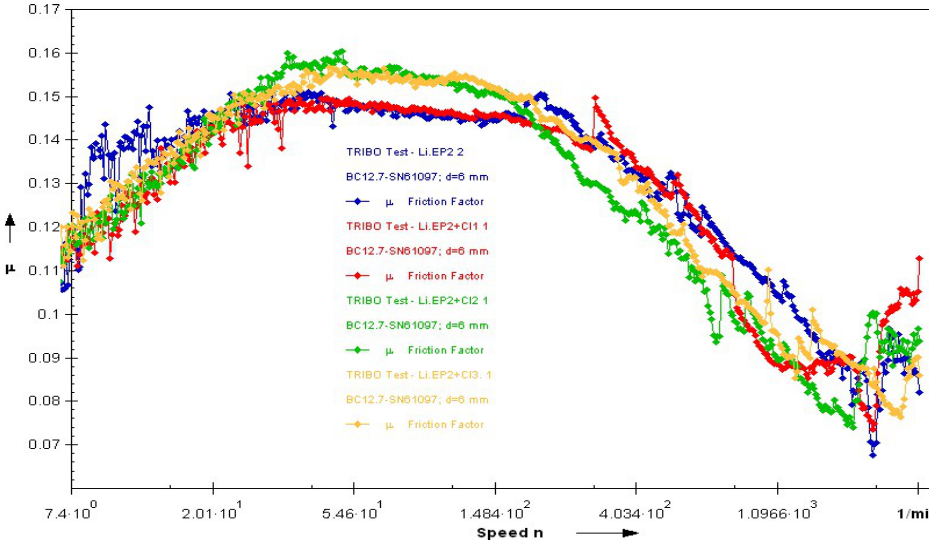


Figure 12: Stribeck Curve lithium base grease with SbDTC and CI additives.

Similarly as shown in Figure 13, Li-Gr-EP3 with MoS_2 found to show lower friction coefficient alone while combination with CI at lower speeds show high friction and at higher speeds friction coefficient of the CI additized greases was lowered indicating formation of tribo layer.

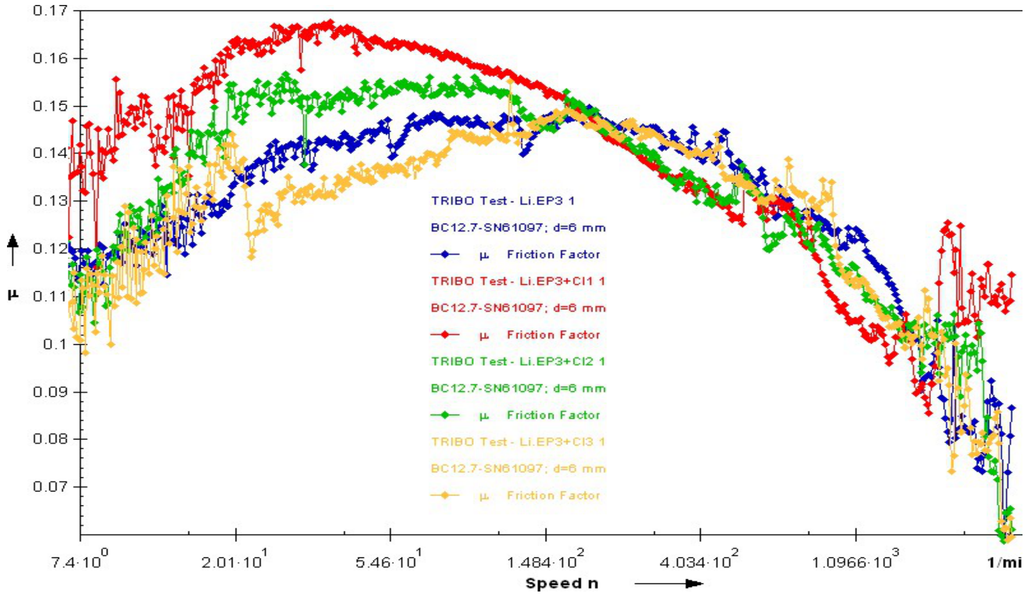


Figure 13: Stribeck Curve lithium base grease with MoS_2 and CI additives.

From tribo rheological experiments it is understood that at lower speeds lubrication is by thickener/oil based films. At higher speeds lowering of friction coefficient is seen as a result of surface active additive tribo film formation. In further work effect of load, type of surfaces and temperature variations will be studied.

Conclusions

1. Studied three commonly used EP additives namely sulfurized olefins, antimony dialkyl dithiocarbamate and molybdenum disulfide in combination with commonly used CI additives amine phosphate, half ester of succinic acid and barium sulfonate.
2. It was found that competition between EP and anti rust additives is evident in a grease resulting in antagonistic effect; lower weld load stages for EP additive compared to the grease without CI additive.
3. EP and CI combination not only effect EP and CI properties they also effect certain other properties such as water resistance, copper corrosion, consistency etc.
4. Initial selection of EP and CI additive combination is very critical to minimize antagonistic effect between the EP and CI additives.
5. Multi functional additive ZDDP found to show synergy with SO+AmPh system.
6. Further multifunctional additive response and other additives combination such as antiwear, friction modifier, dropping point enhancers etc will be required to develop complete grease formulation for desired application.

References:

1. Gatto., V., The chemistry and function of lubricant additives, Tribology & Lubrication Technology, November, 2017, www.stle.org.
2. a) Lubricant Additives Chemistry and Applications Second Edition, editor, Leslie R. Rudnick. -- 2nd ed.p. cm. -- (Chemical industries ; 124), ISBN 978-1-4200-5964-9. b) Polishuk, A. (1998), "A Brief History of Lubricating Greases," *Grease Technology*, Lima, Pa. c) A comprehensive review of lubricant chemistry, selection and design, Syed Q. A. Rizvi, "ASTM stock number: MNL59."ISBN 978-0-8031- 7000-1
3. Grease additives: Important contributors not to be overlooked, Canter, Neil. Tribology & Lubrication Technology; Park Ridge Vol. 68, Iss. 12, (Dec 2012): 28-32,34-38.
4. "The Chemistry and Physics of Grease-The Advantages of Grease," *Axel Christiernsson White Paper*, 2004 (01) http://www.axelch.com/composite-74.htm?catid=4.
5. Kaperick, J. (2010), "Grease – The 'Other Lubricant,'" STLE Philadelphia Section presentation, April 15, 2010.
6. Extreme Pressure Performance of Greases: Testing and Additive Solutions, Grease Tech India, Vol XVI, No.4, April1-June 30, 2014.
7. a) Canter, N., Special Report: Trends in extreme pressure additives, Tribology & Lubrication Technology, September, 2007. b) Mandakovic,R., *J.Syn.Lubr.*, 16(1), 13-26, 1999.
8. a) Fish, G., & Ward Jr., W. C. (2011) -Extreme pressure performance of greases: testing and additive solutions, NLGI Spokesman, volume 75(3), pages 12-27. b) Fish, G, Additives for lubricating grease_A skillfully formulated grease brings a host of good things, www.stle.org, Tribology & Lubrication Technology, December, 2015.
9. a) Mistry, K., Neville, A., Morina, A., Webster, M.N., Lubricant/surface interactions under extreme pressure conditions: Corrosion inhibitor interacting extreme pressure/anti-wear additives on steel surface, Proceedings of the Institution of Mechanical Engineers Part J Journal of Engineering Tribology 1994-1996 (vols 208-210), 222(3):315-323 DOI: 10.1243/13506501JET391. b) Bala, V., Hunt, J., Performance Considerations in Formulating Multi-Purpose EP Greases, September / October 2020 NLGI Spokesman.
10. Molecular Science of Lubricant Additives, Appl. Sci. 2017, 7, 445; doi:10.3390/app7050445
11. Sanyal, B. Organic compounds as corrosion inhibitors in different environments – a review. *Prog. Org. Coat.*, 1981, **9**, 165–236.
12. a) Myers, H., Lubricating Compositions Containing Polysulfurized Olefi n, US Patent No. 3,471,404, 1969; b) US Patent Nos. 3,703,504 and 3,703,505 (1972). Davis, K.E., Sulfurized

Compositions, US Patent Nos. 4,119,549, 1978 and 4,191,659, 1980. c) Davis, K.E. and Holden, T.F., Sulfurized Compositions, US Patent Nos. 4,119,550, 1978 and 4,344,854, 1982.

13. Hunter, M., Rizvi, S. and Baker, R. (2001), "Ashless Rust Inhibitors for Greases," *NLGI Spokesman*, 65 (3), pp. 24-32. (2004)
14. Ward Jr., W.C., Fish, G., Najman, M., and McFadden, C. H., -Extreme Pressure and Tribochemical Film Comparisons of Antimony and Non-Antimony Additive-Containing Lithium Complex Grease NLGI 75th Annual Meeting Williamsburg, Virginia, June, 2008.
15. Risdon, T.J. —Molybdenum Disulfide in Greases - A Review (2005) Presented at the NLGI 72nd Annual Meeting San Antonio, Texas October 30 – November 1, 2005.
16. Heyer P., and Läuger J., A Flexible Platform for Tribological Measurements on a Rheometer, Annual Transactions of the Nordic rheology society, vol. 17, 2009.
17. a) Stribeck, R. (1901), Kugellager für beliebige Belastungen (Ball Bearings for any Stress), Zeitschrift des Vereins Deutscher Ingenieure 45., b) Stribeck, R. (1902), Die wesentlichen Eigenschaften der Gleit- und Rollenlager (Characteristics of Plain and Roller Bearings), Zeit. des VDI 46.

Low Temperature Fluidity of Polymer-Modified Greases

Erik Willett, PhD; Functional Products Inc.

24th NLGI-IC Lubricating Grease Conference (2022) - Visakhapatnam, Andhra Pradesh, India

1. Introduction

Polymers and Grease

Polymer additives are often used to modify the interaction of greases with surfaces or other materials.[1] High speed couplings may use a tackifier to reduce the fling-off of the grease under centrifugal forces.[2] Water-resistant grease may require a functionalized grease polymer.[3] [4] Internal interactions like incompatibility between a very non-polar synthetic base stock and highly charged thickener like lithium or calcium salts which results in oil bleed can be mitigated by the oil swell effect of polymers.[5] [6] Some polymers can even reinforce the mechanical stability of greases when picked correctly.[7]

Various polymers can be used to achieve the desired effects depending on the grease type, base oil, and additive. Polymer may be picked from oil-soluble viscosity modifier grades used to prepare fluids and lubricants or from specialized semi-crystalline or oil-insoluble 'grease polymer' grades.

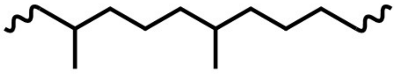
It is rare that an additive can solve many problems without causing a few problems of its own. The question then becomes: for all the benefits of polymers in grease, what is being given up? Traditionally the answer for polymers in grease has been fluidity. This has been investigated previously with Lincoln ventmeter at near ambient conditions for various functionalized polymers.[8] This current work focuses specifically on the chemical structure of several more simple polyolefins, the resulting tackiness properties based on polymer type and loading, and the ultimate effect on grease fluidity as low as -40°C.

Polymers Under Study

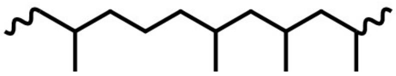
Three low-to-high MW polymer chemistries (PIB, OCP, CRY) were evaluated alongside greases made with paraffinic oil, naphthenic oil, and mPAO 100. The three polymer chemistries were chosen based on good solvency in petroleum oil and solubility in PAO6 which is the preferred base oil in this study. The PIB, OCP, and CRY polymers and mPAO are suitable for NSF H1 grease formulations due to their high purity and lack of reactive functionality – many are already NSF-listed as one or more products.

Polyisobutylene ("PIB")

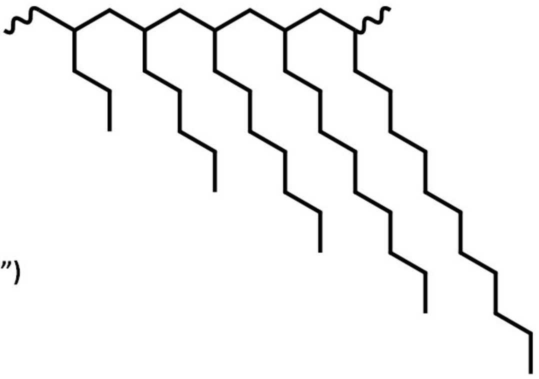
Ethylene-Propylene Copolymer ("OCP")



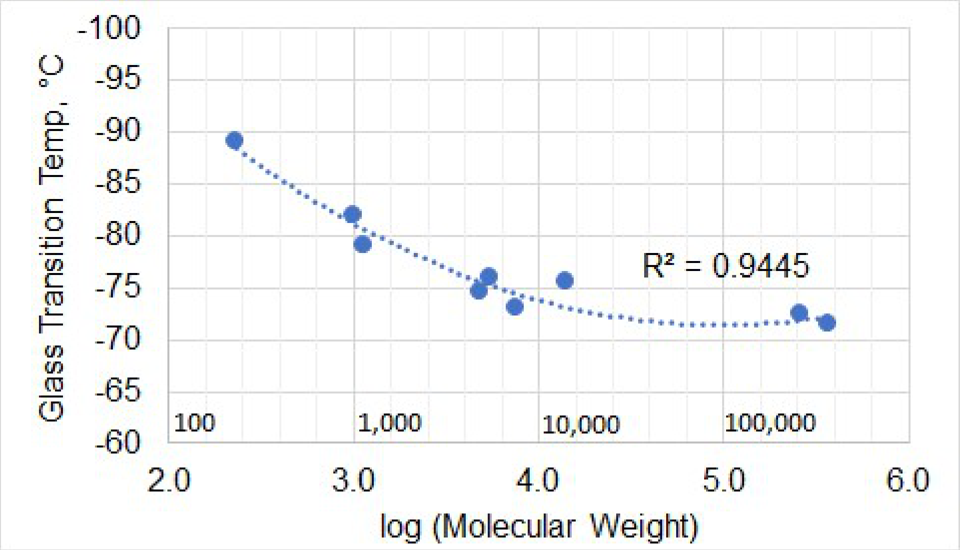
Semi-Crystalline Ethylene-Propylene ("CRY")



mPAO (C4 – C12 shown)



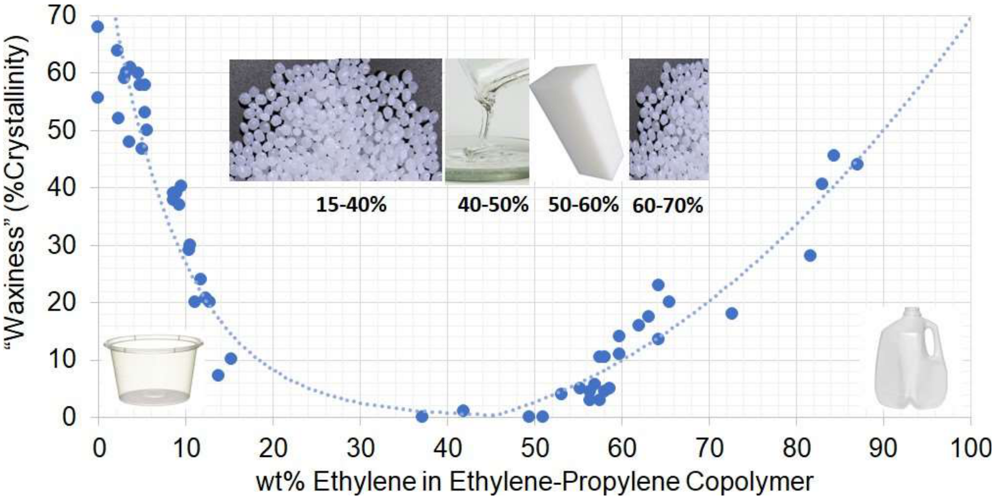
"PIB" is a pure homopolymer ('same monomer') of isobutylene prepared from very low to very high molecular weights for a wide range of applications in lubricants, coatings, and consumer goods. PIB's glass transition temperature (Tg) which is discussed later but is essentially a molecular pour point for polymers remains <-70°C even at hundreds of thousands molecular weight.[9][10] In theory, the low temperature fluidity of a polymer chemistry is best at low MW but plateaus at medium MW and remains constant from there up to very high MW.



“OCP” is a copolymer of ethylene-propylene with 40-60% ethylene which results in very low wax-like structure and is called “amorphous” as it is free flowing as either a liquid or a very soft solid bale.

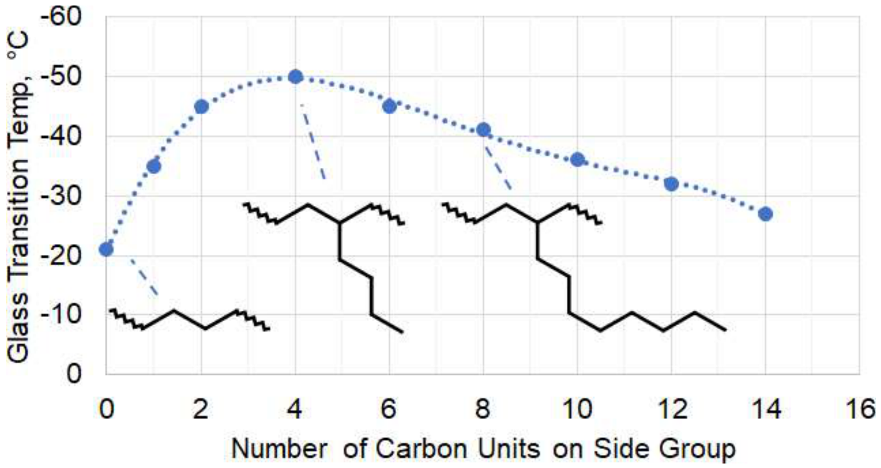
“CRY” is a copolymer of ethylene-propylene with <40% ethylene which results in crystalline regions of polypropylene forming within the polymer that can behave much like a wax. These grades are called “semi-crystalline” and occur as solid pellets which require heat and long stirring times to properly incorporate into oil.

The more common form of semi-crystalline OCP is when ethylene is >60% which results in crystalline regions of polyethylene that behave more gel-like. CRY chemistry with low ethylene content tends to produce small, localized crystallites or “spherullites” microparticles which improves low temperature fluidity but can greatly affect product clarity. CRY chemistry can be used as a viscosity modifier in high solvency Group I or naphthenic oils while the high ethylene semi-crystalline chemistry rapidly gels any petroleum or synthetic base oil.



“mPAO” chemistry is a proprietary copolymerization of short, long, and even branched straight chain alpha olefins. The mixture of monomers can suppress the high crystallinity of short olefins (like the polypropylene previously discussed) or waxy nature of longer olefins (like the polyethylene discussed). mPAOs are typically produced in the thousands of molecular weight and which grants some additional low temperature fluidity. mPAO 100 is itself a polymer since mPAO molecular weights can range from 5000 – 10000 g/mol which implies 36 to 72 decene units or 360 to 720 carbon atoms.

One way to compare the relative low temperature performance of different polymer chemistries is through “glass transition temperature” or Tg. Tg is essentially a measure of ‘molecular pour point’ where polymers lose their flexibility and become highly structured which may result in brittleness or loss of fluidity. The series of poly(n-alpha olefins) is a good demonstration of how monomer selection can affect low temperature fluidity in the form of glass transition temperature, Tg.[11]



When diluted in fluids, Tg may manifest as aggregation of individual polymer chains to form a solid or semi-solid network. Tg comes about through waxy interactions like long runs of ethylene or propylene in the semicrystalline olefin copolymers; or through polar attractions on polymeric esters. Tg is dependent on molecular weight up to a few thousand g/mol and then remains constant and independent of molecular weight. Only mPAOs or low MW PIBs would be of sufficiently low MW to gain this benefit.

Summary of Notable Properties Between Three Polymer Additives and mPAO Base Stock

Name	Chemistry	Glass Transition, Tg	Commercial MW Ranges	Repeat Units per 10,000 MW	Ref
"PIB"	Polyisobutylene	-70°C	1K – 1M	178.3	9 10
"OCP"	Ethylene-Propylene, 40-60% C2 (Amorphous)	-40°C	10K – 20K liquid 100K – 200K solids	285.2	12 13 14
"CRY"	Ethylene-Propylene, <40% C2 (Semi-Crystalline)	-10°C	100K – 200K	254.6	
"mPAO"	Metallocene Polyalphaolefin	-50°C (C6), -65°C (C8), -40°C (C10)	5K – 10K	71.3	11 15 16

Glass transition, molecular weight, and wt% usage may be key factors in comparing the low temperature fluidity of polymer-modified greases. Many more factors like catalyst selection or large-scale branching can also have subtle effects depending on the source of a given polymer.

Low Temperature Grease Testing

Fluids tend to become more viscous with reduction in temperature. The internal molecules have less energy to move quickly and navigate obstacles and this further contributes to resistance to motion known as "viscosity". Viscosity must remain within proper tolerances for lubrication to occur. Lubrication guidelines seek to deliver an appropriate amount of viscosity based on the speed and load of the equipment to minimize wear and friction on the Stribeck curve. When viscosity becomes very high in greased systems it can put excessive torque on moving elements and cause damage. Electric motors can easily stall at startup from only a fraction of their rated torque under the resistance of a lubricant or grease which has thickened. Central lubrication systems pump grease through narrow tubes over up to several hundred feet and any increase in viscosity is quickly magnified to the point that flow stops.

Low temperature test methods are added to grease specifications to ensure adequate flow under cold conditions. The original NLGI grease specification (ASTM D4950) covered automotive chassis greases and limited low temperature testing to simply the ASTM D4693 low temperature torque on wheel bearing test. Since the intended purpose for the specification was wheel bearing and chassis grease this made sense.

However many industrial greases with no application in automotive have been developed to the NLGI GC-LB specification which does not test for performance under low temperature conditions relative to their specific application. The NLGI High Performance Multiuse specification (HPM) was developed in recent years to include test methods to ensure performance in a wide range of non-automotive uses. The Low Temperature subcategory (LT) adds two new test methods and is the only specification to test more than one type of low temperature property.

Specification	Test Methods	Test Type	Limits
ASTM D4950 – NLGI GB (1989)	Low Temperature Torque, ASTM D4693	Rotational Torque	< 15.5 N-m @ -20°C
ASTM D4950 – NLGI GC, GC-LB (1989)	Low Temperature Torque, ASTM D4693	Rotational Torque	< 15.5 N-m @ -40°C
DIN 51825 (2004)	Low Temperature Torque, IP 186	Rotational Torque	Used to determine lower operating temp. -10°C to -60°C
ISO 12925-3 (2004)	Low Temperature Cone Penetration, ISO 13737	Consistency	> 300 1/10mm
NLGI HPM (2020)	Low Temperature Torque, ASTM D1478	Rotational Torque	< 1000 mNm startup @ -20°C < 100 mNm after 1hr @ -20°C
NLGI HPM-LT (2020)	Low Temperature Torque, ASTM D1478	Rotational Torque	<1000 mNm startup @ -30°C < 100 mNm after 1hr @ -30°C
	US Steel Mobility, LT-37	Confined Flow	> 10 g/min @ -20°C
	Kesternich, DIN 51805-2	Confined Flow	< 1400 mbar @ -30°C

ISO 12925-3 provides an international specification for grease for gears and includes ISO 13737 low temperature cone penetration test but allows for any suitable low temperature test as long as the grease does not channel at the lowest operating conditions and the customer agrees.

