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Synthesis, Characterization, and Tribological Evaluation of Reduced GrapheneOxide Added Grease through SRV-5

Sooraj Singh Rawat[1], A. P. Harsha[1*] and O. P. Khatri[2]
[1]Department of Mechanical Engineering, Indian Institute of Technology
(Banaras Hindu University), Varanasi, India
[2]Chemical Science Division, CSIR-Indian Institute of Petroleum, Dehradun India

Keywords: Paraffin grease; friction; wear; rGO nanosheets; four-ball tester

Abstract

The present study focused on the formulation and dispersion of reduced graphene oxide (rGO) nanomaterials in the paraffin grease. The tribological behavior of grease was investigated using the SRV-5 test machine as per the ASTM D 5707 standard. Graphene oxide nanosheets were synthesized by conventional Hummer's method. Further, hydrazine hydrate was used as a reducing agent for the development of rGO nanosheets. Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) analytical tools were used to affirm the formulation of rGO nanosheets. The high-resolution transmission electron microscopy (HRTEM) was used to probe the microstructural features of rGO nanosheets. Paraffin oil was used as base oil, and lithium soap opted as a thickener. The dispersion of rGO nanosheets in the grease was done through the in-situ method, and their concentration was varying in the range between 0.01-0.05% w/w. The drop point and cone penetration of paraffin grease were also evaluated according to ASTM D566 and D1403 standards, respectively. The tribological test results showed a maximum reduction in average coefficient of friction (COF) and mean wear volume (MWV) was ~18.15% and ~21.35% at a concentration of 0.03% w/w of rGO nanosheets, respectively. Energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) were used to characterize the wornsurfaces.

Introduction

In a recent development, two-dimensional (2D) nanomaterials are preferred as lubricant additives.[1] Molybdenum disulfide (MoS_2), graphite, and graphene are well-known solid lubricants. Graphene is largely produced with chemical exfoliation, micromechanical, electrochemical, chemical vapor deposition (CVD) reduction routes.[2] Graphene has distinctive properties such as high thermal conductivity, large specific surface area, high transparency, and high mechanical strength. Therefore it is used in enormous applications in sensors, capacitors, touch screens, transparent conductive films, batteries, toxic material removal, fuel cells, spintronic devices, solar cells, ceramic and metal matrix composites.[3] Apart from this, graphene demonstrated unique friction and wear reduction properties as an additive in water-based lubricant[4], oil-based lubricant[5], and grease.[6]

The present investigation focused on tribological study on the formulated paraffin grease homogeneously mixed with rGO nanosheets by the in-situ scheme. A fresh formulated paraffin grease without any additive/s was termed as 'base grease' and set a reference to equating the physical and tribological properties of the greases. Antiwear (AW) and antifriction (AF) characteristics of paraffin grease mixed with and/or without rGO nanosheets have been explored using the SRV-5 test machine as per ASTM D5707 standard.

Experimental details

Synthesis and characterization of rGO nanosheets

The synthesis procedure of GO nanosheets is reported in the article.[7] The rGO nanosheets were prepared from GO nanosheets. Hydrazine hydrate (Sigma Aldrich) was used as a reducing agent to eliminate the oxygen functionalities from its basal plane. The aqueous solution of GO with hydrazine hydrate was refluxed for 24 h. The dark brown colored GO which was turned into black colored as aggregated rGO. Subsequently, rGO was washed thoroughly with distilled water several times to remove residual hydrazine hydrate traces. The black color rGO nanosheets were filtered out using a membrane filter and dried at 105 ^{o}C for 6-7 h. The dried powder of rGO was grounded into a fine powder and kept for further use.

The structure of rGO nanosheets were examined by XRD (Cu Kα radiation, Rigaku Miniflex 600 D/teX Ultra) in the 2θ range from 3 to 70 deg. FT-IR (Bruker ALPHA ECO-ATR) was used to affirm rGO nanosheets in a transmittance spectrum range of 400 and 4000 cm^{-1} with the resolution of 4 cm^{-1} and a scan rate of 40 cm^{-1}. The nanostructural morphology of rGO nanosheets were investigated by HRTEM (JEM 2100, JEOL Ltd., Japan).

Synthesis of grease and characterization of physical properties

The synthesis technique of paraffin grease was followed in the present study is reported in the our earlier article.[8] The concentration of the thickening agent was taken 14% w/w. The blending concentration of rGO nanosheets in the grease were varied in the range between 0.01 to 0.05% w/w. Paraffin grease mixed with rGO nanosheets termed as 'rGO grease,'.

The consistency and dropping point of the base and rGO greases were examined as per ASTM D 1403 and D 566 standard, respectively. Each experiment was repeated thrice with fresh grease to precise the test results, and the average value was reported.

Tribological characterization of the grease and analysis of worn surfaces

High frequency linear-oscillation (SRV-5 model) test machine was used to evaluate AF and AW of synthesized greases as per the ASTM D 5707 standard. In this test, steel ball (100Cr6, dia. 10mm, 60±2 HRC) and steel disc (100Cr6, 24x7.85mm, 60±2 HRC) were used as test specimens. The detailed test specifications are summarized in **Table 1**. The wear scars on the surface of disc and ball were probed with an SEM. EDS was attachment with SEM machine, and it was used to examine the elemental characterization of worn surfaces.