DIN 51825 specification requires setting a lower limit for operating temperature using IP 186 low temperature torque. This is unique as the ASTM, HPM, and ISO standards only test the grease at one arbitrary temperature and do not specify exactly how the minimum operating temperature should be determined.

Several other low temperature grease test methods are popular but no officially listed as testing requirements. Lincoln ventmeter is another popular method of determining the pumpability of grease through 25 feet of ¼" tubing and has direct application to how far grease can be pumped in central lubrication lines. Prior work has evaluated the effects of polymer additives on Lincoln ventmeter pumpability down to -1°C / 30°F.[8] ASTM 1092 apparent viscosity of grease is another 'confined flow' type of test which forces grease under high pressure at low temperature through a narrow tube and measures the mass flow rate. Test setup is similar to US Steel Mobility.

2. Materials

A range of base stocks and polymeric additives were used to evaluate the effects of different polymer chemistries and molecular weights on the tackiness and low temperature fluidity of synthetic #2 simple lithium grease.

Base Stocks:

Abbreviation	Base Stock
PAO6	6 cSt Polyalphaolefin
mPAO100	100 cSt Metallocene Polyalpaholefin
WO600	600 SUS White Oil
Naph750	750 SUS Naphthenic Oil
SN600	600 SUS Group I
BS150	150 Bright Stock

ISO 150 base oil blends without polymer were prepared as:

- PAO ISO 150 = 50wt% PAO6 + 50wt% mPAO100
- White Oil ISO 150 = 95wt% WO600 + 5wt% PIB1 (below)
- Paraffinic ISO 150 = 85wt% SN600 + 15% BS150
- Naphthenic ISO 150 = Naph750

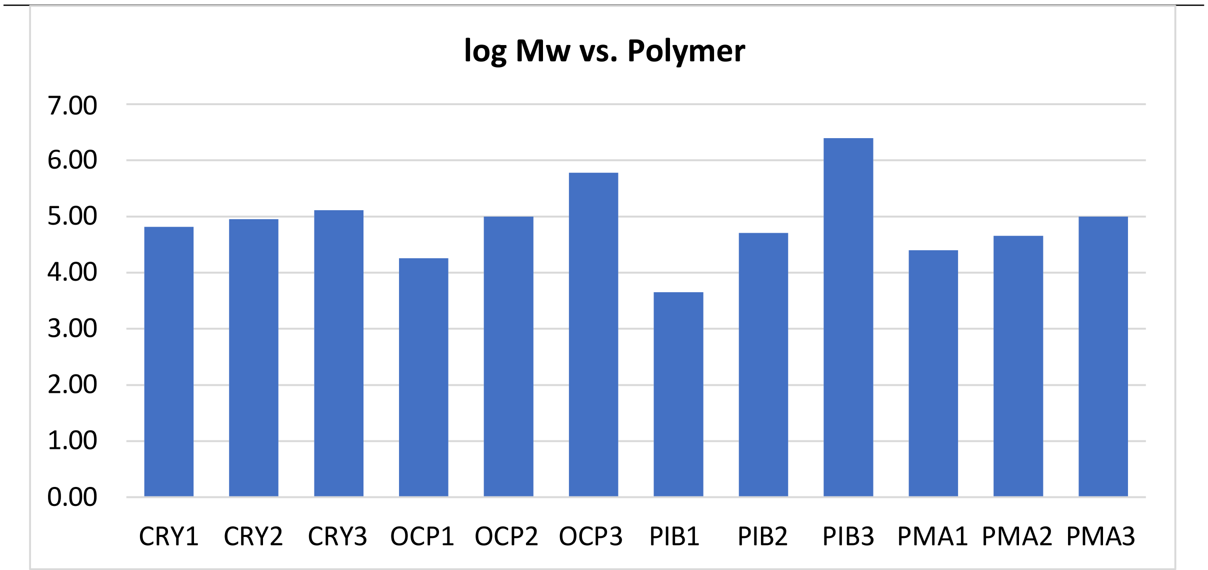
Polymers were diluted into light petroleum oil (ISO 22-25) such that 20wt% of the concentrate gave an ISO 150 viscosity in PAO6. This allows a repeatable preparation of the base fluid mixture and a standardized viscosity. PAO6 was chosen due to its very low pour point (<-50°C) which allows clear observation of any effects from polymer.

PMA polymethacrylate polymers (PMA1, PMA2, PMA3) were adjusted with the diluent oil such that 30wt% of PMA+oil produced ISO 150 blends in PAO6. The lower thickening efficiency of the PMAs required higher treat than 20wt%. The PMA polymers are only used in this study for additional tackiness testing with TAA to establish a wider dataset – no low temperature testing was performed with PMA greases but may be tested at a later date when the TAA data interpretation has been further matured.

Name	Polymer	Original Form	MW Range Category	Typical Use
OCP1	Ethylene-propylene, amorphous (40-60% ethylene)	Liquid	Low	Base Stock
OCP2	Ethylene-propylene, amorphous (40-60% ethylene)	Bale	High	Viscosity Modifier
OCP3	Ethylene-propylene, amorphous (40-60% ethylene)	Bale	Very High	Tackifier
PIB1	Polyisobutylene	Liquid	Very Low	Base Stock
PIB2	Polyisobutylene	Bale	Low	Viscosity Modifier
PIB3	Polyisobutylene	Bale	Very High	Tackifier
CRY1	Ethylene-propylene, semi-crystalline (<40% ethylene)	Pellet	Medium	Viscosity Modifier
CRY2	Ethylene-propylene, semi-crystalline (<40% ethylene)	Pellet	Medium	Viscosity Modifier
CRY3	Ethylene-propylene, semi-crystalline (<40% ethylene)	Pellet	High	Viscosity Modifier
PMA1	Polymethacrylate, 0 SSI by D6278 (gear oil grade)	Liquid	Low	Viscosity Modifier
PMA2	Polymethacrylate, 1 SSI (hydraulic grade)	Liquid	Low	Viscosity Modifier
PMA3	Polymethacrylate, 36 SSI (engine oil grade)	Liquid	High	Viscosity Modifier

Molecular weight (MW) is noted by weight-average (Mw) GPC molecular weight:

	“Very Low”	“Low”	“Medium”	“High”	“Very High”
MW Range	< 15,000	15,000 – 50,000	50,000 – 100,000	100,000 – 200,000	>200,000



ISO 150 base oil blends are shown below with comparisons for KV100, KV20, and KV-20 assuming all oils were prepared at a perfect 150 cSt @ 40C. The fluidity and pour point of the base oil is considered to be a limiting factor in the lower operating temperature of grease. KV20 and KV-20 are extrapolated from ASTM D341 calculation. “Tack Type” is a metric developed and discussed later in this work describing the tackiness behavior of the grease.

						wt% Li-2HSA by NLGI Grade			**Viscometrics if KV40=150.0 cSt**			
Base Oil Blend	**wt% Polymer in Base Oil Blend**	**Mw Average of Base Fluid**	**VI (D2270)**	**Pour Point °C (D97)**	**Tack Type**	**#1**	**#2**	**#3**	**KV100 (D445)**	**KV40 (D445)**	**KV20 (D341)**	**KV-20 (D341)**
Naphthenic ISO 150	0	405	54	-21	1	6.9	9.1	11.8	11.3	150	686	127289
Paraffinic ISO 150	0	520	104	-15	1	9.3	12.1	15.8	15.3	150	526	29250
White Oil ISO 150	5	690	122	-18	2	13.0	15.4	18.3	16.9	150	486	19335
PAO ISO 150	5	3022	177	-48	2	8.7	11.9	16.2	22.3	150	396	7050
OCP1 ISO 150	15 – 25	3510	194	-45	2	13.5	16.4	19.9	24.2	150	376	5470
OCP2 ISO 150	1 – 5	2840	203	-51	4	7.1	9.8	13.3	25.2	150	365	4777
OCP3 ISO 150	1 – 5	8900	213	-51	4	14.8	17.7	21.3	26.3	150	355	4201
PIB1 ISO 150	15 – 25	1335	162	-51	2	10.8	13.8	17.7	20.8	150	417	9038
PIB2 ISO 150	5 – 10	4500	219	-51	3	15.3	18.4	22.2	27.1	150	348	3850
PIB3 ISO 150	<1	23080	233	-45	4	12.6	16.2	20.7	28.8	150	335	3238
CRY1 ISO 150	1 – 5	2640	166	-33	2	15.7	19.3	23.8	21.2	150	411	8382

CRY2 ISO 150	1 – 5	3070	200	-48	3	14.9	18.1	21.9	24.9	150	368	5000
CRY3 ISO 150	1 – 5	4140	210	-44	3	10.2	14.5	20.7	26.0	150	358	4378
PMA1 ISO 150	25 – 50	10730	175	-30	4	10.6	15.5	22.6	22.2	150	399	7251
PMA2 ISO 150	15 – 25	16530	163	-15	1	12.5	16.2	21.1	20.8	150	416	8935
PMA3 ISO 150	15 – 25	23080	264	-27	2	13.9	17.40	21.7	33.0	150	308	2240

3. Methods

2.1 Simple Lithium Soap Base Preparation

Soap bases for later cut-back to prepare #2 simple lithium greases were initially prepared using Blachford Lith12 HX-1 preformed lithium 12-HSA powder.

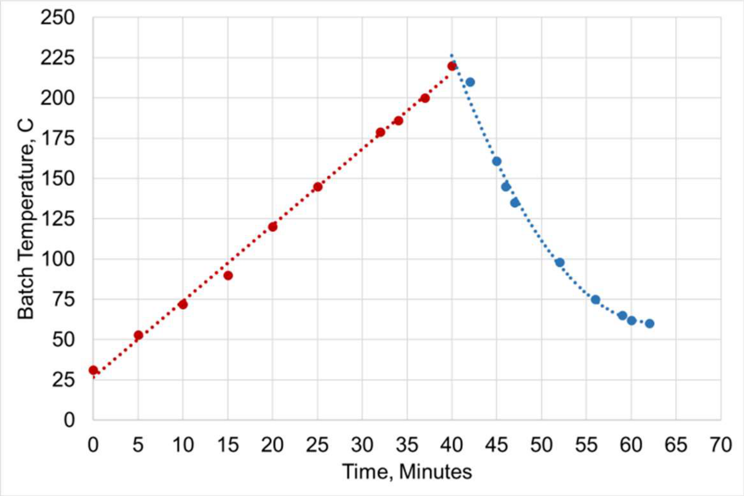
Basic recipe for the ISO 150 Base Oil Blends, the Simple Lithium Soap Bases, and the heating profile are organized below:

ISO 150 Base Oil Blend	wt% *
PAO6	80%
Pre-Dissolved or Pure Liquid Polymer	1 - 20%
Diluent Oil (100 SUS)	19 - 0%

Simple Lithium Soap Base	wt%
Lithium 12-HSA (NSF HX-1 grade) **	25%
Antioxidant Blend (Phenolic + Aminic)	0.75%
ISO 150 Base Oil Blend	74.25%

* mPAO grease uses 50% mPAO + 50% PAO6; PMA greases use 30% polymers/oil + 70% PAO6

** Naphthenic base oil blend starts with 20% Lithium 12-HSA preform.



400 gram batches of soap base were prepared from pre-formed thickener in a three-speed Hobart C-100 mixer with a 10-quart bowl, a B-style Hobart agitator paddle, and an electronic heating mantle (Glas-Col, 600 W, 5000 mL, silicone- impregnated fiber glass, #100AO414). A 120 V Variac was used to regulate the heating mantle power and batch temperature.

Temperature was ramped up using a Variac to control the power level of the electric heating mantle at a rate of +5°C/minute. The batch was held above 220°C until the lithium salts became molten and in full synthetic base oil blends temperatures up to 230-240C may be required. Once molten, the batch was mixed for five minutes before removing the electric heating mantle and continuously stirring down to 60°C.

Greases were milled to good texture with a two-roll mill (Seattle Findings #28-281) adjusted to the finest gap setting that would allow material to pass through. The mill was modified with a motor (Dayton 6A198; 1/20 HP, 154 rpm, 20 ft-lbs torque) to power the rollers. Material was passed through the rollers three times. However, full synthetic greases with no diluent petroleum oil produced larger, coarser grains of thickener that required up to six passes.

The ISO 150 Naphthenic base oil was prepared with 20wt% lithium 12-HSA instead of 25wt% due to the higher yield in the naphthenic oil which produced soap bases too thick to properly mix in the kettle.

2.2 Adjusting Greases

Soap bases with simple lithium thickener were cut back with 10wt%, 25wt%, and 50wt% more ISO 150 base oil blend. These three preparations were milled on a simple two-roll mill three times at the lowest gap setting. The consistencies of milled greases were measured by ASTM D1403 quarter cone penetration. A linear or logarithmic plot of wt% thickener versus full-scale cone penetration was used to determine the middle of the NLGI #2 grease consistency range.

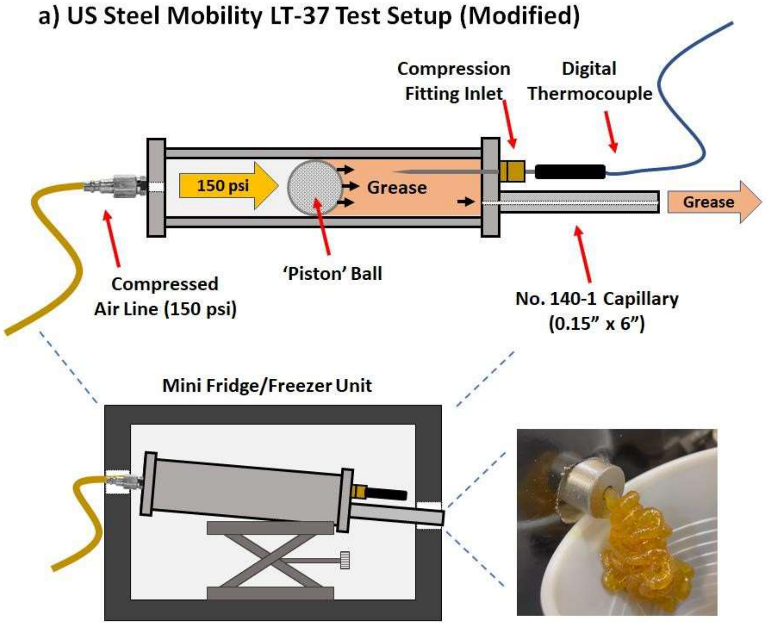
The remainder of the grease batch was cut back using the three-point calibration curve and milled to good texture.

2.3 Low Temperature Testing

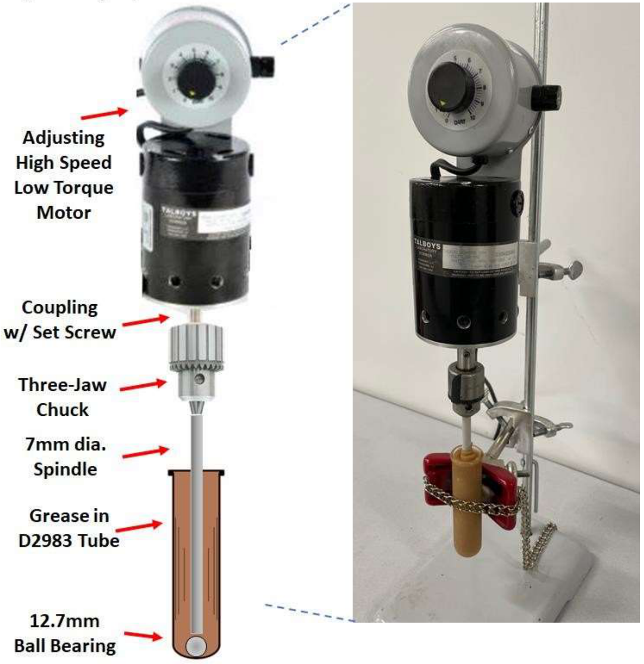
Two methods were used to scan the low temperature rheology of the polymer-modified greases and control greases. US Steel Mobility LT-37 (in Figure on left) allows the flow of grease in central lubrication systems to be modeled. This type of testing ensures that changes in grease's resistance to flow with temperature does not affect pumpability in narrow, high pressure lines. Lincoln ventmeter or the DIN 51805-2 Kesternich method achieve similar goals with varying amounts of difficulty in setting up the experiment.

The Spindle Stall Test (in Figure on right) is a house-made test to emulate the investigate the resistance of very viscous and tacky greases on the motion of rotating elements like bearings or shafts upon startup where the machinery's torque is lowest and risk of stalling is highest. This test is intended to be a simple and quick alternative to methods like Low Temperature Ball Bearing Torque (ASTM D1478) or Low Temperature Wheel Bearing Torque (ASTM D4693).

a) US Steel Mobility LT-37 Test Setup (Modified)



b) Heavy Spindle Test



Details on the two low temperature tests are detailed below.

2.3.1 Modified US Steel Mobility (LT-37)

US Steel Mobility was measured using an LT-37 unit in a modified procedure to allow the unit to run in a sideways
orientation in a small consumer 'mini-fridge'.

The unit was placed sideways into the freezer of 3.1 cubic foot combination refrigerator/freezer (Whytner MRF-310DB) with 1" diameter holes drilled to allow the pressure inlet and grease outlets to be accessible. An adjustable lab jack was used to position the unit in the center of the freezer at an approximately 15 degree downward slope. Pressure was provided by a Craftsman air compressor (2.6 SCFM, 6 gallon capacity, 150 psi).

Initial testing showed channeling of the grease sample which caused the 150 psi gas to blow through the grease sample even when filled with grease. To evenly distribute pressure across the sample, a golf ball (Titleist II) was found to fit the inner diameter of the LT-37 unit perfectly and was used as a piston (or pig) to great effect. The rubber composition of modern golf balls provides excellent flexibility and compression even at low temperatures.

No blow through occurred.
A digital temperature probe with long wire was inserted into the sample about 5 cm using a NPT-compression fitting adapter and rubber ferrule to prevent leakage. The freezer remained closed after sample preparation. The probe was calibrated at four temperatures from room temperature (~20-25°C) to -40°C against ASTM-certified analog thermometers.

The LT-37 was loaded with a lightly greased 'piston ball' and then 250 grams of grease before sealing and inserting into the freezer. The freezer stabilizes at -29°C and allows readings down to -20°C (-4°F) within 3 hours if the unit and grease are pre-chilled at -6C overnight in the refrigerator section of the cooling unit. If the unit is left in the freezer overnight then samples temperatures can reach down to -25°C.

Temperatures and times for the PAO-based ISO 150 greases are below. Non-PAO greases or PAO greases using the highest MW polymers for a given category were given twice the flow time due to slower flow rates. Roughly, every 10°F reduction causes flow rate to half for the majority of grease formulations in this study.

Temperature	**Flow Time, seconds 150 psi**	**Time to Reach Temperature from Warm Start**	**Time to Reach Temperature from Pre-Chilling**
30°F / -1.1°C	10 seconds	65 minutes	18 minutes
20°F / -6.7°C	10 seconds	90 minutes	37 minutes
10°F / -12.2°C	20 seconds	130 minutes	65 minutes
0°F / -17.8°C	40 seconds	180 minutes	110 minutes
-4°F / -20.0°C	80 seconds	240 minutes	160 minutes

Samples were degassed by cycling 5 minutes on and off under vacuum (25-27 in Hg vacuum) until pressurization and depressurization of the vacuum chamber did not cause the grease to expand or contract. Typically five purge cycles are sufficient to remove any entrained air.

2.3.2 Low Temperature Spindle Test

Several attempts at modifying ASTM D2893 low temperature Brookfield viscosity method were made using partial penetration of the #4B2 Brookfield spindle into the grease to give a qualitative measure of grease viscosity versus temperature. Reproducibility was poor due to the very high viscosity of the #2 grease samples which are far above the 6,000,000 cP limit of a Brookfield unit.
Instead, a low power 110V electric motor (Talboys, Model 103A, 1/12 HP, 1000-10000 rpm, 120VAC, 110W) with three- jaw chuck was used to hold a 7 mm diameter steel rod immersed approximately 100 mm in a tube of grease (115x25 mm tube from ASTM D2893). A 0.5" AIST steel ball bearing was placed at the bottom of the tube beneath the grease to serve as a support and to prevent the rod from accidentally breaking through the tube. The grease was charged to the tube using a 3-oz scale grease gun.
The startup RPM of the motor versus the temperature of the grease was used to emulate conditions of low temperature torque tests but provide a 'scanning' mode for evaluating the torque on the grease at various temperatures quickly. The first measurement was made at 22°C, then after 30 minutes in the -6°C refrigerator, and then after 1 hours in the -29°C freezer unit, and then 1 hours in -40°C Brookfield viscometer bath (ASTM D2893).
The startup speed (in rpm) of the motor was measured as the number of rotations in 30 seconds at each temperature before moving the sample to the next cooling zone. A black line marked on the chuck allowed visual counting. If the motor stalled then this was noted as "0 rpm". After stopping the motor at 30 seconds any partial rotations are included to nearest ¼ turn which provides improved accuracy at very low rpms. At high rpms or if the motor begins to accelerate then the number of turns in 15 seconds is used to calculate rpm; otherwise the motor is operating out of startup torque conditions or the tacky grease may begin to climb the rod.
Startup RPM versus temperature of the grease is reported. The startup torque may be calculated through the equation: Torque (mN-m) = -0.0226 * (RPM) + 11.79. A calibration curve was established by measuring RPM

versus the weight (in Newtons) of various weights pulled up by a string attached to the spindle. The torque required to stall the motor at startup was 11.8 mN-m, equivalent to pulling up a 300 gram weight. Startup RPM and torque will greatly vary from the rated capacity under steady state operation.

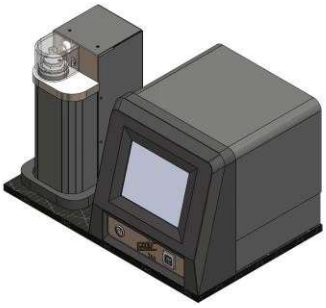
2.4 Falex TAA Tack Testing

Adhesion and cohesion of the greases were measured by a Falex Model 200 Tackiness Adhesion Analyzer (TAA) using software version 1.3.3. Data processing was performed through an included Excel macro, software version 1.2. Work has been previously demonstrated using the TAA method on #1 calcium sulfonate greases with various grease polymers.[5]

The 15-well sample carousel was loaded with fifteen repeat samples of each grease to allow for automating scanning at different probe retraction speeds. Compression energy and separation energy were calculated in microjoules. Thread length was calculated in millimeters.

Approach and retraction speeds were varied at 0.1, 0.5, 1.0, 2.0, and 5.0 mm/s per the default “Round Robin 2021” procedure below. One full run tests each speed fifteen times (5 cycles per well on three wells) and calculates averages for each tackiness parameter from all fifteen runs. The first few cycles may vary from the last cycles per well.

Well #	Speed	Well #	Speed	Well #	Speed
1	0.1	6	1.0	11	0.1
2	0.1	7	2.0	12	0.5
3	0.5	8	2.0	13	1.0
4	0.5	9	5.0	14	2.0
5	1.0	10	5.0	15	5.0



The probe approaches the sample at the approach speed, waits 1 second, embeds into the grease to produce a force of 50 mN, then holds for 3 seconds before retracting (same speed as approach). A micro force gauge measures the push and pull on the probe as it manipulates the grease and this information is recorded for later analysis.

3. Results and Discussion

Testing for Different Types of Tackiness in Grease

Our goal is to relate tackiness to quantified measurements of low temperature fluidity in the LT-37 US Steel Mobility test and the custom-made Spindle Stall Test. For this, we must also quantify tackiness to create and investigate a correlation.

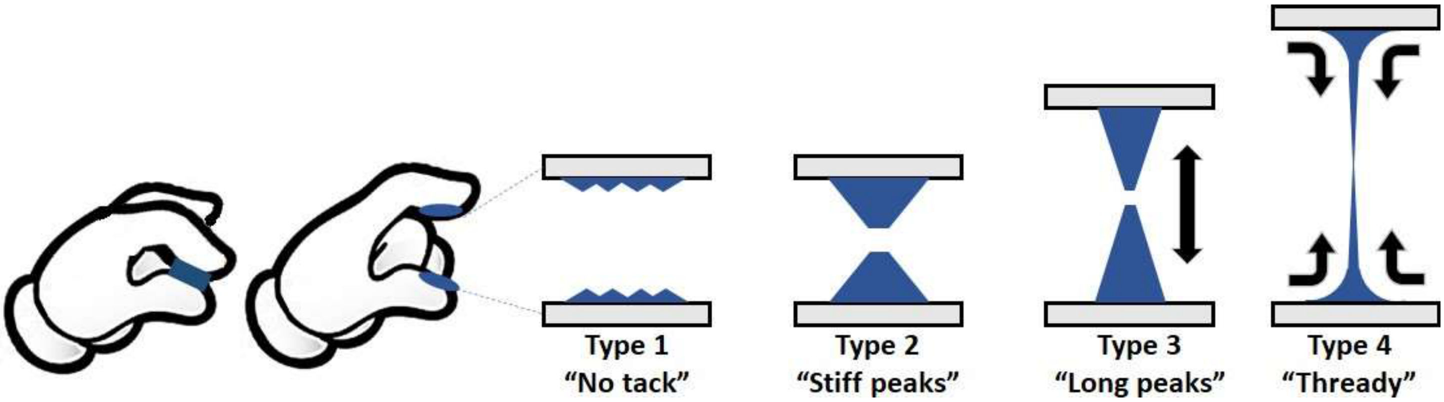
Four types of tacky behavior were observed in the various grease formulations. It was hypothesized that these different types of behavior would be the result of different adhesion and cohesion parameters. Therefore it was important to classify these types before using the Falex TAA to quantify the tackiness parameters. Different polymer structures in the greases should cause differences in the adhesion and cohesion properties which causes differences in the observed tackiness performance – this is a fundamental concept for material science.

The four behaviors observed with manual thumb and finger tack testing were:

- **Type 1 – “No Tack”** – The grease sample pulls apart into two thin, slightly bumpy layers.
- **Type 2 – “Stiff Peaks”** – There is some structuring occurring where the grease pulls into two

triangular peaks reminiscent of a dolphin or shark fin.

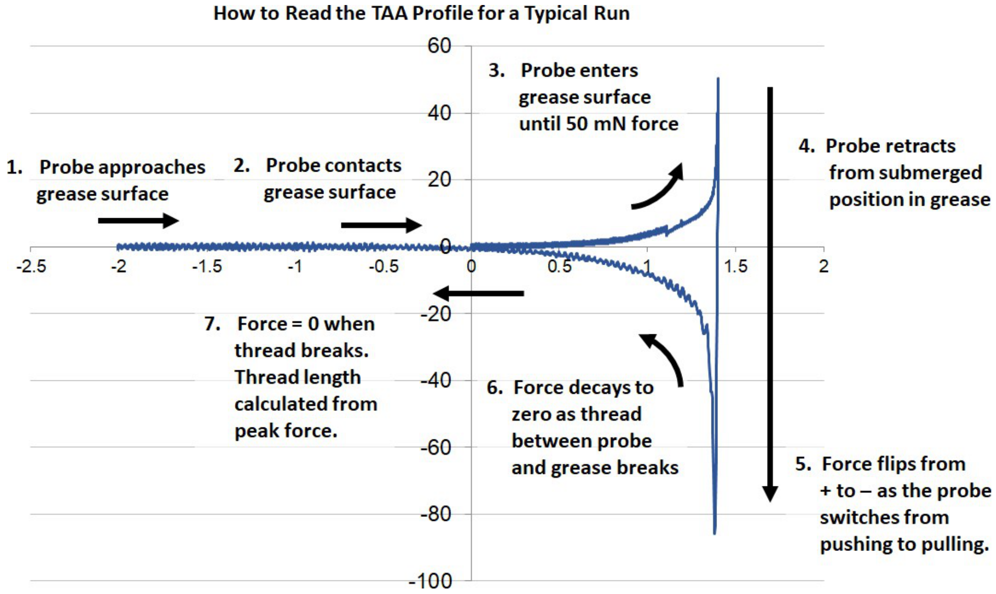
- **Type 3 – "Elastic"** – The grease exhibits elastic behavior and elongates over a longer distance and narrows in the middle into an hourglass shape. The narrow region will snap and result in two long peaks. The thick thread of grease elongates by stretching of the material already between the two surfaces.
- **Type 4 – "Threading"** – The grease immediately pulls into narrow threads which elongate rather than thin and can produce quite long strands. The thread appears to be extending not through stretching of the material in the thread but by pulling in surrounding grease from the two surfaces.



Type 1	Type 2	Type 3	Type 4
Paraffinic, Naph.	mPAO, White Oil		
PMA2	PMA3		PMA1
	PIB1	PIB2	PIB3
	CRY1	CRY2, CRY3	
	OCP1		OCP2, OCP3

Can a highly precise microscale force gauge (the Falex TAA instrument) capture this behavior in some fashion?

The Falex TAA unit can measure: thread length (length before breakage), compression energy, separation energy, peak force to pull the thread, and all as a function of time or distance between the grease sample and the moving probe.
Conditions can also change and be measured for various probe movement speeds and timing. There are several opportunities to find unique correlations between those pieces of data and the four tack behaviors observed.



Pull off force (Fn) exhibited during retraction of the probe from the grease samples was typically highest in greases with Type 1 "no tack" behavior (120-140 mN) while peak force trended lowest for Type 4 "thready" greases (60 - 110 mN) from speeds of 0.1 to 5.0 mm/sec. Type 2 and Type 3 greases exhibited similar (80 – 130 mN) levels of intermediate peak force. Peak force could be read as the stress required to cause the grease to yield and allow the probe to pull away. Higher peak forces demonstrate a tougher or less yielding grease and vice versa for lower peak forces.

Separation energy increases with retraction speed for all greases. However, Type 1 and Type 3 tackiness behavior show a rather linear steady increase from 0.1, 0.5, 1, 2, and 5 mm/sec while Type 2 and Type 4 behaviors show disproportionately low separation energy at low speeds (0.1) and much higher separation energy at high speeds (5.0). The slope of separation energy vs. retraction speed is steeper for Type 2 and 4 which implies the formation of stiff peaks or narrow threads is speed dependent as all non-Newtonian behavior should be. The lack of tackiness in Type 1 or the elastic, Newtonian behavior of Type 3 (where the thicker thread stretches and snaps) would be more Newtonian and less speed dependent.

Compression energy during embedding the probe into the grease sample did not vary with speed, with approach speed into the sample equal to the retraction speed. Type 2 and Type 4 greases trend higher in compression energy with a wide variations between different grease formulations. Type 1 and Type 3 greases are lower in compression energy on average and more consistent between different grease formulas.

Thread length versus retraction speed follows a similar trend to separation energy. Type 2 ("stiff peaks") and Type 4 ("thready") show exaggerated speed dependence with low retraction speeds showing low thread lengths and higher retraction speeds showing higher thread length. Type 3 ("long peaks") are slightly speed dependent but all samples fall within a narrow band of thread lengths versus speed. The ratio of thread length at 5.0 mm/sec to thread length at 0.1 mm/sec was typically 1.5 – 2.0 for most greases yet two greases with Type 4 behavior showed ratios of 2.7 and 3.9 from the very high MW PIB3 and OCP3 greases. Thread length tends to plateau for Type 1 greases above 1 mm/sec.

Thread length divided by separation energy ("length/energy") against follows the trend of separation energy and thread length with Type 2 and Type 4 showing high contrast in length/separation energy from low (0.1 mm/sec) to high (5.0 mm/sec) speeds. Again, Type 1 and Type 3 greases show very similar results for this metric despite the very different physical effect of no tack in Type 1 and very elastic tack in Type 3. Overall, the length/energy increases as Type 1 < Type 3 < Type 4 < Type 2.

From these findings, the Falex TAA using the default ‘Round Robin 2021’ protocol of testing can separate greases with Type 1 and Type 3 tack behavior (more Newtonian based on the TAA data) from greases with Type 2 and Type 4 behavior (more non-Newtonian based on the speed dependency observed in the TAA data). Yet the default information cannot separate Type 1 from Type 3 or Type 2 from Type 4.

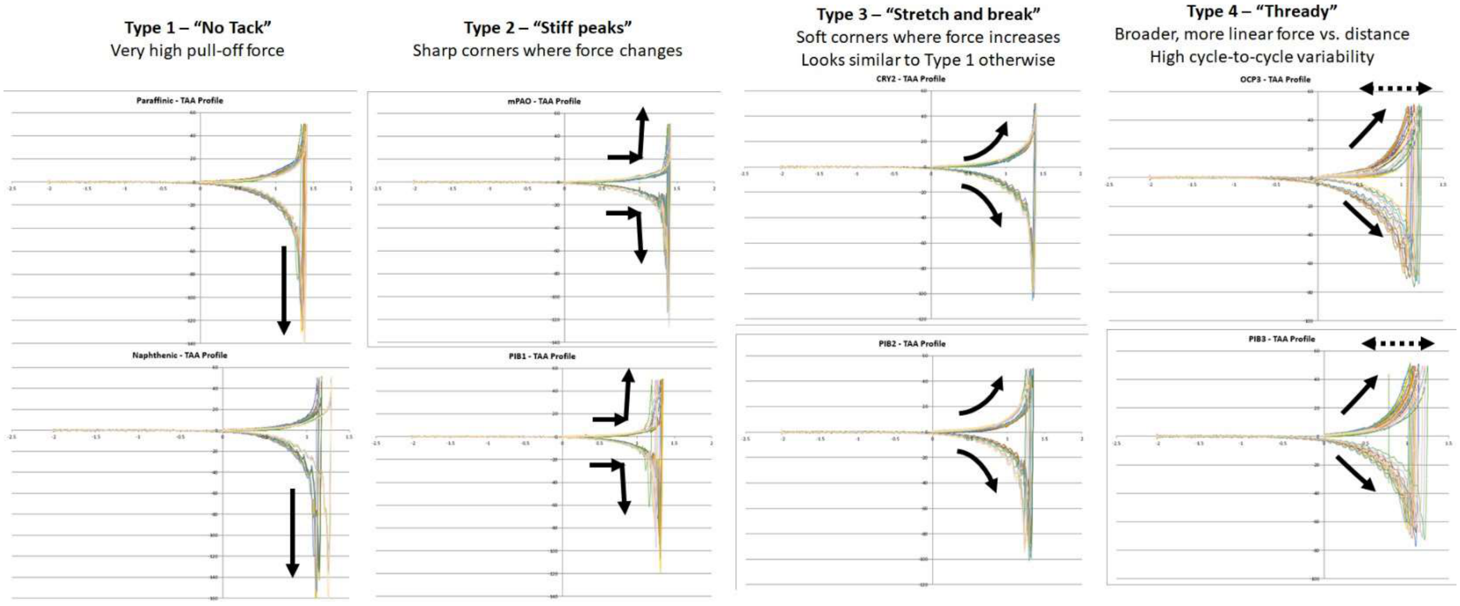
Comparison of measured values for the different types of grease tack behavior. Key characteristics are highlighted.

	Type 1	**Type 2**	**Type 3**	**Type 4**
Pull Off Force	Highest 120-140 mN	Medium 80-130 mN	Medium 80-130 mN	Lowest 60-110 mN
Separation Energy	Energy increases slowly with speed (more Newtonian)	Energy increases quickly with speed (more non-Newtonian)	Energy increases slowly with speed (more Newtonian)	Energy increases quickly with speed (more non-Newtonian)
Compression Energy	Low, Consistent 2-9 µJ	High, Highly Variable 2-14 µJ	Low, Consistent 4-10 µJ	High, Highly Variable 2-12 µJ
Thread Length	Plateaus with increasing speed above 1 mm/sec	Second highest speed dependence	Some speed dependence	High at high speeds and lowest at low speeds
Length/Energy	Lowest	Highest	Second lowest	Second highest

The parameters above are automatically calculated from the average of three 5-cycle runs for each approach/retraction speed. Averaging the TAA force-distance profile may remove subtle details that may further help sort different grease behaviors into the four types experimentally observed with the simple finger tack test.

It is acceptable if Type 2 and Type 4 greases, both objectively tacky, cannot be differentiated by a tack tester but Type 1 (not tacky) and Type 3 (very elastic and tacky) ought to be easily distinguishable. Looking at all the evidence it may take a combination of factors to be assessed to quantitatively separate Type 1 from Type 3 in testing. Type 1 grease behavior has very high pull off forces with low change in thread length at higher speeds (≥1 mm/sec). Type 3 behavior comes with moderate pull off force and thread length which continues to increase with retraction speed. The differences exist but are subtle and no one clear feature distinguishes the two.

The figure below compares two representative samples from each tack behavior type at 5.0 mm/sec speed. The main difference occurs in the curvature of the force versus distance plots, specifically on the shoulder as force increases or decreases rapidly when the probe enters or exits the bulk of the grease sample. Comparing the TAA profile for Type 2 to Type 3 to Type 4 shows continuously broadening of this shoulder as the increase in force with distance becomes less ‘sharp’.



However, Type 1 and Type 3 exhibit similar features and, much like the parameters discussed previously, the only difference appears to be the very high pull-off force of the Type 1 greases versus the Type 3 grease. It seems possible that Type 1 and Type 3 belong to one single type of grease behavior since these numerous comparisons show very few concrete differences that could separate the two types definitively. While no parameter or TAA profile can distinguish the two clearly it is still very apparent that Type 1 and Type 3 greases show obviously different behavior to any casual observer.

We can identify four different types of grease tackiness behavior but the default TAA test protocol did not produce any clear singular value for "tack" that all formulations could be measured against. Thread length would be most useful but all greases from Type 1 (no tack) up to Type 4 (very thready and tacky) show that all the greases are forming threads which break at in the range of 0.4 – 2.0 mm depending on the retraction speed from 0.1 – 5.0 mm/sec. The finger tack method can pull threads of grease several orders of magnitude longer for Type 4 greases.

Future work will entail optimizing the TAA test conditions to better isolate the key parameters that govern the four types of grease behavior and distinguish between greases with higher precision. It is to note that this preliminary test shows that certain speeds of retraction can begin to show different phenomena. 0.1 mm/sec appears too low a speed and many times the TAA profile shows irregularities. 1.0 mm/sec is a good transition point above which non-tacky greases don't increase in thread length much with increasing speed. 5.0 mm/sec is interesting since thready/tacky greases will show high cycle-to-cycle variability.

Key points from section:

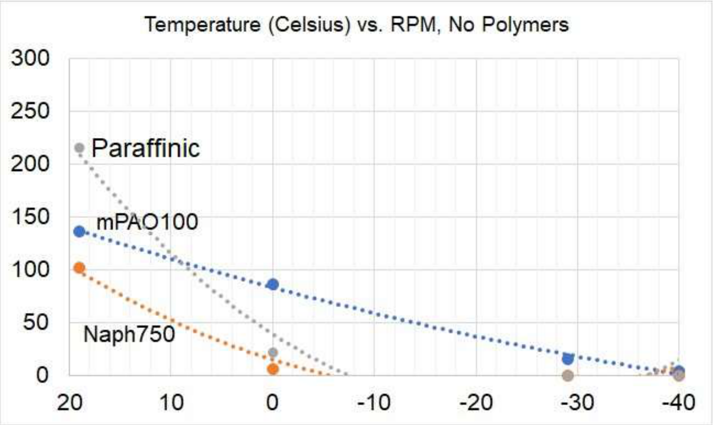
- Falex Tack Adhesiveness Analyzer (TAA) measures quantities like pull-off force, separation energy, and thread length as a function of grease composition and the protocol which consists of different test speeds and cycles.
- Four empirical 'types' of tackiness behavior were seen in the many polymer-modified greases prepared in the study – from 'no tack' to formation of 'stiff peaks' to 'elastic, stretch and break' to 'thready'.
- The default "Round Robin" parameter for the TAA unit can distinguish between three of the four grease behavior types based on qualitative features like curvature of force vs. distance and pull-off force.

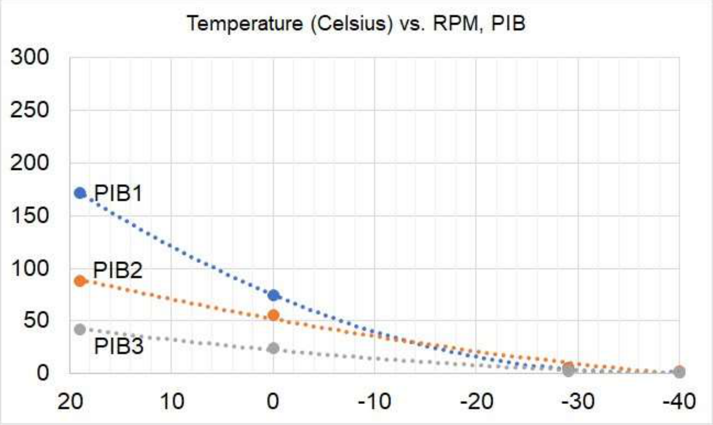
- Type 1 and Type 3 greases are very hard to differentiate in the TAA test but the difference is obvious to the
  ‘finger tack’ method. Type 1 and Type 3 behavior may actually be two opposite ends of one single behavior type.
- A more specific TAA testing protocol needs to be developed that can separate the four tackiness behavior types.

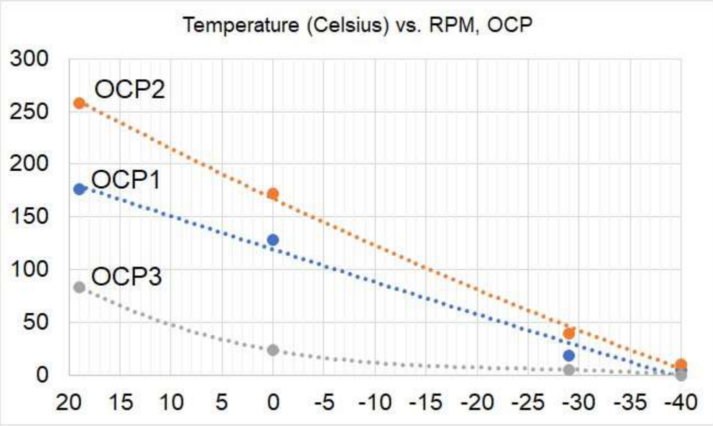
Spindle Stall Test

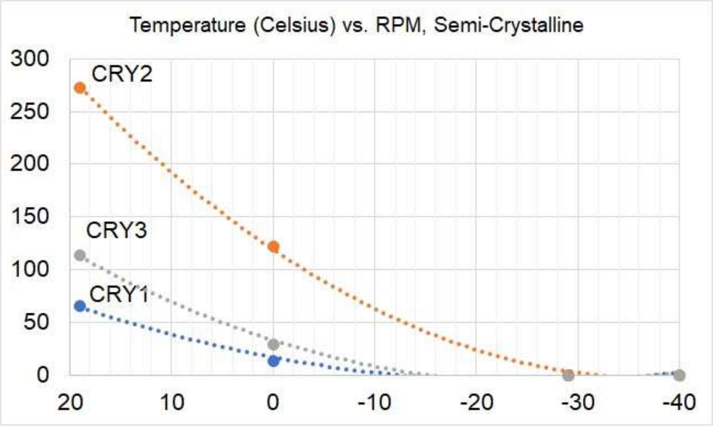
The Spindle Stall test shows a wide range of effects of polymer-modified greases on the resistance of grease on a moving element in terms of RPM versus temperature. For an electric motor, increasing torque from the resistance between the rotating shaft and the viscous grease causes the RPM to decrease until the motor stalls when the resistance equals the torque output and the RPM becomes zero.

Only the non-polar PIB, OCP, CRY, mPAO polymer formulations were evaluated to simplify the study.









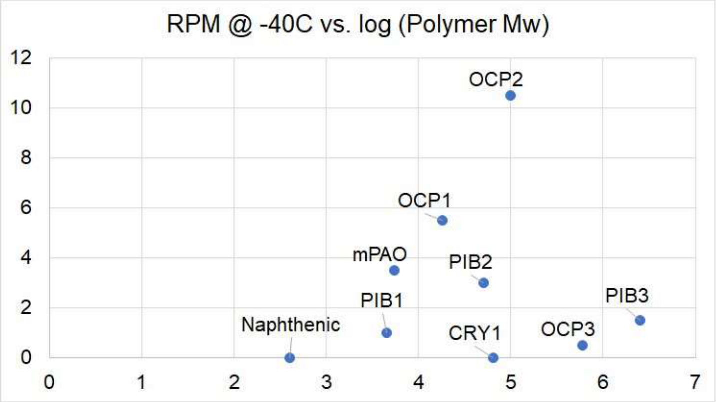
Since the majority of greases were synthetic-based, most greases did not stall the motor at -40°C. Only the Paraffinic, Naphthenic, and CRY polymers (semi-crystalline OCP) based greases exhibited 0 RPM at -40°C which is the test temperature for ASTM D1478 on the NLGI HPM-LT low temperature grease specification. These samples were the highest, i.e. worst, pour points at -15°C, -21°C, and -33°C for Paraffinic, Naphthenic, and CRY2 base oil blends. It is a common rule of thumb that a grease's lower limit for operating temperature is the pour point of the grease's base fluid and all three base fluids for the greases that stalled were above -40°C. The CRY polymer blends have Tg, molecular pour points, of roughly -10°C which appears to dominate the low temperature fluidity even though isolated CRY2 and CRY3 base fluid blends had pour points of -48 and -44°C (< -40°C).

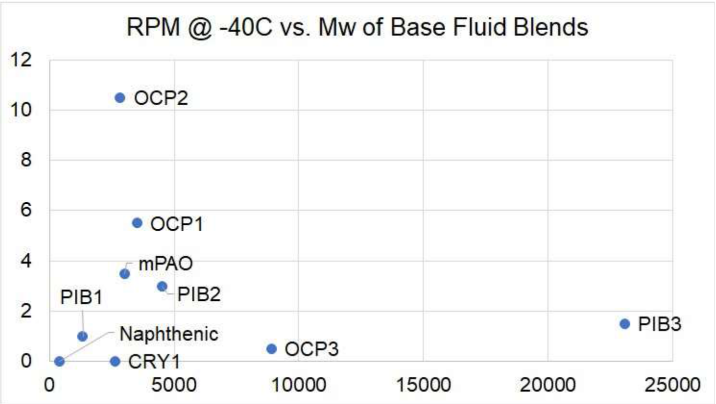
Interestingly, measuring RPM versus temperature from 20°C to -30°C show that the medium molecular weight polymers OCP2 and CRY2 are far more favorable than their low molecular weight counterparts OCP1 or CRY1. At -40C, even the PIB2 outperforms the PIB1 and allows the highest RPM of the PIB series. In all cases the highest molecular weight polymers PIB3, OCP3, and CRY3 produced the lowest RPM which implies the highest resistance to spindle rotation at low temperature. However for OCP and CRY polymer chemistries the best performer was neither lowest or highest molecular weight. Why is this so?

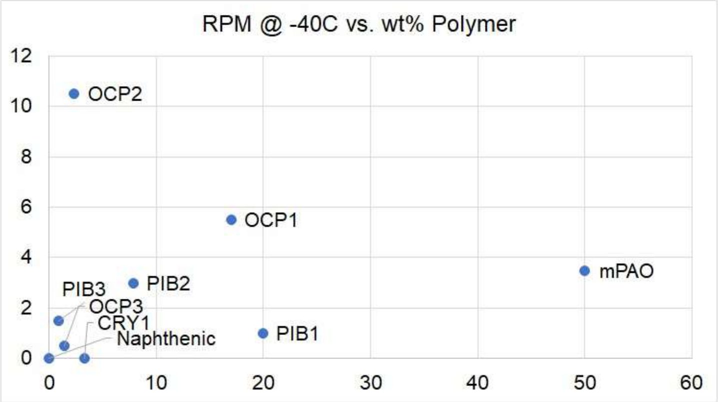
The results highlight a key dilemma in formulating with polymers. Is it better to formulate with a low wt% of high MW polymer or a high wt% of low MW polymer to achieve a target viscosity? In fluids, the low wt% / high MW option typically produces higher low temperature fluidity since more of a lighter base oil can be used which ultimately drives the fluidity. Yet for applications like gear oil or industrial HF where stringent limits of shear stability are placed the high wt% / low MW strategy provides the best mechanical stability.

The way to compare low wt% / high MW vs. high wt% / low MW is to calculate a molecular weight average which gives a single number to rank the formulations against their low temperature fluidity or the RPM on the motor. Molecular weight average Mw is an arithmetic average of each component (PAO6, polymer, diluent oil) versus their respective wt% in the base oil.

Shown below are comparisons of the startup RPM at -40°C versus the log of the molecular weight of the respective polymers, the Mw average of the base fluid blends, and the wt% polymer. Looking at the dataset from these three perspectives shows that the highest RPM was not achieved by the highest or lowest molecular weight polymer (first plot). The highest performance was centered around the medium MW polymers with an average MW of 5000 in the base oil blend (second plot). Several blends fell within the ~5000 MW average but the third plot comparing wt% polymer used clearly separates performance of the OCP2 vs. OCP1 vs. mPAO100 which compete as the highest RPM formulas.





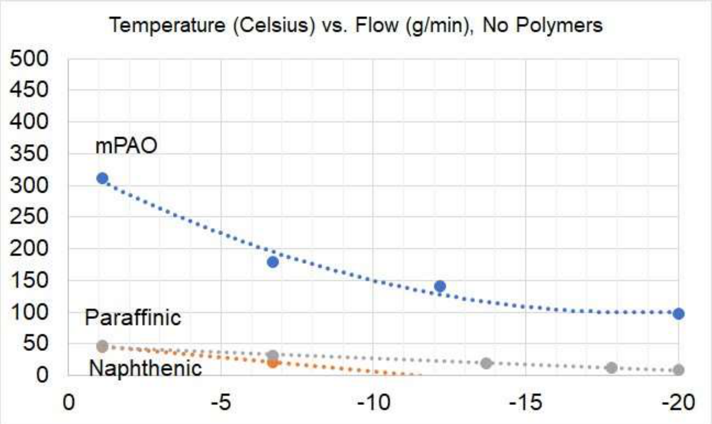


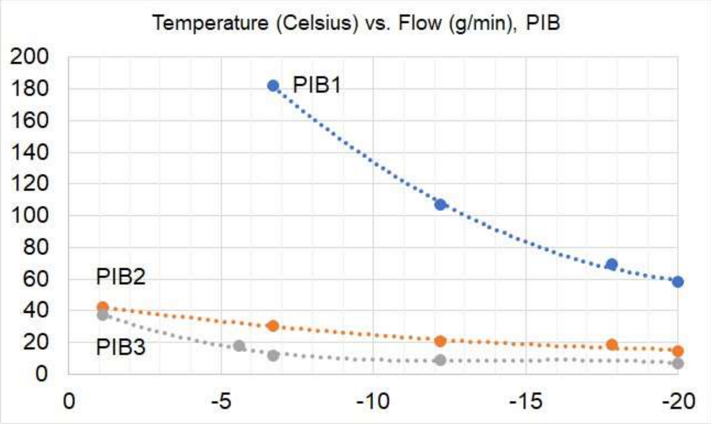
It appears that too much polymer is negative and the lower MW grades (OCP1, PIB1, CRY1) plus mPAO will require more polymer than other formulations to achieve the ISO 150 base oil viscosity. It also appears that too high a molecular weight is also negative for OCP3 and PIB3 though the PIB is higher MW and outperforms the OCP slightly. A moderation between suitably low MW and good thickening efficiency (low wt% polymer needed to meet ISO grade) appears to occur around 5000 MW average which coincide with OCP2 which does so with the least amount of polymer. OCP1, mPAO, and PIB2 also fall into the 5000 MW average region but have notably more polymer and produce lower startup RPMS.

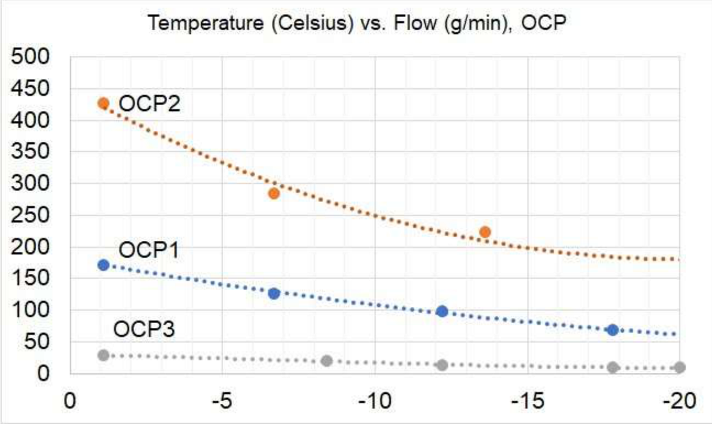
Why does OCP1 outperform the similar PIB2? PIB2 has lower polymer wt% and similar MW average of ~5000. However, the OCP modified greases all appeared to be more yielding and shear thinning than PIB or CRY modified greases despite all greases testing as NLGI #2 on the ASTM D1403 cone penetration test. This is also apparent on the higher startup RPMs at room temperature (20°C) which indicate the OCP greases have lower startup resistance. Cone penetration is very simple test which only captures the rheology of the grease under one arbitrary condition and though all greases are NLGI #2 they present differently under different shearing tests.[17]

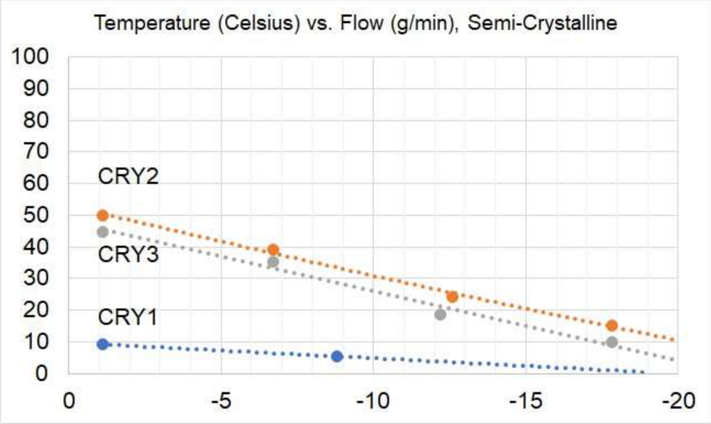
US Steel Mobility - LT-37 Results

The flow rate on US Steel Mobility LT-37 at -20°C is required to be >10 g/min to meet the Low Temperature category of the new NLGI High Performance Multiuse grease specification. Previous discussion on polymers, measuring tack, low temperature fluidity, and the simple Spindle Stall Test have all served as groundwork to discuss the effects of polymers on performance in US Steel Mobility down to -20°C.









The majority of greases were able to flow at -20°C though not every grease met the >10 g/min requirement for HPM-LT subcategory.

Comparing the US Steel Mobility flow rates versus the Spindle Stall test it is apparent that there is good correlation between grease that stall the spindle motor at -40C versus greases that fail the HPM-LT flow rate of 10 g/min. CRY2 was the only grease that failed the Spindle Stall but passed HPM-LT but the CRY2 grease only exceeded the limit by 1.6 which may be well within experimental error for US Steel Mobility.

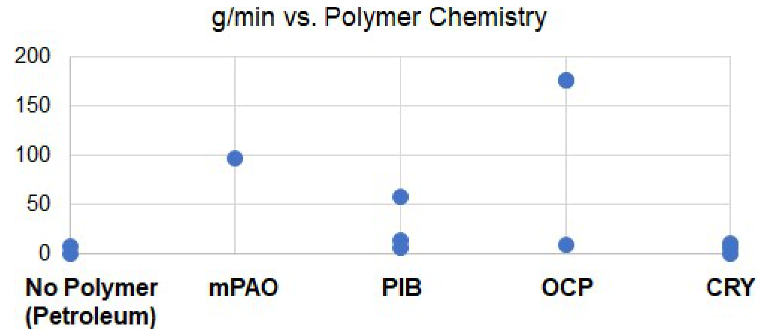
Low Temperature Test Results from Highest Flow Rate in US Steel @ -20°C to Lowest

	US Steel Mobility			Spindle Stall, RPM		
	-20C	**-1C**	**HPM-LT?**	**-40C**	**20C**	**-40C Stall?**
OCP2	175	426.8	Pass	10.5	258	Pass
OCP1	175	172.3	Pass	5.5	176	Pass
mPAO	97.2	311.5	Pass	3.5	136	Pass
PIB1	58.2	182.1	Pass	1	172	Pass
PIB2	14.3	42.2	Pass	3	88	Pass
CRY2	11.6	50.1	Pass	0	272	Fail
OCP3	8.9	28.7	Fail	0.5	84	Pass
Paraffinic	8.5	46.3	Fail	0	216	Fail
PIB3	7.1	37.7	Fail	1.5	42	Pass
CRY3	6.4	44.8	Fail	0	114	Fail
Naphthenic	0	45.7	Fail	0	102	Fail
CRY1	0	9.2	Fail	0	33	Fail

The very high MW polymers PIB3, OCP3, and CRY3 appear very poor on the Spindle Stall test yet do flow at -20°C in US Steel Mobility. No formulation here was optimized and with some adjustment it would likely be possible to meet the 10 g/min limit if starting from the 6 – 9 g/min starting formulations demonstrated here.

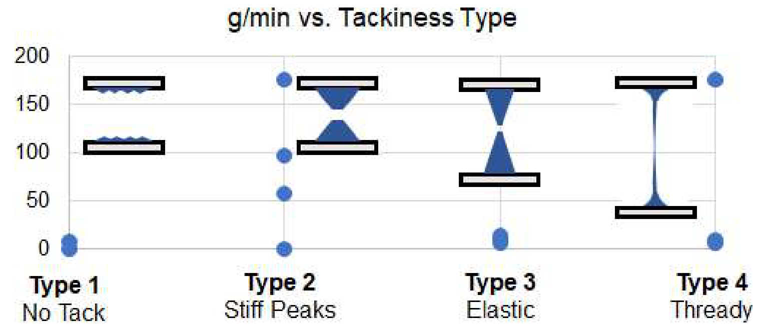
Spindle Stall test at -40°C appears to be a good pass/fail or go/no-go indicator for US Steel Mobility @ -20°C. Setup is minimal and results can be obtained within 2 hours.

Which other factors in grease composition and properties can also help to predict US Steel Mobility success?

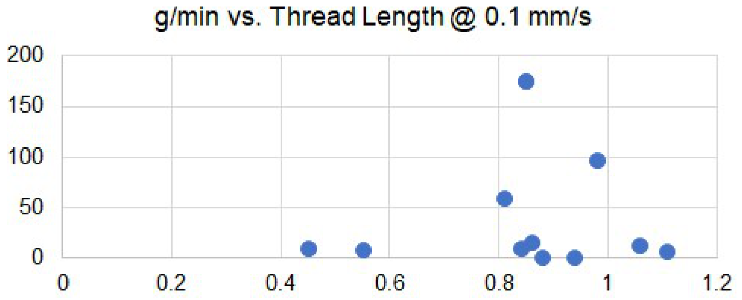


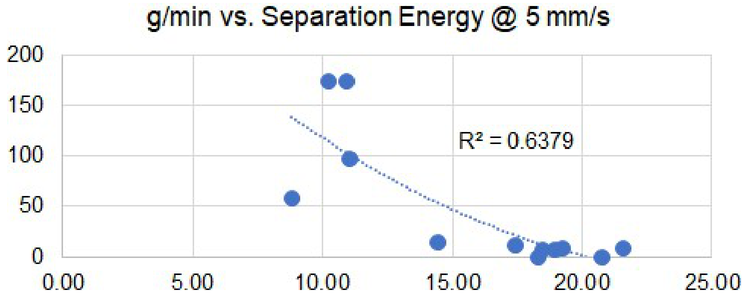
Polymer chemistry appears to matter. The use of polymers, if mPAO is included, to create a synthetic base fluid appears to be required for -20°C flow.
Indeed, the original US Steel Mobility testing only calls for testing down to -1°C/0°F when conventional base stocks were most prevalent. The ISO 150 Group I and naphthenic base stocks both failed HPM-LT with the Naphthenic sample giving no flow.

The interesting point is that PIB, even low MW PIB1, give relatively low flow rates despite having the best Tg of the four polymers (~-70°C). It could be due to the poor thickening efficiency of PIB polymers which requires them to be used at higher wt% which causes overtreat of the polymer.



Tackiness type – whether no tack to some structure to very thready behavior – gave well-defined results. Only the conventional greases were Type 1 so all Type 1 greases gave poor flow rate. All Type 3 greases (elastic) failed the HPM-LT spec and were the worst performers. 3 of 4 Type 2 greases passed while only 1 of 3 Type 4 greases passed (OCP2).

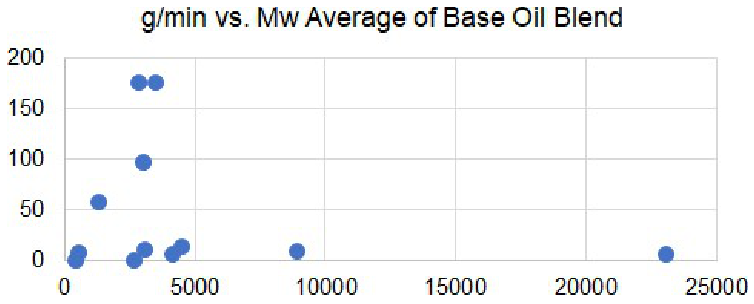




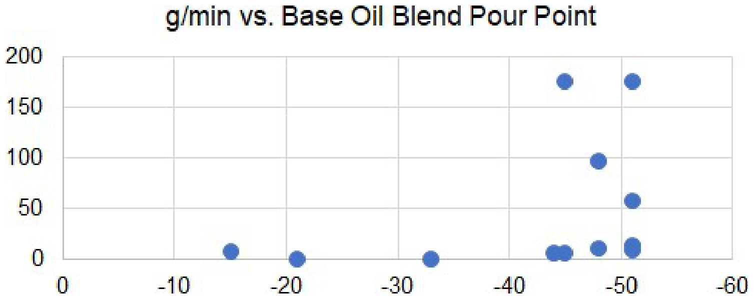
TAA test parameters that best fit US Steel Mobility trends were **Thread Length** at low speed (0.1 mm/s) and **Separation Energy** at high speed (5.0 mm/s).

The Thread length plot shows the familiar ‘triangular’ shape seen in other figures above where flow rate increases to a maximum and then decreases beyond that value.

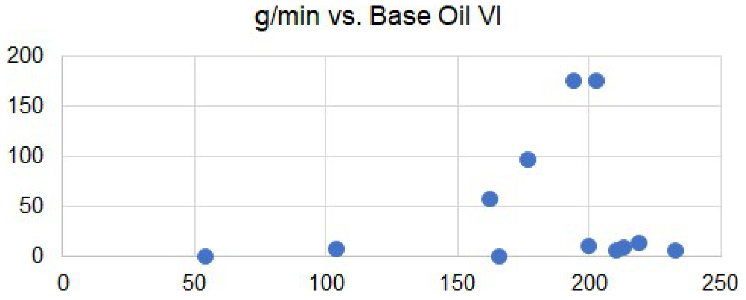
Higher separation energy at higher speeds typically produced better flow rates in low temperature US Steel Mobility. Separation energy tends to be reduced by high MW polymers and is very low in the Type 4 “thready” greases as the threads are pulled very easily.



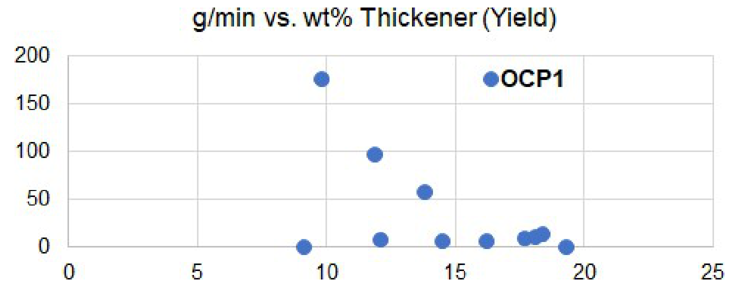
Average molecular weight of the base oil blend had a strong effect on the US Steel Mobility. Much like the Spindle Stall test, the most successful and highest flow greases were centered around Mw = 5000 g/mol.



Pour point of the base oil blend shows a strong effect. No base fluid with a pour point warmer than - 40°C gave a passing flow rate in US Steel Mobility at - 20°C. This may be the reason behind the good correlation between Spindle Stall at -40°C versus US Steel Mobility at -20°C. Low pour point was a necessary but not sufficient parameter for success.

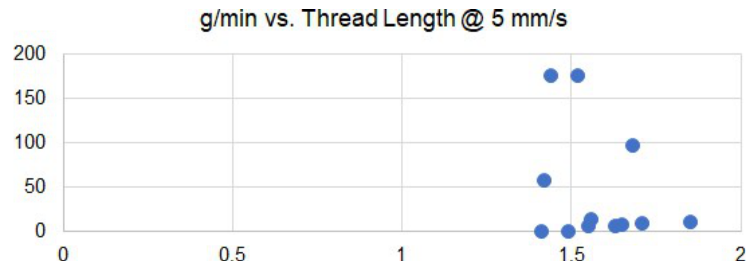


Base oil viscosity index (VI) shows an interesting, ramp-like relationship. VI 150 to 200 produced good flow rates at -20°C but exceeding VI 200 suddenly gave very poor results. The highest VI base oil blends were from the highest MW polymer grades while the medium MW polymers preferred for low temperature fluidity produced the 150-200 Vis.



Thickener wt% showed a ramp-like trend with higher amounts of thickener showing a strong decline in flow rate. The low MW OCP1 stood out with very high flow rate but otherwise higher thickener content was unfavorable.

Many of this factors may be the result or symptom of other, more fundamental factors. Which factors did not greatly affect US Steel Mobility in a systematic way?



Thread length at high speed (5 mm/sec) has notably low correlation with flow rate. Overall thread lengths were much lower on the TAA tack test than could be pulled by the simple finger test. More work is needed to refine the testing protocol to emulate the exact conditions. US Steel Mobility flow rates tend to be quite low so high speed tackiness may not be applicable due to the difference in time frame.

4. Conclusions

A range of greases were prepared using ISO 150 synthetic base stocks adjusted with different molecular weights (base stock, viscosity modifier, tackifier) from three different polymer chemistries (PIB, OCP, CRY). The resulting greases show a wide range of tackiness which can be summarized as four different types of tack behavior.

Quantification of tackiness behavior with the Falex TAA has been moderately successful in corroborating the empirical, visual finger tack results with real force and energy numbers. However this preliminary work with the Falex TAA does not yet produce a singular measure of tack that we can line up all the greases against. Knowing that there are different regimes of tackiness behavior will help to guide careful consideration of future testing protocols with TAA.

Low temperature testing with the in-house Spindle Stall test and the US Steel Mobility LT-37 methods give insight into the balance of wt% polymer versus polymer molecular weight and chemistry.

The Spindle Stall test demonstrates that the best low temperature fluidity and low resistance to torque are achieved when the molecular weight average of the base fluid blend (between polymer, base oils, and synthetic base stocks) is limited to 5000 g/mol. The limitations of mPAO became apparent due to the very high (50%) treat rate which made the mPAO control grease less fluid than the OCP chemistries.

US Steel Mobility results at -20°C correlate well with the more convenient testing of Spindle Stall at -40°C. Similar phenomena are in effect between the resistance to rotation of a spindle versus grease being pushed through a confined metal tube – the difference is whether it is the metal substrate or the grease sample which is in motion. Not all greases that passed US Steel Mobility passed the Spindle Stall test and vice versa. Thus it is important to screen multiple types of grease flow (i.e. rotational torque, confined flow, consistency changes) to cover possible failure in different end uses.

5. Acknowledgements

Thank you to Jim Cordek (Functional Products Inc.) for the numerous soap bases and characterizing each base fluid blend; and to Pat Stockton (Clark Testing) for discussions on US Steel Mobility method. Thank you to Falex Tribology (US and European teams) and Compass Instruments Inc. for continued discussion and training with the Falex TAA tack tester equipment and to H.L. Blachford for supplying the NSF HX-1 lithium 12-hydroxystearate preformed grease thickener.

6. References

1. Vargo, D. M. Polymers to Enhance the Performance of Inorganic Grease. NLGI Spokesman 32–36 (2017).
2. Vargo, D. The Adhesiveness of Grease. NLGI 81st Annual Meeting (2014).
3. Willett, E. Overcoming Obstacles in Water Resistant H1 Specialty Greases Using Polymer.
4. T.G. Musilli. Water Spray-off Characteristics of Lubricating Grease. NLGI Spokesman **December**, (1982).
5. Georgiou, E. et al. Measuring Grease Tackiness Objectively. ELGI AGM (2019).
6. Gonçalves, D. et al. Formulation, rheology and thermal ageing of polymer greases—Part I: Influence of the thickener content. Tribology International **87**, 160–170 (2015).
7. Willett, E. The Mechanical Stability of Polymer-Modified Greases.
8. Vargo, D., DeVore, D. & Lipowski, B. The Effect of Polymer Additives on Grease Flow Properties. NLGI 81st Annual Meeting (2014).
9. Kunal, K. et al. Polyisobutylene: A most unusual polymer. Journal of Polymer Science, Part B: Polymer

Physics **46**, 1390–1399 (2008).

10. Malhotra, S. L., Minh, L. & Blanchard, L. P. Thermal Decomposition and Glass Transition Temperature of Poly(isobutylene). http://dx.doi.org/10.1080/00222338208056515 **18**, 455–475 (2006).
11. NATTA, G., DANUSSO, F. & MORAGLIO, G. ISOPHASIC TRANSITIONS OF POLYMERS OF n-ALIPHATIC α-OLEFINS.
    Stereoregular Polymers and Stereospecific Polymerizations 386–387 (1967) doi:10.1016/B978-1-4831-9883- 5.50068-4.
12. Linnig, F. J., Parks, E. J. & Wood, L. A. Ethylene–propylene copolymers: Crystallinity, infrared, and creep studies.
    Journal of Applied Polymer Science **8**, 2645–2651 (1964).
13. Gahleitner, M. et al. Propylene–ethylene random copolymers: Comonomer effects on crystallinity and application properties. Journal of Applied Polymer Science **95**, 1073–1081 (2005).
14. Tammy Uan-Zo-li, J., Marand, H. & Brian Love William Reynolds Alan Esker Richey Davis, C. J. Morphology, Crystallization and Melting Behavior of Propylene-Ethylene Statistical Copolymers. (2005).
15. US20090281360A1 - Polyalphaolefins and processes for forming polyalphaolefins - Google Patents. https://patents.google.com/patent/US20090281360A1/en.
16. US8080699B2 - Two-stage process and system for forming high viscosity polyalphaolefins - Google Patents. https://patents.google.com/patent/US8080699B2/en.
17. Flemming, W. & Sander, J. Is It Time to Retire the Grease Penetration Test? NLGI Spokesman 14 (2018).

Evaluation of EP Components for Gear Oil Packages

Rolfe J. Hartley
Kemipex Chemicals Trading LLC

Abstract

A chemical bench test involving soaking a copper strip in EP additive and measuring weight loss has been shown in the patent literature to predict performance in shock-bump hypoid gear lubrication performance. However, the bench test yields no chemical information to guide the development of new components, formulation of new packages or selection of purchased components. The chemical bench test was used in the patent to select a purchased component to develop an automotive gear oil formulation. The component described in the patent has been analyzed with modern analytical methods to yield compositional and structural information. The compositional data provides insight into structure/activity relationships as predicted by the bench test. The analytical tools are demonstrated to be capable of providing guidance in process development for new components. The analytical tools are also shown to be capable of doing a detailed analysis of purchased components. There is a high potential to use compositional data to make formulation and component selection rather than relying on empirical methods. The empirical methods and analytical methods are shown to complement one another.

Keywords: polysulfide, EP additives, gear oil components, gear oil formulations, analysis of lubricants

1.0 Introduction

The lubricant industry is highly reliant on mechanical tests to determine if a lubricant is fit for its purpose. Tests can be quite expensive and time-consuming. When developing a new formulation, it is desirable to be able to screen for performance. To maximize the speed of product development and minimize product development costs, the screening methodology should be fast, cheap, repeatable, and reliable.

The single largest amount of additive in a gear oil package is the Extreme Pressure (EP) additive. The choice of additives is in a state of flux. Traditionally sulfurized isobutylene by the chlorine process has been used. However, the manufacture of these additives in certain geographical areas have been curtailed due to environmental concerns. The supply is either limited or no longer exists.

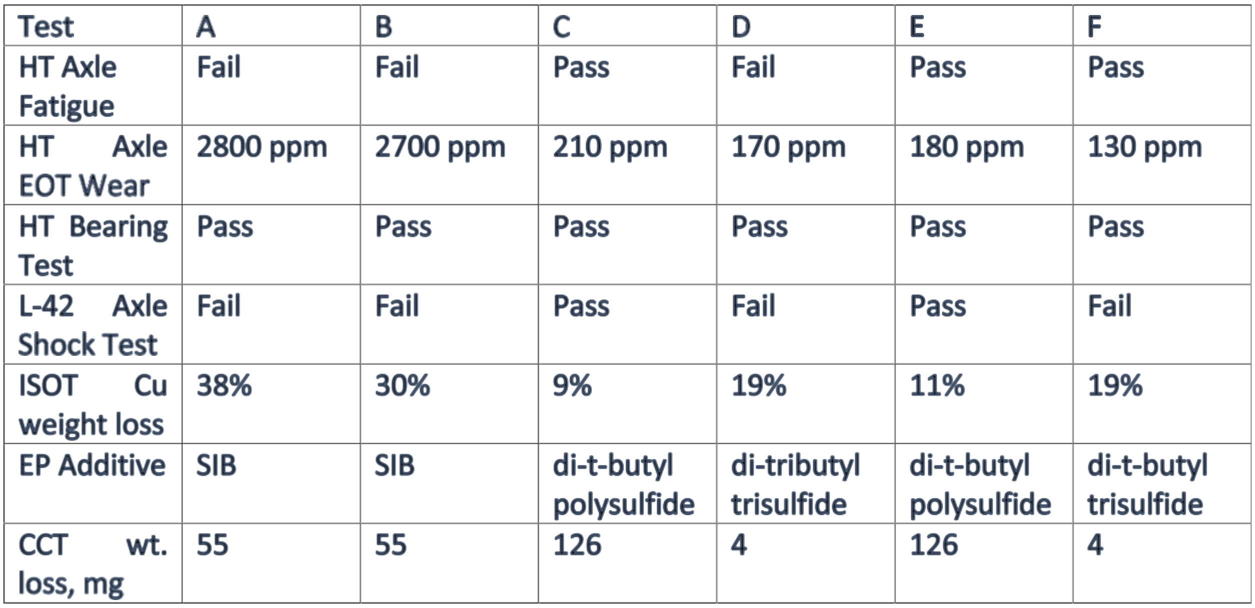
Polysulfides are an alternative to SIB. There are two types of polysulfide available based on the type of reaction used to produce the component. The first type uses t-butyl mercaptan as a starting material. The resultant t-butyl polysulfide is an excellent material but is expensive because t-butyl mercaptan is expensive. The second type is made by direct sulfurization of isobutylene. However, there can be issues, and not all products are equivalent.

Chlorine process SIB yields a complex product that is difficult to analyze. As a young chemist, the author observed over 80 major peaks by liquid chromatography (LC). Polysulfides yield a mixture of products that are simple enough that they can be characterized with modern analytical methods.

Previous work (1) in characterizing the balance between EP activity and copper corrosion in polysulfides had focused on gravimetric methods like reaction with copper metal. These gravimetric techniques allowed an accurate prediction of performance. However, the results were empirical. There was no compositional information about the components tested.

2.0 Screening EP additives

US patent 7,888,299 B2 teaches a screening method for EP additives. The name of the method is the Copper Corrosion Test (CCT). The method is shown to be able to predict performance in key rig tests. The method is based on the weight loss of a copper strip immersed in the additive at the specified time and temperature. Weight loss is determined by removing the corrosion by a soak in sodium cyanide—weight after is subtracted from weight before. The patent gives detailsof the procedure.



Test	A	B	C	D	E	F
HT Axle Fatigue	Fail	Fail	Pass	Fail	Pass	Pass
HT Axle EOT Wear	2800 ppm	2700 ppm	210 ppm	170 ppm	180 ppm	130 ppm
HT Bearing Test	Pass	Pass	Pass	Pass	Pass	Pass
L-42 Axle Shock Test	Fail	Fail	Pass	Fail	Pass	Fail
ISOT Cu weight loss	38%	30%	9%	19%	11%	19%
EP Additive	SIB	SIB	di-t-butyl polysulfide	di-tributyl trisulfide	di-t-butyl polysulfide	di-t-butyl trisulfide
CCT wt. loss, mg	55	55	126	4	126	4

Table 1 – Table 2 from US patent 7,888,299 B2

Basically, what the patent says is that the correct EP agent to give passing CRC L-42 EP performance and axle fatigue performance can be selected by screening the component in the CCT bench test.

The inventors evaluated several candidate EP sources in the CCT.

EP Component	CCT
SIB	55
Di-t-butyl polysulfide	126
Di-t-butyl disulfide	2
Di-t-butyl trisulfide	4
Di-t-butyl pentasulfide	466
Di-t-nonyl polysulfide	731

Table 2 – Table 3 from US Patent 7,888,299

Additives having more active sulfur are predicted to have better EP performance. However, the point of diminishing returns is reached due to the difficulty in being able to inhibit copper corrosion in a finished oil formulation.

Since the time this patent was filed, there has been an increased awareness of safety and environmental issues. The original CCT procedure called for the use of a sodium cyanide solution to strip off the corrosion. Cyanide is a toxic substance, and handling and disposal must be carefully considered. The decision was made to eliminate the cyanide stripping step and to try to remove the corrosion by abrasion with a towel.

The CCT is a method that gives empirical data but no information about the chemical structure. Modern analytical techniques like Gas Chromatography and Liquid Chromatography have become routine. When coupled with a mass spectrum (MS) detector, a powerful tool has become available to characterize the molecular weights of chemical species in a complex mixture.

2.1 GC/MS of t-butyl polysulfide

The t-butyl-polysulfide shown in tables 1 and 2 is a well-known commercial component that has been successfully used to formulate GL-5 level automotive gear oil packages. The issue with t-butyl polysulfide is cost. The manufacturing process uses t-butyl mercaptan as a starting material. The product is very clean, with very few side reactions.

Two different lots of t-butyl polysulfide were obtained. GC analyzed the samples with an MS detector. The MS spectra were used to characterize the samples' molecular weight of the constituent compounds.

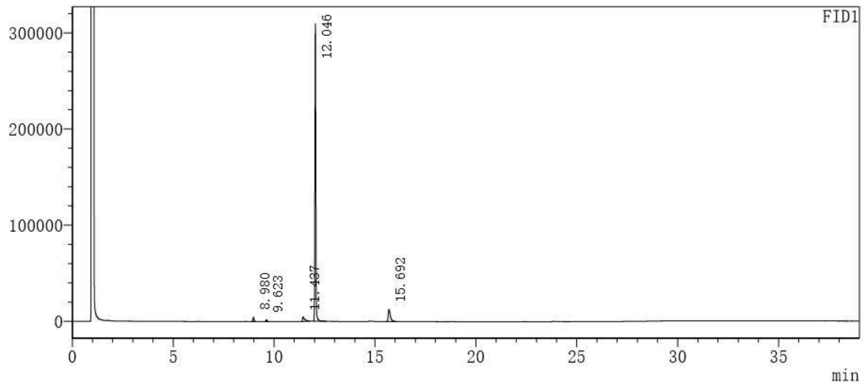


Figure 1 – polysulfide sample 1

The GC of the first sample is shown in Figure 1. There is one major peak and four minor peaks.

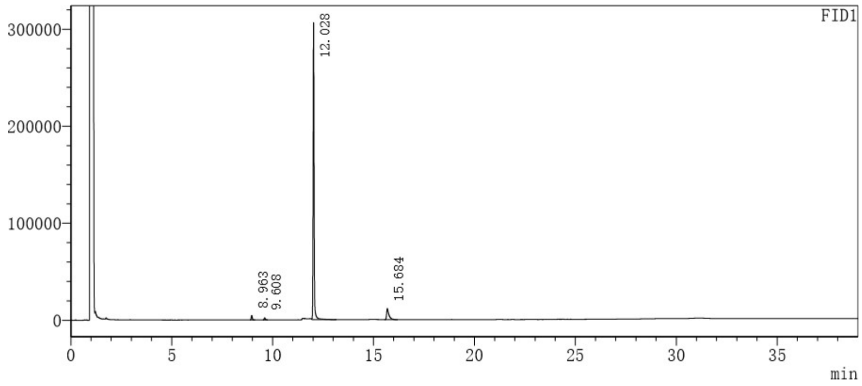


Figure 2 – polysulfide sample 2

The GC of the second sample is shown in Figure 2. There is one major peak and three minor peaks. The two samples are not the same.

	Retention time, min.	Mwt.	Likely identity	Sample 1, area %	Sample 2, area%
1	8.96	178	Disulfide or isomer	1.339	1.36
2	9.601	178	Disulfide or isomer	0.576	0.608
3	11.44	209	Suspected ring compound	3.148	
4	12.028	210	Tri sulfide	86.659	90.071
5	15.684	242	Tetra sulfide	8.278	7.961
Total				100	100

Table 3 – Mass spectrum identification of species.

Both samples had minor components of 178 Mwt. Since the molecular weights are the same butthe retention times are different, it can be inferred that these are isomers. The compound at 209 Mwt is one mass unit less than the trisulfide. The bulk of both samples are comprised of trisulfideand tetra sulfide.

In the patent, di-t-butyl trisulfide gave failing results in the L-42. The di-t-butyl trisulfide gave passing results. The difference between the two is that the t-butyl polysulfide contains ~ 8% of the tetra sulfide. This argues that the difference between the two in performance is the 8% of tetra sulfide.

Mass spectroscopy gives information about molecular weight, but ^{13}C NMR would be required to confirm the exact identity. For the purposes of this study, it was not deemed essential to confirm exact structures.

3.0 Applications

This section discusses the applications of modern analytical methods to process development and selection of 3rd party components.

3.1 Process Development

The approach of using isobutylene as one of the starting materials rather than t-butyl mercaptan was decided, primarily for economic reasons. GC/MS was used as a tool to characterize the reaction products. The analysis results would be used to guide decisions about new experiments.

Identity	t-butyl polysulfide from patent, area %	Developmental t-butyl polysulfide A, area %	Developmental t-butyl polysulfide B, area %	Developmental t-butyl polysulfide C, area %
t-butyl disulfide or isomer	1.36	0.03	.06	0.08
t-butyl disulfide or isomer	0.608	6.80	9.52	13.02
t-butyl trisulfide	90.071	87.44	79.85	71.73
t-butyl tetra sulfide	7.961	5.33	9.95	14.66
t-butyl penta sulfide		0.05	.08	.12
t-butyl hexa sulfide		0.04	.08	.12
Sum	100	100	100	100
CCT, mg. weight loss	85	134	257	290

Table 4 – Developmental t-butyl polysulfide versus t-butyl polysulfide from the patent

GC/MS was used to characterize the reaction products during process development experiments. Table 4 shows the estimated chemical compositions of three developmental t-butyl polysulfide products versus the t-butyl polysulfide from the patent. Also shown is the CCT data.
The value of the CCT for t-butyl polysulfide from the patent (85 mg) was lower than the value reported in the patent (126 mg). This could be because it was run at a different time by a different operator using a modified procedure. However, it looks like the trend in the data is similar. The CCT data for the developmental samples is substantially higher than the CCT data for the t-butyl polysulfide from the patent. The main difference in composition between the developmental polysulfides and the patent example are small amounts of t-butyl pentasulfide and t-butyl hexa sulfide. This implies that small amounts of these compounds are very corrosive toward copper.

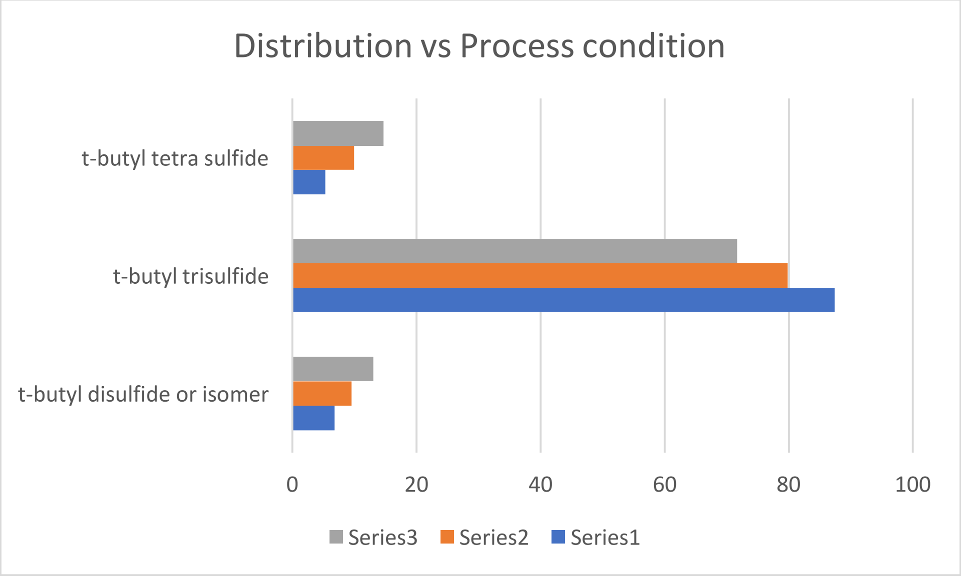


Figure 3 – Distribution of polysulfide as a function of process condition

As shown in Figure 3, the experiment showed that process conditions could be manipulated to control the level of t-butyl tetra sulfide, t-butyl disulfide, and t-butyl trisulfide in the product, albeit not in an independent manner.

3.2 Purchased components

Building a manufacturing plant from scratch to make t-butyl polysulfide requires capital investment. There are also health, safety and regulatory concerns that must be addressed. If building a plant is not an option, components can be purchased if the component can be supplied with the required timing, quality, and volumes. The methodology outlined in this paper can also be used to screen candidate components before committing to more exhaustive and expensive testing.

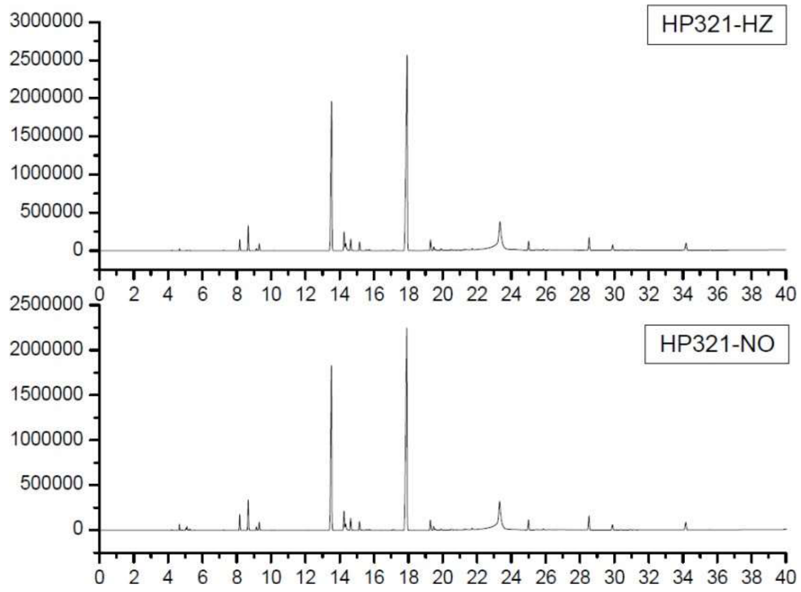


Figure 4 – Market samples

Figure 4 shows the GC of two market samples. These samples are like the developmental samples. However, there are differences. Most of the composition is t-butyl di sulfide, t-butyl tri sulfide and t-butyl tetra sulfide. Also present are small amounts of t-butyl penta sulfide and t-butyl hexa sulfide suggesting these samples may be corrosive toward copper. Also present in minor amounts are t-butyl mercaptan, t-butyl-S-S-H and others.

The two neat components had a strong odor of rotten eggs. Due to odor, it was impossible to blend an additive package without causing the laboratory to evacuate.

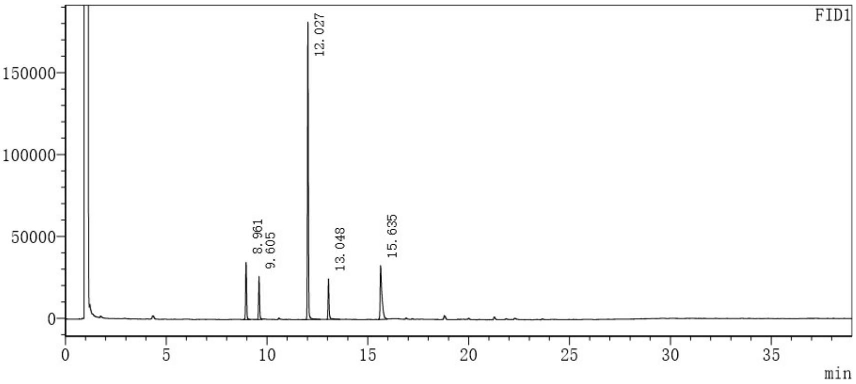


Figure 5 – Market sample A

The GC trace of market sample A is shown in Figure 5. It is known with certainty that his component has been used to formulate an API GL-5 level of the quality additive package. The GC is very clean and simple.

Peak No.	Retention Time	Area %	Identity	Mwt
1	8.961	11.369	t-butyl disulfide or isomer	178
2	9.605	8.450	t-butyl disulfide or isomer	178
3	12.027	53.036	t-butyl trisulfide	210
4	13.048	8.258	Isomer of t-butyl trisulfide	210
5	15.635	18.887	t-butyl tetra sulfide	242
Total		100		

Table 5 – Composition of Market Sample A

Table 5 summarizes the composition of market sample A. The MS data gives molecular weight but cannot distinguish between isomers to give complete structural information. Follow-up work by ^{13}C NMR would be required to define exact structures. Of note are the missing minor impurities that could cause a large issue with formulating a finished oil.

4.0 Soft ionization methods

Soft ionization methods as applied to EP sources are discussed.

Ionization type	Ionizing species	Comment
Electrospray ionization (ESI)	Sample solution is aspirated across a high potential difference, heat, and gas flow desolvates clusters.	Good for charged, polar or basic compounds, multiply charged species are common, good for LC-MS, mass range to 200 k
Matrix-assisted laser desorption ionization (MALDI)	Analyte dissolved in a matrix that is UV active, on a Laser target, matrix absorbs laser pulse.	Very high mass range–up to 500,000 AMU, requires pulsed mass analyzer, not compatible with LC-MS.

Table 6 – Soft ionization MS techniques

Two common soft ionization MS techniques are shown in Table 6. The great thing about soft ionization MS is that no prior separation is required. The author has found that ESI is useful in the analysis of competitors' additive packages and finished oils. For example, consider the analysis of a finished engine oil. ESI can show the exact alkyl groups used in the detergents, the type of detergent (sulfonate, phenate, salicylate, carboxylate, etc.), the exact alcohols used to make the ZDDP and the details of the antioxidant system all without having to do a separation.

Di isobutylene can be reacted with sulfur to give a sulfurized olefin. This type of component is sold by several additive suppliers primarily for metal working applications.

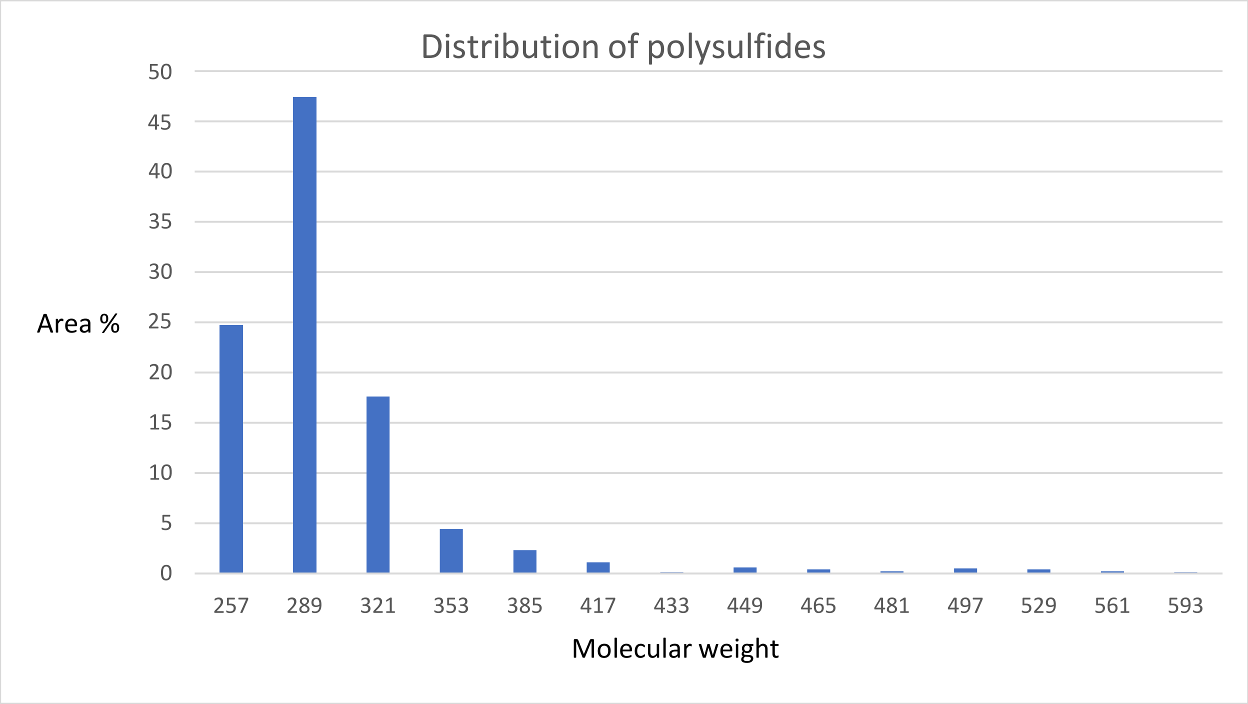


Figure 6 – MALDI data for sulfurized di isobutylene.

Figure 6 shows the mass distribution for a commercial sample of sulfurized di isobutylene obtained by MALDI. All the major peaks differ from each other by 32 (the atomic weight of sulfur).Thus, the major peaks are mono, di, tri, tetra, penta, etc. di isobutyl sulfides.

5.0 Conclusions

1.) A wet chemical procedure exists (CCT) to screen sulfur compounds for their potential for inclusion at the EP additive for high-quality gear oils. The procedure was published in the patent literature.
2.) The CCT has the drawback of not giving any chemical information.
3.) GC/MS gives detailed information about the chemical composition of a mixture of polysulfides. Performance can be inferred from the chemical composition.
4.) Taken together, the CCT and GC/MS are synergistic in providing insight into the performance of polysulfides.
5.) GC/MS is a powerful tool to guide process development. 6.) GC/MS is a powerful tool to screen candidate components.
7.) Higher polysulfides (n > 4) are very corrosive toward copper
8.) If mercaptan can be detected by GC/MS, the odor is most likely unacceptable.
9.) Soft ionization techniques are demonstrated to be able to characterize candidate components.

References:

1.) Extended Drain, Thermally Stable, Gear Oil formulations, US patent 7,888,299 issued Feb. 15, 2011, to Milner, Sheets, Seki and Yatsunami.

2.) Johnson, D. W., 2017, 'Applications of Mass Spectrometric Techniques to the Analysis of Fuels and Lubricants', in M. Aliofkhazraei (ed.), Mass Spectrometry, IntechOpen, London. 10.5772/intechopen.68592.

Impact of Friction Modifiers and Viscosity Modifiers in the formulation ofEnergy Efficient Automotive Gear Oils

Jencen Mathai Arivannoor*, Sanjay Kumar, Chidambaram C T, Botta Sudhakar, Dr KavirayaniNavinkiran, Dr Karthika C, V Vidhya
Gulf Oil Lubricants India Limited

Abstract

The efficiency of an automotive transmission can be improved with the selection of suitable energy- efficient transmission fluids, which can reduce friction losses in the system. There are two methods to reduce friction between two surfaces - reduction in coefficient of friction in boundary regime by employing friction modifiers, and reduction in fluid friction in hydrodynamic regime by reducing viscosity. This study focuses on the effects of friction modifiers, viscosity modifiers, and combinations thereof in the reduction of friction in four conventional automotive gear oils of different viscosity grades. The various formulations were evaluated in two tribological test rigs. The SRV linear reciprocating tester was used to evaluate friction reduction in boundary conditions with moderate temperatures. The Mini Traction Machine was used in the measurement of traction coefficient with varied speeds, spanning all the lubrication regimes at higher temperatures. The study shows that the addition of different additives has a marked effect on the coefficient of friction across all the regimes. The study shows a selection of appropriate friction modifiers and viscosity modifiers can further improve the formulation of energy-efficient gear oils.

Introduction

The main driver in modern vehicle development is emission control. Since the introduction of the concept of emission regulation in 1963, vehicle emission standards have become increasingly stringent with every revision. With the introduction of Corporate Average Fuel Economy (CAFÉ) standards in India, vehicle manufacturers have been imposed a limit for carbon dioxide (CO_2) emissions of 130 g/km by 2023, and 113 g/km afterwards [1]. The emission regulations for passenger cars are even more stringent in the European Union, where the CAFÉ limits are 95 g/km of CO_2. [2]

The primary approach is to make the vehicle more energy efficient, thereby reducing the fuel consumed for the same amount of work and reducing the associated emissions. In addition to emission control, increased energy efficiency can also reduce a dependency on petroleum-based fuels such as petrol and diesel, improving energy security. This approach has led to multiple overhauls in design over the last few decades. Several design changes and additions have been made over the years to improve the fuel efficiency of vehicles. The majority of these improvements were made in increasing engine efficiency, such as improving the combustion characteristics through modified injection timings and injection patterns, downsizing the engine, introducing turbochargers, and even electrification. Reduction of losses across the powertrain, such as frictional losses, can also increase the output of the vehicle. [3]

As evaluated on the EPA drive cycle, only 38 per cent of the combusted fuel is obtained as available horsepower. The rest is lost through the exhaust and the coolant. After consideration of pumping losses and friction losses in the engine, 25 per cent is transferred to the rest of the drivetrain. Further losses occur in the transmission system and axles, such as braking and coasting and idle. Only 12 per cent of the total energy produced is available for motion, in overcoming tyre-to-road friction and aerodynamic drag. In essence, as determined in the EPA drive cycle, about 7 per cent is lost as friction in the engine, and 3 per cent in transmissions. [4]

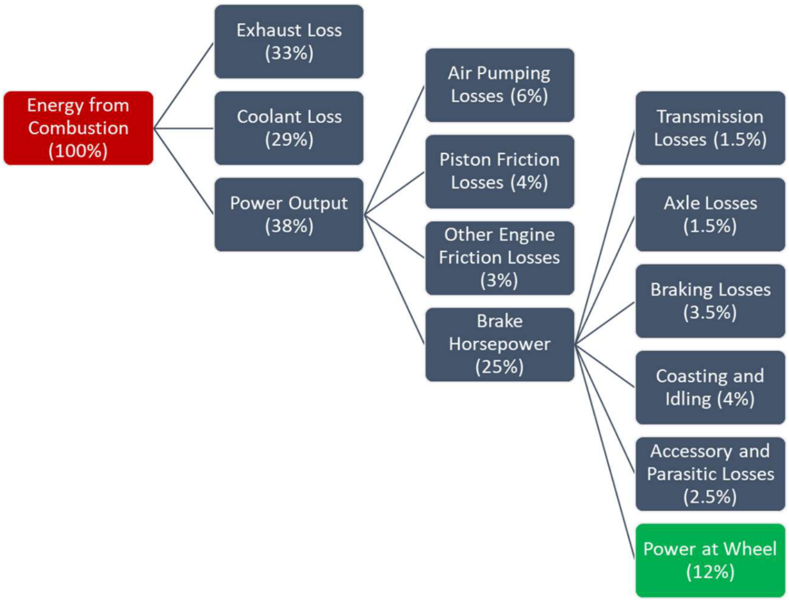


Figure 1. Representation of efficiency of energy transfer from the combustion of fuel to traction in a typical passenger car. Adapted from [4]

Friction is reduced by improving the design and geometries of the various engine and transmission components, improving the surface finish or textures, the addition of surface coatings, and by lubrication [3]. Of these, lubricants are increasingly becoming a point of focus for energy efficiency.

In a fluid lubricating system, such as engines and transmissions, different lubrication regimes can be observed between the various moving parts. The lubrication regimes are defined based on the surface roughness and the thickness of lubricant film, which depends on the load applied, relative speed and the viscosity of the lubricant. Four lubrication regimes are typically described based on these parameters: boundary lubrication regime, mixed lubrication regime, elastohydrodynamic lubrication regime (EHD) and hydrodynamic lubrication regime. The coefficient of friction (COF) in the boundary regime is high, in the range of 0.10 to 0.15 due to metal surface contact. It begins to drop in the mixed lubrication regime and is lowest in the hydrodynamic regime, around 0.01. However, with an increase in viscosity or speed, the COF increases significantly due to viscous drag.

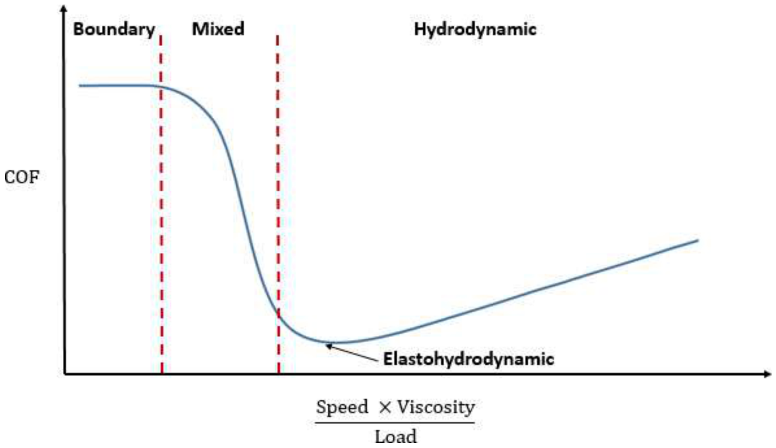


Figure 2. Pictorial representation of the Stribeck curve, and the four lubrication regimes

In the transmission system, the surfaces of concern are the contact between the gears. The three regimes observed in gears are boundary lubrication at the top face or the tip and bottom face or the root due to the pure sliding contact, elastohydrodynamic lubrication in the pitch point due to the pure rolling contact, and mixed lubrication in between [5]. COF in the boundary regime is dependent on the surface roughness and asperities, and the interactions between the surfaces in contact. COF in the hydrodynamic regime is dependent on viscosity. Figure 3 shows the different types of relative motion observed in gear contact. Sliding can occur in both the same direction as rolling and the opposite direction.

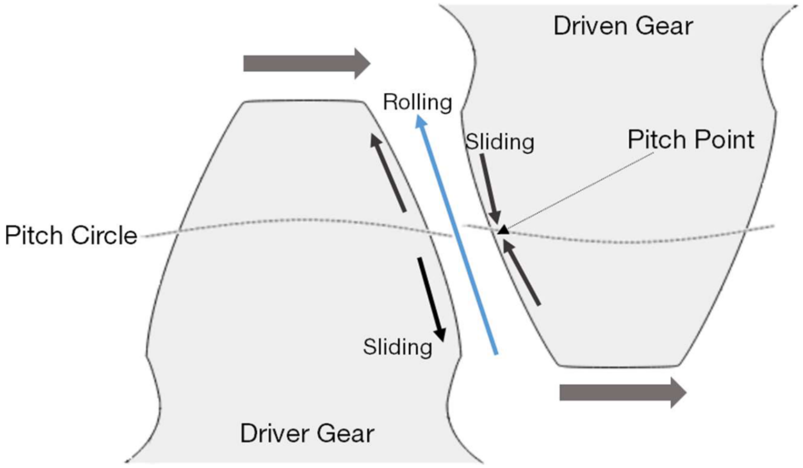


Figure 3. Pictorial representation of the rolling and sliding motion in the gears

To reduce friction between the gears in a transmission, two methods can be considered. Friction in the boundary regime can be reduced by using friction modifiers in lubricant. Fluid friction in the hydrodynamic regime can be decreased by using lubricants of lower viscosity which offer lower viscous drag.

Friction modifiers are surface active additives which form low shear films on surfaces which promote slippage. These are typically highly polar molecules which bond easily with the metal surface and reduce the coefficient of friction during relative motion. Their ability to reduce COF has made them a popular addition to fuel economy providing engine oils. Additionally, they can also help reduce system temperature by reducing the frictional heat generated. Broadly, they can be classified as organomolybdenum friction modifiers and organic friction modifiers. Organomolybdenum friction modifiers refer to those which contain molybdenum, such as molybdenum disulphide (MoS2) molybdenum dialkyl dithiocarbamate (MoDTC), molybdenum dialkyl dithiophosphates (MoDTP) and other organo-metallic compounds of molybdenum. Organic friction modifiers refer to purely organic chemistries such as glycerol monooleates (GMO), fatty acid esters, oleylamides, phosphate esters or polymeric esters. Although its consideration in gear oil formulations is recent, usage of fatty acid amides, phosphoric acid amide and ester derivatives as friction modifiers in gear oils have been documented. [6]

Viscosity modifiers (VM) are long-chain polymeric additives which affect the dependency of viscosity of a lubricant on the temperature, or the viscosity index (VI). Usage of VMs can reduce the drop in viscosity as the temperature increases. This is critical because this can prevent a significant change in viscosity in operation as the system reaches the operating temperature. They are extremely popular in usage in multigrade engine oils and are also used often in gear oils, automatic transmission fluids and hydraulic oils. VMs help develop formulations which have lower viscosity at lower temperatures,which aids in reducing friction at system starts and low temperatures. VMs also improve film thicknessin the elastohydrodynamic regime. Additionally, they can impart the ability of shear-thinning or temporary viscosity loss, which can reduce viscosity at high shear applications. [7]

While several additives play a role in determining the anti-friction performance of a lubricant, the present study is concerned with studying the effect of using viscosity modifiers and friction modifiers, and combinations thereof, in the formulation of energy-efficient lubricants. Several automotive gear oil formulations are evaluated in three tribological tests under different conditions to evaluate the effect of these additives in reducing friction.

Literature Review

The effect of lubricants in transmissions, particularly on gear efficiency and gear fatigue, has been well documented over the years. Some of the earlier studies reviewed are summarized in this section.

Viscosity and viscosity index of the oil has an effect on the system efficiency of engines, hydraulic systems and gearboxes at lower temperatures, while the viscosity-pressure (VP) coefficient affected COF in the EHD regime. Gr. III mineral base oils and synthetic base oils had better efficiency due to the higher VP coefficient. [7]. Low viscosity oils increased overall gearbox efficiency at low loads due to reduced churning losses, even though the gear mesh efficiency was reduced [8] [9]. But in severe load cycles, low viscosity oils increased friction losses [9]. In general, high viscosity index oils were found better for axle gear transmission [10].

Several studies reveal a positive effect of the chemistry of viscosity modifiers on system efficiency. The addition of polymethylmethacrylate (PMA) viscosity modifier generally reduced the torque losses in hydraulic motors [11]. A highly branched polyethylene or olefin copolymer type viscosity modifier with a tapered topology of copolymer could work both as a viscosity modifier and friction modifier [12]. Similarly, star-shaped polyalkylmethacrylate (PAMA) polymers with high polar content or higher molecular weight polymer fractions reduced friction [13]. A study modelling the effect of lubricants on hypoid gear efficiency suggested that viscosity modifiers improved shear thinning characteristics and VP coefficient, which in turn improved axle efficiency [14]. Extensive studies on the effect of viscosity modifiers on spur gear efficiency showed that using viscosity modifiers like polyisobutylene (PIB) and PAMA over bright stock can significantly improve efficiency at both high and low temperatures and durability [15] [16].

Studies show that friction modifiers can improve overall efficiency by reducing friction between the gears. Organic friction modifiers were observed to have improved performance for low contact pressures and in rolling-sliding contacts [17]. Organomolybdenum friction modifiers improved efficiency in rear axles [9], and the effect improved with increasing doses of the friction modifier and was dependent on the temperature [18]. Friction modifiers with lower decomposition temperatures were found to reduce torque losses better. However, it is noted that the effectiveness of friction modifiers in transmission oil is also dependent on the extreme pressure (EP) additives present. Friction modifiers can have an antagonistic effect on efficiency and EP properties when used with an unsuitable EP additive [19].

Methodology

Several studies show that there is a positive effect in the usage of viscosity modifiers and friction modifiers in transmission gear oils. This study focuses on examining the effect of different types of viscosity modifiers for oils of different viscosity in all lubrication regimes. In some oils, the combined effect of viscosity modifiers and friction modifiers is studied. The purpose is to ascertain the effect of these additives and obtain a direction in the formulation of energy-efficient gear oils for automotive transmissions. This is done by evaluating the oils in three friction tests, on two tribological test rigs.

Test Lubricants

All formulations use the same core additive package at a fixed treat rate, meeting the API GL-4 performance level. Two viscosity modifiers of different chemistries and two friction modifiers of different chemistries are also studied. All the additives selected are commercially available. A description of these additives is provided in Table 1.

Additive Name	Function	Chemistry
VM-1	Viscosity Modifier	PIB
VM-2	Viscosity Modifier	PAMA
FR-1	Friction Modifier	MoDTC
FR-2	Friction Modifier	Fatty acid ester

Table 1. Description of the evaluated viscosity modifiers and friction modifiers

Automotive gear oils of four different viscosity grades were formulated and evaluated in this study. The SAE 75W-90, SAE 80W-90 and SAE 90 oils have been formulated with the same kinematic viscosity at 100°C of about 15.0 cSt. The SAE 85W-140 oils were formulated for a kinematic viscosity at 100°C of around 26.5 cSt. The formulation and properties of the lubricants are summarized in Table 2.

Sample ID	SAE Viscosity Grade	Base Oil Type	Viscosity Modifier (Treat Rate)	Friction Modifiers (Treat Rate)	Kinematic Viscosity at 100°C, cSt	Viscosity Index
F1-75W	75W-90	Polyalphaolefins (PAO)			15.00	149
F2-75W-1	75W-90	Gr. III Mineral Oil	VM-1 (22.0%)		15.05	165
F3-75W-2	75W-90	Gr. III Mineral Oil	VM-2 (32.0%)		15.01	203
F4-75W-1-1	75W-90	Gr. III Mineral Oil	VM-1 (22.0%)	FR-1 (0.5%)	15.09	165
F5-75W-1-2	75W-90	Gr. III Mineral Oil	VM-1 (22.0%)	FR-2 (0.5%)	15.10	164
F6-75W-2-1	75W-90	Gr. III Mineral Oil	VM-2 (32.0%)	FR-1 (0.5%)	15.19	202
F7-75W-2-2	75W-90	Gr. III Mineral Oil	VM-2 (32.0%)	FR-2 (0.5%)	15.23	201
F8-80W	80W-90	Gr. II Mineral Oil and Bright Stock			15.12	101
F9-80W-1	80W-90	Gr. II Mineral Oil and Bright Stock	VM-1 (5.0%)		14.92	110
F10-80W-2	80W-90	Gr. II Mineral Oil and Bright Stock	VM-2 (5.0%)		15.11	112
F11-90	90	Gr. II Mineral Oil and Bright Stock			15.06	99
F12-90-1	90	Gr. II Mineral Oil and Bright Stock	VM-1 (5.0%)		15.17	108
F13-90-2	90	Gr. II Mineral Oil and Bright Stock	VM-2 (5.0%)		14.99	111
F14-140	85W-140	Gr. II Mineral Oil and Bright Stock			26.40	97
F15-140-1	85W-140	Gr. II Mineral Oil and Bright Stock	VM-1 (5.0%)		26.84	105
F16-140-2	85W-140	Gr. II Mineral Oil and Bright Stock	VM-2 (5.0%)		26.50	106

Table 2. Description of the evaluated test oils, their composition and viscometrics

SRV Experiment

The Optimol SRV®5 oscillation system was selected for evaluation of the performance of the test oils at high load and high-speed boundary lubrication regimes under a pure sliding contact. A 10 mm steel ball is loaded against a stationary steel disc. The specimens are lubricated only at the point of contact, by a small amount of the test oil. The steel ball oscillates at high frequencies, with a small amplitude.

The test was based on the test method ASTM D6425. The conditions were modified in terms of the test temperature, to simulate boundary lubrication regimes for gears under high loads. The COF was measured for the duration of the test, and the diameter of the wear scar on the steel ball was recorded. The test conditions are summarized in Table 3.

MTM Experiments

The Mini Traction Machine of PCS Instruments was selected for the evaluation of the performance of the test oils in mixed, EHD and hydrodynamic lubrication regimes. A steel ball 19mm in diameter is loaded on a steel disc, where both the ball and disc can rotate at independent speeds. This permits the simulation of rolling contact, with varying slide-to-roll ratios (SRR). The disc is completely submerged in the test lubricant. The traction coefficient is recorded during the test.

Two tests were performed on the MTM instrument in each run. The first test was to generate Stribeck curves for the oils, measuring traction coefficients over a range of speeds at a constant SRR. Immediately after, the second test was performed to generate the traction curve for a range of SRRs at a constant speed. Both negative and positive SRR is considered as sliding in gears can happen in negative and positive directions to the rolling motion (as shown in Figure 3).

The test conditions for the MTM test are selected to simulate the low load operation of transmission and are summarized in Table 3.

Test Conditions	SRV	MTM Stribeck	MTM Traction
Test Duration, min	120	-	-
Load, N	300	30	30
Contact Pressure, GPa	3.0	0.9	0.9
Speed, m/s	0.05	0.003 – 3.00	2.00
Temperature, °C	100	80	80
SRR, %	-	50	(-50) - 50
Running-in Duration, Load	50	3	-
Running-in Duration, min	0.50	10	-

Table 3. Summary of the test conditions for the SRV and MTM experiments

Results

SRV Friction Test

The COF of the oils were plotted against the duration of the test. Figures 4 to 10 show the results of the tests, comparing test samples of each viscosity grade, highlighting the effect of additives in the different viscosity grades

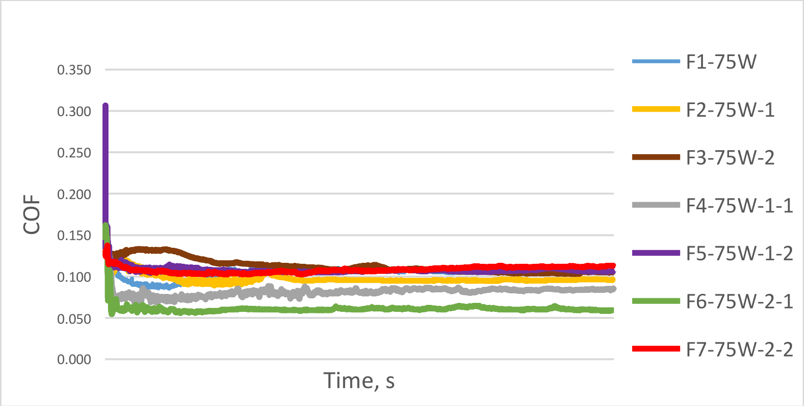


Figure 4. SRV Friction curve for evaluated SAE 75W-90 oils

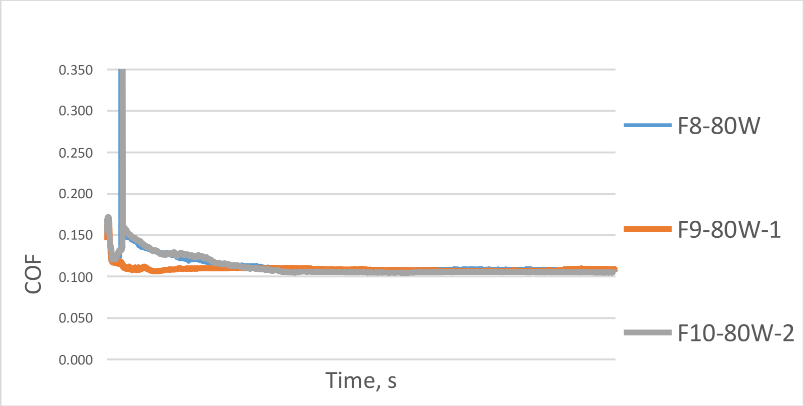


Figure 5. SRV Friction curve for evaluated SAE 80W-90 oils

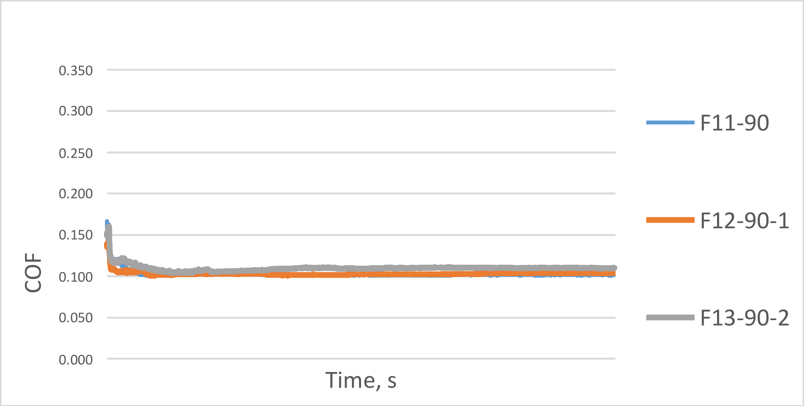


Figure 6. SRV Friction curve for evaluated SAE 90 oils

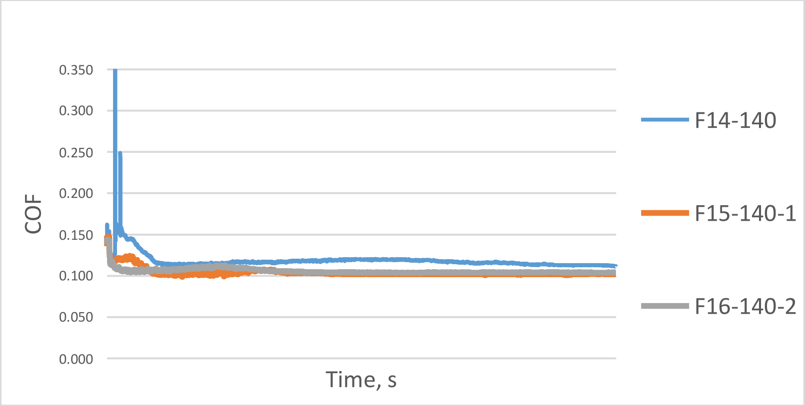


Figure 7. SRV Friction curve for evaluated SAE 85W-140 oils

For the SAE 75W-90 oils in Figure 4, it is observed that the VM-1 based oil F2-75W-1 performed similarly to the PAO-based F1-75W. However, the VM-2 based oil F3-75W-2 had significantly higher COF than the two. The oils containing the organomolybdenum FR-1 (Oils F4-75W-1-1 and F6-75W-2- 1) has lower COF than all the other. Of the two, F6-75W-2-1 had lower friction than F4-75W-1-1 (19% lower in terms of minimum COF recorded). The oils containing the organic friction modifiers FR-2 (Oils F5-75W-1-2 and F7-75W-2-2) performed similar to each other and F1-75W but were about 11 per cent lower than F3-75W-2. In all the other viscosity grades, no significant difference was observed for the COF despite the addition of viscosity modifiers in the samples.

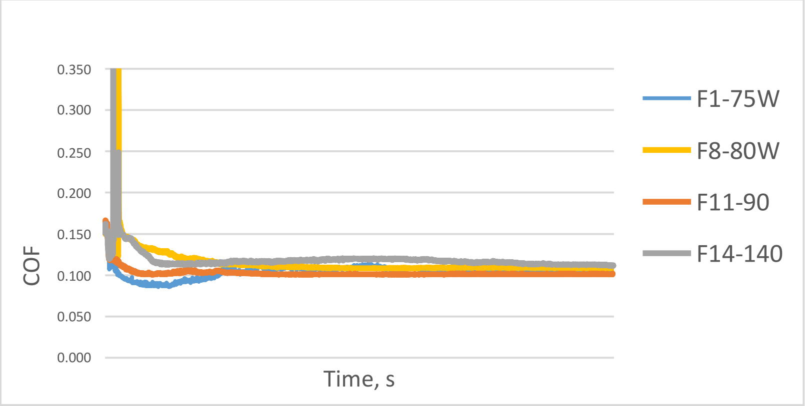


Figure 8. SRV Friction curve for oils of different viscosity grades, containing no viscosity modifiers or friction modifiers

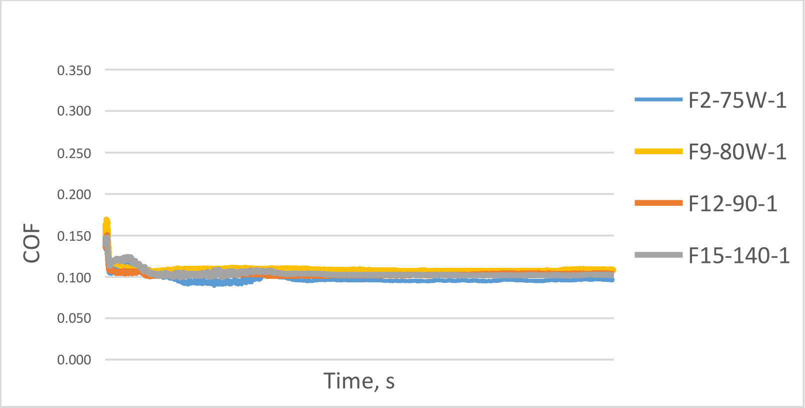


Figure 9. SRV Friction curve for oils of different viscosity grades, containing VM-1 but no friction modifiers

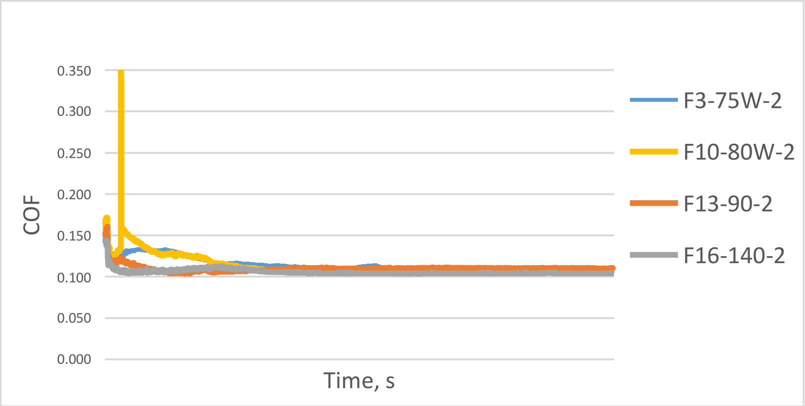


Figure 10. SRV Friction curve for oils of different viscosity grades, containing VM-2 but no friction modifiers

In Figures 8 to 10, which compare oils of different viscosity grades, there is no significant difference inCOF despite the change in viscosity grades.

SRV Anti-Wear Results

Sample ID	**SAE Viscosity Grade**	**Base Oil Type**	**Viscosity Modifier (Treat Rate)**	**Friction Modifiers (TreatRate)**	**Wear Scar Diameter on Ball, mm**
F1	75W-90	Polyalphaolefins (PAO)			0.66
F2-75W-1	75W-90	Gr. III Mineral Oil	VM-1 (22.0%)		0.64
F3-75W-2	75W-90	Gr. III Mineral Oil	VM-2 (32.0%)		0.58
F4-75W-1-1	75W-90	Gr. III Mineral Oil	VM-1 (22.0%)	FR-1 (0.5%)	0.57
F5-75W-1-2	75W-90	Gr. III Mineral Oil	VM-1 (22.0%)	FR-2 (0.5%)	0.56
F6-75W-2-1	75W-90	Gr. III Mineral Oil	VM-2 (32.0%)	FR-1 (0.5%)	0.55
F7-75W-2-2	75W-90	Gr. III Mineral Oil	VM-2 (32.0%)	FR-2 (0.5%)	0.50
F8-80W	80W-90	Gr. II Mineral Oil and Bright Stock			0.72
F9-80W-1	80W-90	Gr. II Mineral Oil and Bright Stock	VM-1 (5.0%)		0.54
F10-80W-2	80W-90	Gr. II Mineral Oil and Bright Stock	VM-2 (5.0%)		0.66
F11-90	90	Gr. II Mineral Oil and Bright Stock			0.57
F12-90-1	90	Gr. II Mineral Oil and Bright Stock	VM-1 (5.0%)		0.49
F13-90-2	90	Gr. II Mineral Oil and Bright Stock	VM-2 (5.0%)		0.59
F14-140	85W-140	Gr. II Mineral Oil and Bright Stock			0.70
F15-140-1	85W-140	Gr. II Mineral Oil and Bright Stock	VM-1 (5.0%)		0.62
F16-140-2	85W-140	Gr. II Mineral Oil and Bright Stock	VM-2 (5.0%)		0.59

Table 4. Wear Scar Diameters on the steel ball after the SRV experiment

In the SAE 75W-90 grade oils, there is no effect on the wear scar diameter with the addition of viscosity modifiers. However, the addition of friction modifiers had a significant reduction in the wear scar diameter. Both FR-1 and FR-2 reduced the friction to similar extents.

In the other viscosity grades, the addition of viscosity modifiers improved the anti-wear properties. Particularly for the SAE 80W-90 and SAE 90 grade oils, the addition of PIB (Oils F9-80W-1 and F12-90-1) decreased the wear scar diameter very significantly.

MTM Stribeck Test Results

The traction coefficient curves from the Stribeck curve test are reported in Figures 11 to 17.

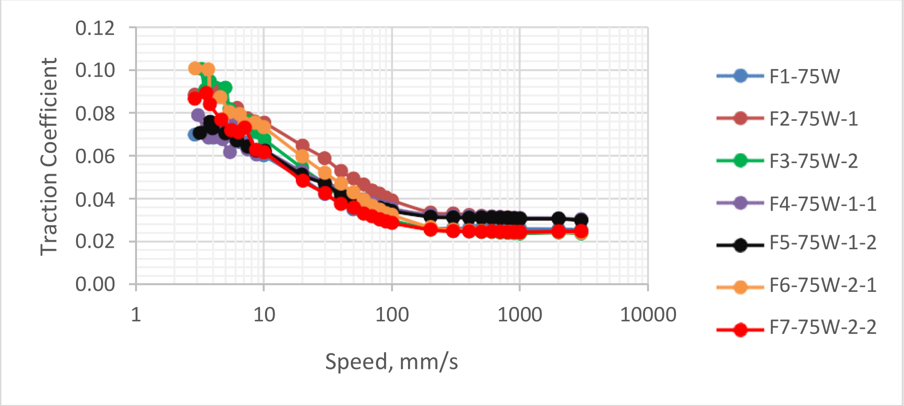


Figure 11. MTM Stribeck curve for evaluated SAE 75W-90 oils

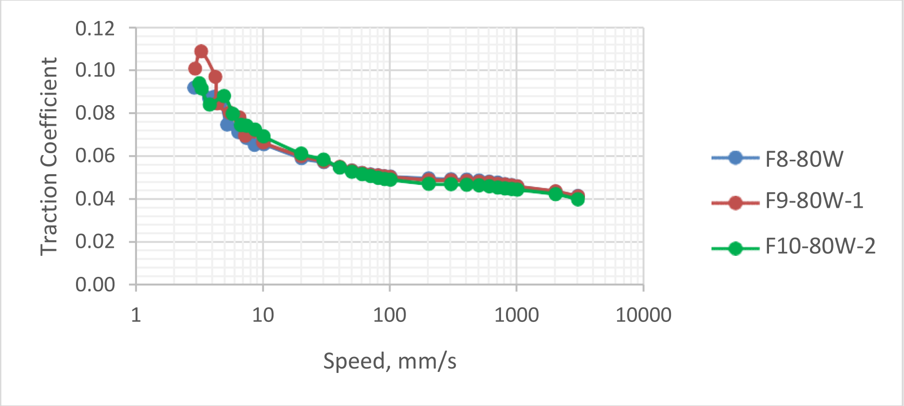


Figure 12. MTM Stribeck curve for evaluated SAE 80W-90 oils

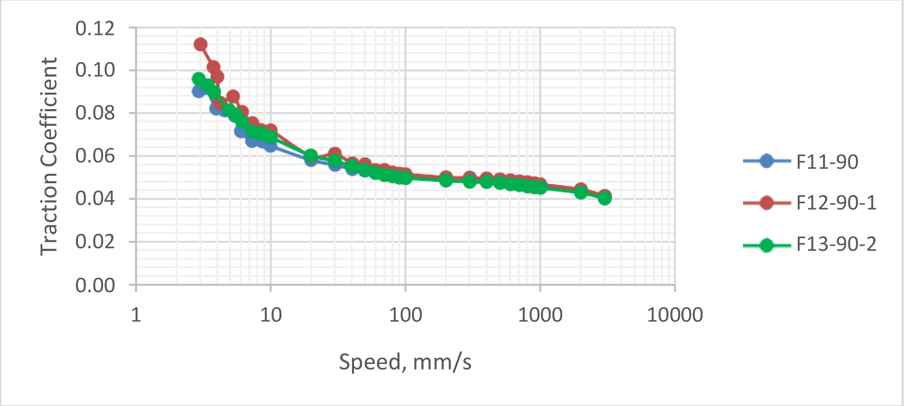


Figure 13. MTM Stribeck curve for evaluated SAE 90 oils

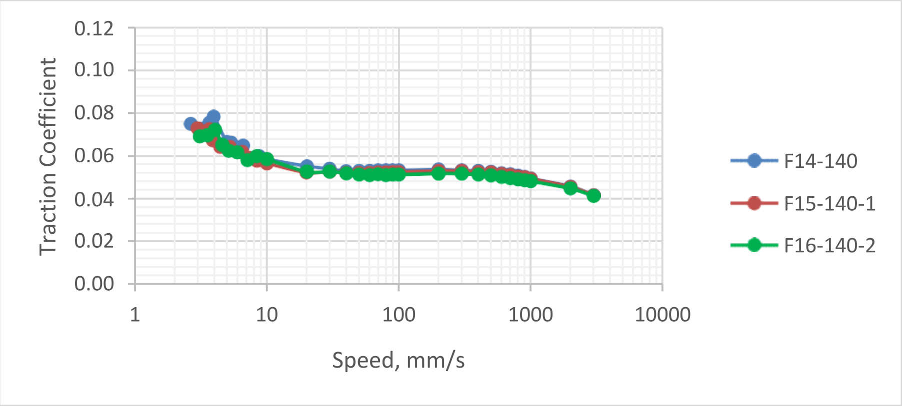


Figure 14. MTM Stribeck curve for evaluated SAE 85W-140 oils

Among the SAE 75W-90 oils in Figure 10, the PAO-based Oil F1-75W has a low traction coefficient in all regimes. The oils containing VM-1 (F2-75W-1, F4-75W-1-1 and F5-75W-1-2) had higher traction at speeds over 10 mm/s. While oils containing VM-2 (F3-75W-2, F6-75W-2-1 and F7-75W-2-2) had lower traction comparable with F1-75W. The performance of the oils containing friction modifiers (F4-75W- 1-1, F5-75W-1-2, F6-75W-2-1 and F7-75W-2-2) was inconsistent. For VM-1 containing oils, F4-75W-1-1 (with MoDTC) had higher traction than F5-75W-1-2, while for VM-2 containing oils, the oil F7-75W-2-2 (with fatty acid ester) had higher traction. For the SAE 80W-90, SAE 90 and SAE 85W-140 oils, the near overlap of the curves shows that there is minimal effect of viscosity modifier in the reduction of COF for oils of a particular viscosity.

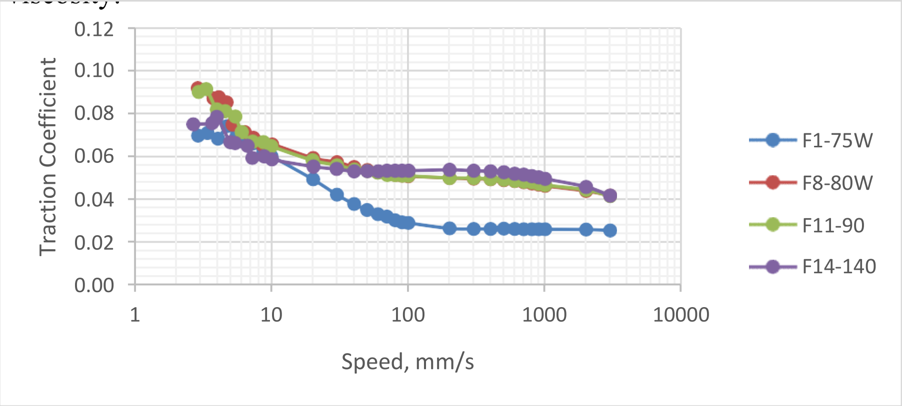


Figure 15. MTM Stribeck curve for oils of different viscosity grades, containing no viscosity modifiers or friction modifiers

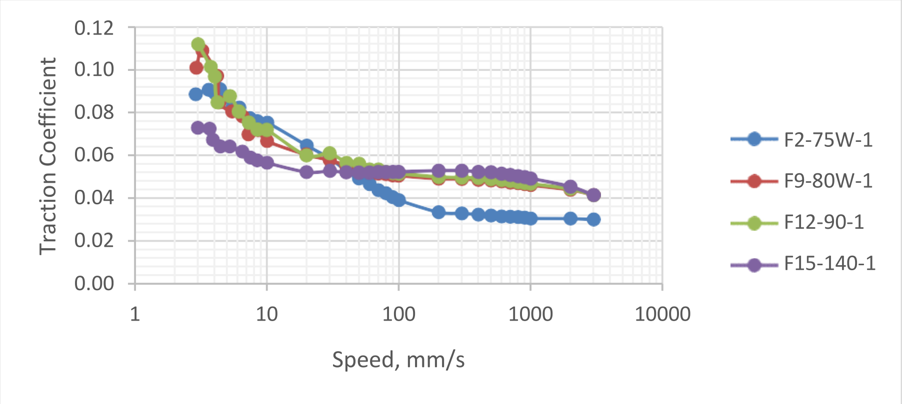


Figure 16. MTM Stribeck curve for oils of different viscosity grades, containing VM-1 and no friction modifiers

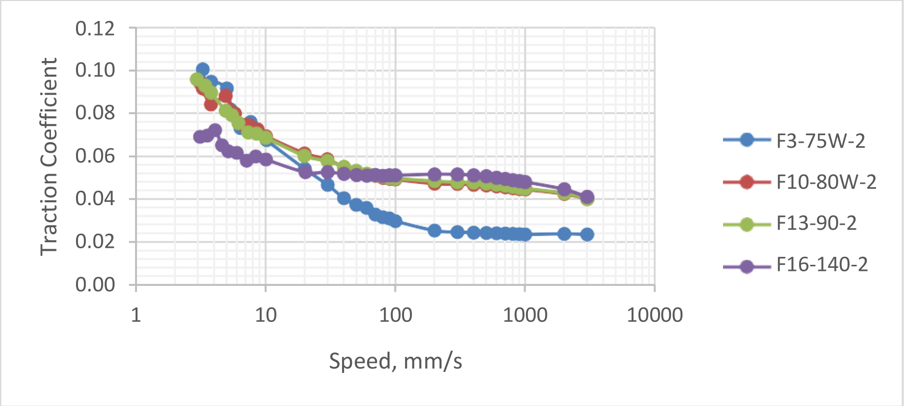


Figure 17. MTM Stribeck curve for oils of different viscosity grades, containing VM-2 and no friction modifiers

Figures 15 to 17 compare the Stribeck curves of oils of different viscosity grades, between the different viscosity modifiers. In each figure, it is observed that the SAE 75W-90 oils have a significantly lower traction coefficient at medium to high speeds, despite having similar performance to the SAE 80W-90 and SAE 90 oils at lower speeds. However, it is also observed that the SAE 85W-140 has a flatter curve in comparison to the rest. The traction coefficient is lower at lower speeds compared to the rest, while higher than the others at medium and higher speeds. Also, there is a dip in the traction coefficient at speeds over 1000 mm/s, which could be attributed to the increase in test temperature.

MTM Traction Test Results

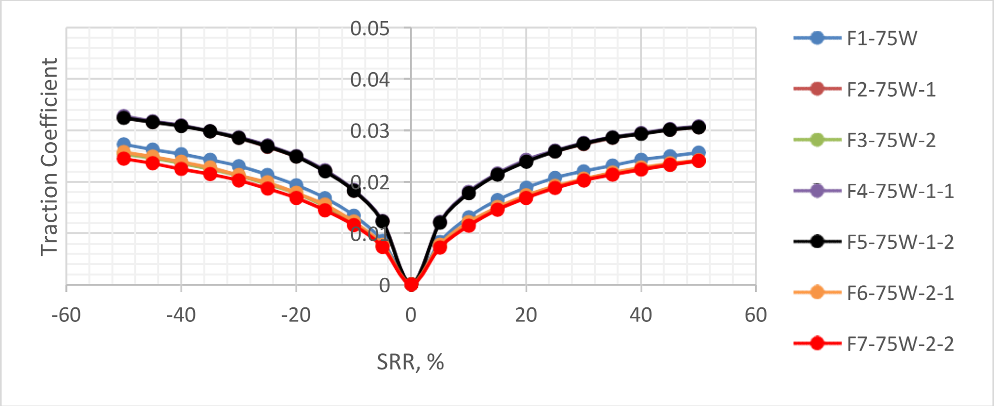


Figure 18. MTM Traction curve for evaluated SAE 75W-90 oils

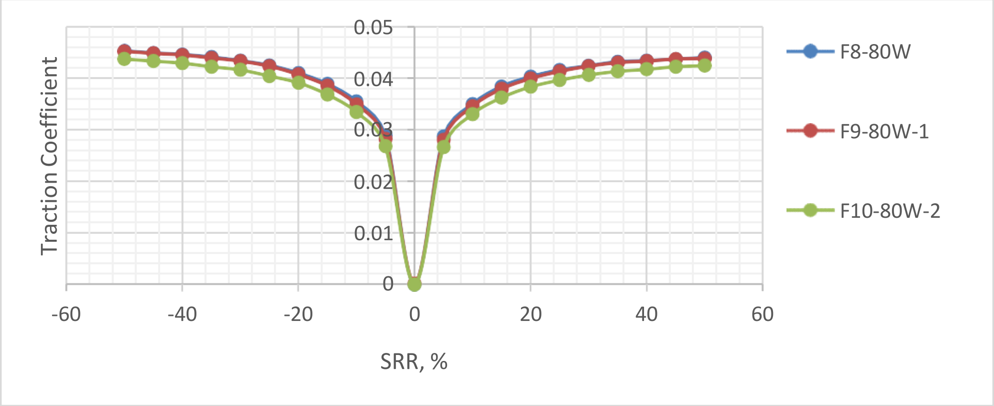


Figure 19. MTM Traction curve for evaluated SAE 80W-90 oils

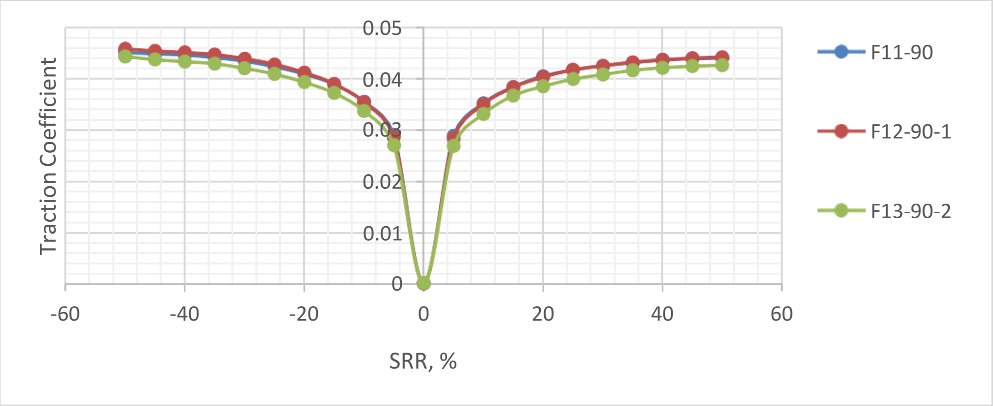


Figure 20. MTM Traction curve for evaluated SAE 90 oils

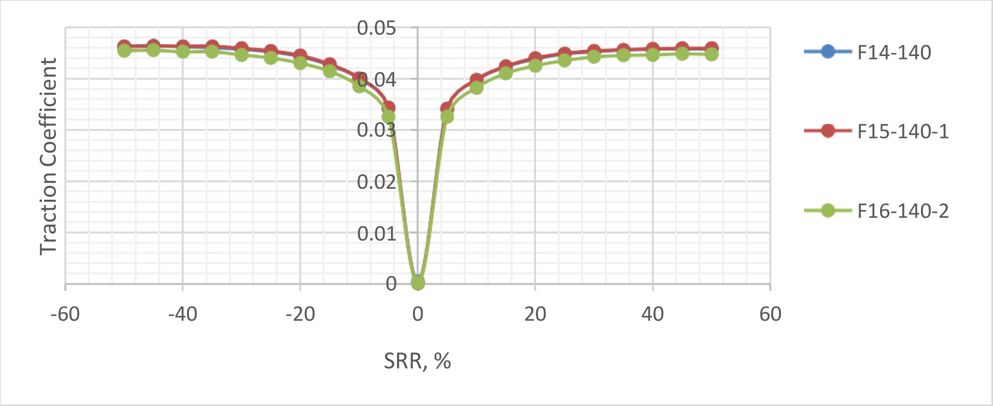


Figure 21. MTM Traction curve for evaluated SAE 85W-140 oils

Similar to what was observed in the MTM Stribeck test, the SAE 75W-90 oils show differentiation of oils containing the different types of viscosity modifiers. The oils containing the PAMA type VM-2 (F4- 75W-1-1, F6-75W-2-1 and F7-75W-2-2) had lower traction coefficients at all SRR than the oils containing PIB. Similar behaviour was noticed for the other viscosity grades. Oils without any viscosity modifier and oils with VM-1 had similar traction coefficients, while the oils with VM-2 had marginally lower traction across all tested SRR.

The PAO-based formulation had a low traction coefficient in all the SRRs evaluated, and was comparable to the SAE 75W-90 oils containing VM-2.

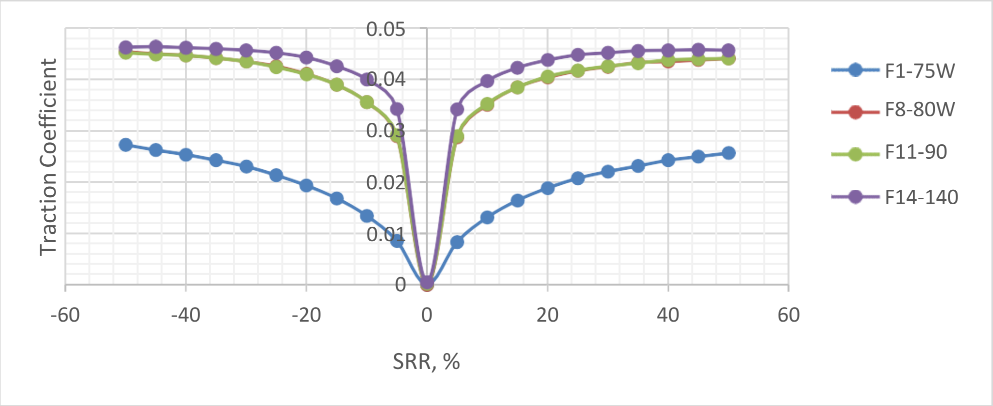


Figure 22. MTM Traction curve for oils of different viscosity grades, containing no viscosity modifiers or friction modifiers

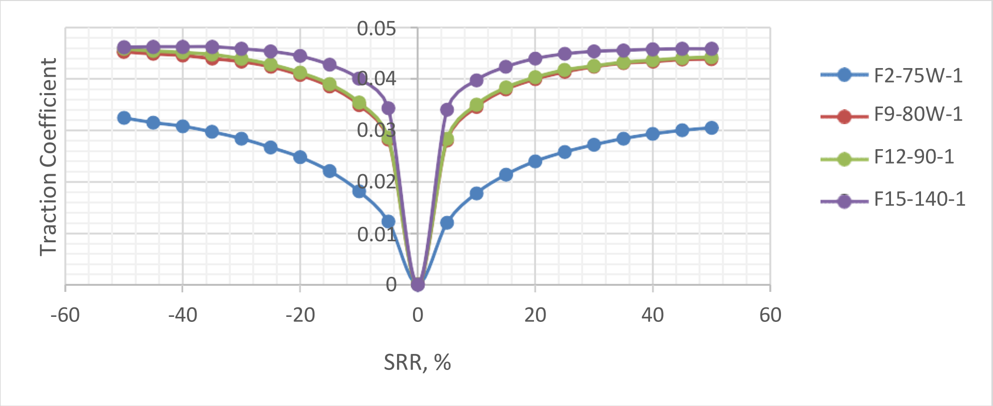


Figure 23. MTM Traction curve for oils of different viscosity grades, containing VM-1 and no friction modifiers

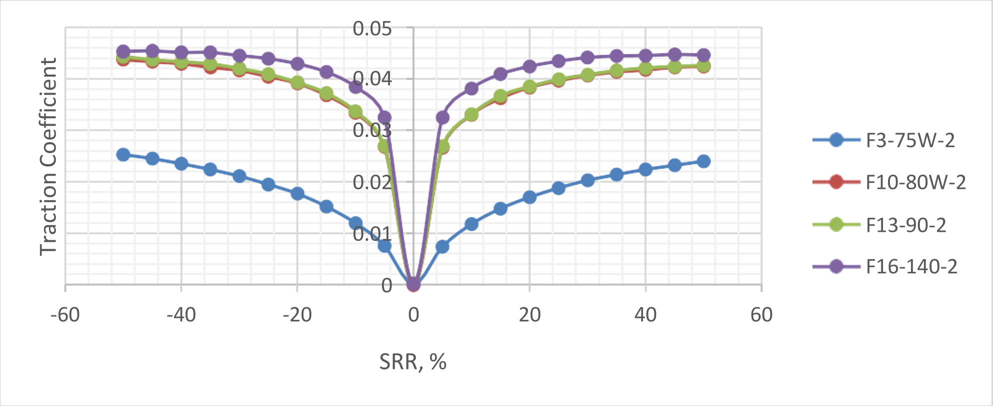


Figure 24. MTM Traction curve for oils of different viscosity grades, containing VM-2 and no friction modifiers

In Figures 22 to 24, the effect of viscosity of an oil and viscosity modifier on the traction in different SRR is observed. Although the SAE 75W-90, SAE 80W-90 and the SAE 90 oils all have the same viscosity, the SAE 75W-90 oils show significantly lower traction coefficient, even at high SRRs. The SAE 80W-90 and SAE 90 oils have similar traction. The 85W-140 oils have a higher traction coefficient at the lower SRRs but converge towards the curves of the SAE 90 oils at higher SRRs.

Discussion

Boundary Friction on SRV and MTM

There seems to be a minimal effect of the viscosity and the viscosity grade on the performance in theSRV test.

Within a particular viscosity grade, there is some effect from the addition of viscosity modifiers. In allthe grades, the addition of the PIB viscosity modifier VM-1 reduced the COF in the beginning stage ofthe test or was on par with the formulations containing no viscosity modifiers. For the SAE 75W-90 grade, usage of the VM-1 with mineral base oils gave a similar performance to that of the PAO-based formulation. Usage of PAMA type VM-2 increased the COF for the SAE 75W-90 grade at the initial section of the test but had no major effect on the other grades.

However, it is observed that using viscosity modifiers seemed to have a positive effect on the reduction of wear on the steel ball during the test for the SAE 80W-90, SAE 90 and SAE 85W-140 grades. This is particularly true for the PIB type VM-1 where a significant reduction in the wear was observed for SAE 80W-90 and SAE 90 This behaviour was not observed in the SAE 75W-90 grade. It is surmised that low treat rates of both the viscosity modifiers can behave like polymeric friction modifiers, and offer anti-wear properties.

However, at higher treat rates, as seen in the SAE 75W-90 oils, they might behave competitively with the anti-wear additives and hence provide no benefit overall.

There is a clear benefit to the addition of molybdenum based friction modifiers to oils, as seen in the SAE 75W-90 test oils. FR-1 in combination with PIB (F4-75W-1-1) had a lower effect on reducing friction than FR-1 with PAMA (F6-75W-2-1). This suggests a mild competition between VM-1 and FR-1. FR-2 did not affect the performance.

No conclusive statement could be made about the performance of FR-1 in the low load MTM test. FR-1 decreased the traction coefficient when used with VM-1 but increased with VM-2. This could be because the loads and temperature were not sufficiently high to activate the action of friction modifiers and increased competition by the viscosity modifiers. However, it was seen that the organic friction modifier FR-2 reduced traction in both boundary and mixed regimes with both VM-1 and VM-2. This is in in-line with some of the reviewed literature that organic friction modifiers perform betterat low load and low-speed conditions.

Mixed and Hydrodynamic Regime in MTM

The viscosity is a critical factor in reducing traction in the mixed and hydrodynamic regimes. Figures 15 to 17 clearly show that for very high viscosities (F14-140, F15-140-1 and F16-140-2), the Stribeck curve is flatter than for the other grades i.e. the traction is lower at low speeds, but higher at high speeds. This is expected because the hydrodynamic regime is reached at lower speeds for the high viscosity oils, shifting its Stribeck curve to the left. However, at higher speeds, the viscous drag increases and prevents further reduction in the traction. But for lower viscosity oils, the viscosity is lower even at high speeds shifting the Stribeck curve towards the right, allowing a reduction in traction.

In Figure 11, the effect of the addition of viscosity modifiers is clear. For the same viscosity and same treat rate of VM-1 and VM-2 in the SAE 80W-90 and the SAE 90 oils (F8-80W to F13-90-2), the Stribeck curves are similar. However, in the case of the 75W-90 grade oils F2-75W-1 and F3-75W-2, where higher treat rates of VM-1 and VM-2 are respectively used, there is a significant drop in traction after 10 mm/s. At high speeds, this is possibly due to the shear thinning effect of the viscosity modifiers coming into play. Shear thinning induces temporary viscosity loss (TVL), which further reduces the viscosity at higher speeds. Hence, as the speed increases the viscosity drops further, subsequently reducing viscous drag. This shear thinning effect of polymers is even more pronounced for VM-2 based oils. This is because of the higher treat rate of VM-2 required to meet the same viscosity, which makes the TVL more pronounced. At medium speeds, the high viscosity index of the oils means that the oil has a lower viscosity than the VM-1-containing oils. These results imply the superiority of the usage of VM-2 as a friction modifier in high-speed applications.

Usage of PAO is shown to have significantly lower traction in all the regimes (F1-75W in Figures 11 and 15). The performance of F1-75W in the mixed and hydrodynamic regime is comparable to the mineral and VM-2 based oils (F3-75W-2, F6-75W-2-1, and F7-75W-2-2). Considering the performance of the PAO-based formulation, further evaluation is warranted to study the effect of the combination of viscosity modifiers or friction modifiers in PAO-based oils.

For VM-1 containing oils, the addition of a friction modifier led to a reduction in traction in the mixed friction regime. For VM-2 containing oils, the addition of FR-1 increased traction (F6-75W-2-1), which is anomalistic and requires further studies. But the addition of FR-2 reduced the traction (F7-75W-2- 2). Friction modifiers had no effect at the higher speeds, as is expected.

In the traction test, it was observed that for a particular SRR, the traction is largely dependent on the viscosity of the oil. Higher the viscosity of the oil, the higher the traction, as seen in Figures 22 to 24. The traction for SAE 75W-90 oils was even lower, either from TVL due to the viscosity modifiers, or the low traction of PAOs.

For SAE 80W-90, SAE 90 and SAE 85W-140 oils, it was observed that VM-2 containing oils performed marginally better at all SRRs, implying a TVL superior to that of VM-1. For the 75W-90 oils, the VM-2 containing oils performed significantly better than the VM-1 oils. This is possibly due to a combination of the superior TVL from VM-2 and the higher treat rate of VM-2. This makes VM-2 highly suited for gear applications due to the reduced tractions at all SRRs, providing an advantage at all points on the gear's face.

In this study, the effect of the additive package, particularly the EP additive used, was not evaluated. Hence, no comments are made on these parameters.

Applications

As transmission systems in different kinds of vehicles operate under different conditions and stress, it will be prudent to formulate gear oils differently for each application. Based on the results obtained from the studies, a direction toward the formulation of energy-efficient gear oils was obtained. It was found that viscosity modifiers can provide a significant advantage when it comes to performance in the mixed and hydrodynamic regimes, and that friction modifiers perform best in higher load boundary conditions.

In low load applications, where torque independent churning or spin losses are high, low viscosity oils will perform the best. With the addition of appropriate viscosity modifiers like VM-2, the traction can be reduced and energy efficiency can be improved. It is also observed that PAO-based formulations have lower traction at all regimes at low loads.

In high load applications, where torque-dependent losses are more significant, friction modifiers play a more significant role. Friction modifiers can reduce friction in the high load boundary regimes, increasing energy efficiency. Of the two friction modifiers evaluated, the MoDTC based FR-1 performed better than FR-2, which is in line with earlier research on gear oils.

For a robust formulation that works across all regimes, a low viscosity oil like the SAE 75W-90 oil with a combination of viscosity modifier and friction modifier can be used in combination to maximize efficiency.

Conclusions

The present studies on SRV and MTM have shown the effects of viscosity modifiers and friction modifiers in a lubricant in improving the efficiency of gears and transmissions. The tests designed on the two instruments are suitable to evaluate automotive gear oils or transmission oils, particularly their performance in boundary and hydrodynamic lubrication regimes.

The viscosity of a lubricant was shown to affect the traction coefficient, particularly in low load applications. Lower viscosity oils reduce traction and help increase the transmission efficiency at low loads.

Viscosity modifiers evaluated can significantly improve the performance in the EHD and hydrodynamic regime, especially when using a viscosity modifier with good shear thinning properties and a higher viscosity index boost. Such a viscosity modifier, such as the PAMA type evaluated in the study, will show its benefits across all points on the gear.

Friction modifiers can improve the energy efficiency in high load conditions by reducing torque- dependent losses, which are prominent in the root and tip of the gear face. Organomolybdenum based friction modifiers were found more suitable than the organic friction modifiers in higher loads, and vice versa in lower loads. However, it is noted that organomolybdenum friction modifiers when used with PIB type viscosity modifiers may have reduced performance at higher loads.

PAOs have shown to be a suitable base oil for high energy efficiency gears, showing reduced friction in all lubrication regimes under lower loads. If a suitable friction modifier is used, it can also improve efficiency in higher loads. The performance of PAO-based formulation can be emulated by using Gr. III base oil with appropriate viscosity modifiers.

Based on earlier research, and this present study, it is evident that it is not possible to generalize the performance of an additive merely by its function or its chemistry. It is highly dependent on the other components used in the formulation. However, certain strategies have been suggested for different applications when using the studied additives.

When formulating energy-efficient gear oils it is necessary to carefully select the appropriate viscosity modifiers and friction modifiers and to ensure synergy with the core additive package and the base oil.

References

1. The Automotive Research Association of India, "India's Initiative Towards Tighter Emission & Fuel Efficiency Norm".
2. Internation Council on Clean Transportation, "EU CO2 Emission Standards for Passenger Carsand Light-Commercial Vehicles," 2014.
3. V. W. Wong and S. C. Tung, "Overview of automotive engine friction and reduction trends - Effects of surface, material and lubricant-additive technologies," Friction, vol. 4, no. 1, pp. 1-28,2016.
4. W. J. Bartz, "Gear oil influences of efficiency of gear and fuel economy of cars," in Proceedings of the Institution of Mechanical Engineers. Vol 214 Part D: Journal of Automobile Engineering, 2000.
5. T. Wang and J. Li, "A Measurement and Testing Method for Lubrication Regimes in GearTransmissions," Tribotest Journal, vol. 2, no. 1, pp. 37-45, 1995.
6. Z. Tang and S. Li, "A review of recent developments of friction modifiers for liquid lubricants(2007-present)," Current Opinion in Solid State and Materials Science 18, pp. 119-139, 2014.
7. R. I. Taylor, "Tribology and energy efficiency: from molecules to lubricated contacts to complete machines," Faraday Discussions, vol. 156, pp. 361-382, 2012.
8. A. Kahraman, T. T. Petry-Johnson, N. E. Anderson and C. D. R, "An Experimental Investigation of Spur Gear Efficiency," Journal of Mechanical Design, vol. 130, pp. 062601-1 - 10, 2008.
9. A. S. Kolekar, O. A. V, S. A. E and L. F. E, "The efficiency of a hypoid axle—a thermally coupled lubrication model," Tribology International, vol. 59, pp. 203-209, 2013.
10. M. Hammami, R. Martins, S. A. Mohamed, H. Mohamed and J. Seabra, "Axle gear oils: Tribological characterization under full film lubrication," Tribology International, vol. 106, pp.109-122, 2017.
11. P. W. Michael, J. M. Garcia, S. S. Bair, M. T. Devlin and A. Martini, "Lubricant Chemistry and Rheology Effects on Hydraulic Motor Starting Efficiency," Tribology Transactions, vol. 55, pp.549-557, 2012.
12. J. W. Robinson, Y. Zhou, J. Qu, J. T. Bays and L. Cosimbescu, "Highly branched polyethylenes as lubricant viscosity and friction modifiers," Reactive and Functional Polymers, vol. 109, pp. 52- 55, 2016.
13. L. Cosimbescu, J. W. Robinson, y. Zhou and J. Qu, "Dual functional star polymers for lubricants," RSC Advances, vol. 6, p. 86259–86268, 2016.
14. L. Paouris, S. Theodossiades, R. Rahmani, H. Rahnejat, G. Hunt and W. Barton, "Effect of Lubricant Rheology on Hypoid Gear Pair Efficiency," in 3rd Biennial International Conference onPowertrain Modelling and Control, Loughborough University, UK, 2016.
15. W. R. S. Barton, J. Payne, M. Baker, B. O'Connor, F. Qureshi, M. Huston and D. Knapton, "Impact of Viscosity Modifiers on Gear Oil Efficiency and Durability," SAE International Journalof Fuels and Lubricants, vol. 5, no. 1, pp. 470-479, 2012.
16. W. Barton, D. J. Knapton, M. Baker, A. Rose, E. A. Schiferl, M. Huston, G. Brown and G. Hunt, "Impact of Viscosity Modifiers on Gear Oil Efficiency and Durability: Part II," SAE InternationalJournal of Fuels and Lubricants, vol. 6, no. 2, pp. 295-310, 2013.
17. B. Vengudusamy, A. Grafl, F. Novotny-Farkas and W. Schöfmann, "Influence of temperature onthe friction performance of gear oils in rolling–sliding and pure sliding contacts," Lubrication Science, vol. 26, pp. 229-249, 2014.
18. A. B. Greene and T. J. Risdon, "The Effect of MolybdenumContaining, Oil-Soluble Friction Modifiers on Engine Fuel Economy and Gear Oil Efficiency," in Fuels & Lubricants Meeting,Tulsa, Oklahoma, 1981.
19. K. Kubo, Y. Shimakawa and M. Kibukawa, "The effect of gear oil viscosity and friction reducertype on transmission efficiency," Tribology International, vol. 19, no. 6, pp. 312-317, 1986.