Table 1: Test parameters for antiwear test of the grease

Test specification	**Antiwear test**
Test standard	ASTM D5707
Load (N)	50 N for 30s (pre load) Then 200 N
Stroke amplitude(mm)	1.0
Duration (min)	120±0.25
Temperature (^{o}C)	80

Results and discussion Characterization of rGO nanosheets

Morphological images of rGO nanosheets characterized with HRTEM is shown in **Figs 1(a-b)**. After treating the GO sheets with a reducing agent, it seems more fluffy appearance. It is a clear indication of the removal of oxygen functionalities and the refurbishment of sp^2 carbon domains. XRD analysis of rGO nanosheets were performed to examine the distinctions in interlayer spacing and structural variations. The diffraction pattern of rGO nanosheets **(Fig. 1(c))** demonstrated a broad peak at 2θ = 25.29 deg along with interlayer spacing 0.351 nm. The hydrazine hydrate, the reducing agent, was used to remove the oxygen defect sites from GO nanosheets through chemical reduction. Carboxylic and hydroxyl vibration peaks did not appear in the FTIR spectrum of rGO nanosheets (**Figure 1(d)**). It is evident that most of the oxygen defect sites have been removed for its basal plane.

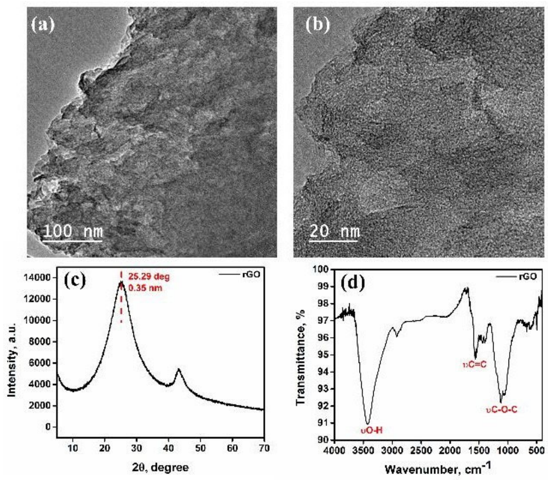

Fig. 1(a-b) Transmission electron microscopic images of rGO nanosheets at low and high resolutions **(c)** XRD diffraction pattern **(d)** FT-IR pattern of rGO nanosheets

Physical and tribological characterization of the grease with rGO nanosheets

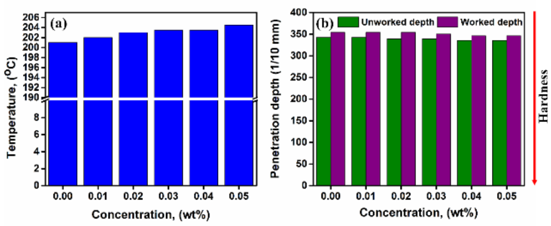

Fig. 2 Variation in **(a)** drop point temperature and **(b)** unworked and worked penetration depth with varying concentration of rGO greases

The base grease is referred to as standard grease and compared with rGO nanosheets dispersed grease for various physical and tribological properties. Drop point test results are shown in **Fig. 2(a)**. The test result showed that the dropping point of greases increases gradually with the increment of concentration of nanosheets, but the difference was 4 °C, only and it is not a significant change in the dropping point. Cone penetration test results are depicted in **Fig. 2(b)**.

According to the cone penetration test results, theformulated base and rGO greases are semi-solid and can be classified as NLGI 1 grade. No significant changes were observed between unworked and worked penetration depth of grease samples. It indicates that formulated greases have excellent shear stability.

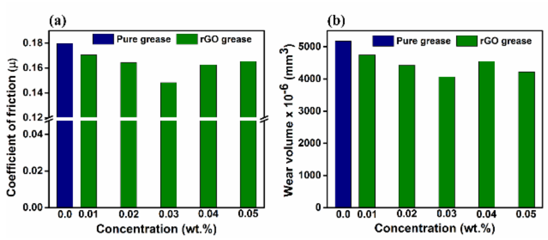

Fig. 3(a) Variation in COF with varying concentration of rGO nanosheets **(b)** Variation in WV with varying concentration of rGO nanosheets

The variation of average COF and MWV with increasing concentration of rGO nanosheets are shown in **Figs. 3(a-b)**. The highest COF (0.18106) was shown by base grease. The highest reduction in COF and MWV was achieved with 0.03% w/w dispersion of rGO nanosheets, and it was ~18.15% and ~21.36%, respectively. The AF and AW test results show a significant reduction in COF and MWV. It is a shred of evidence that such little fraction of rGO nanosheets have a noteworthy potential to enhance the tribologicalperformance of the formulated grease.

Study of worn surfaces area of ball and disc

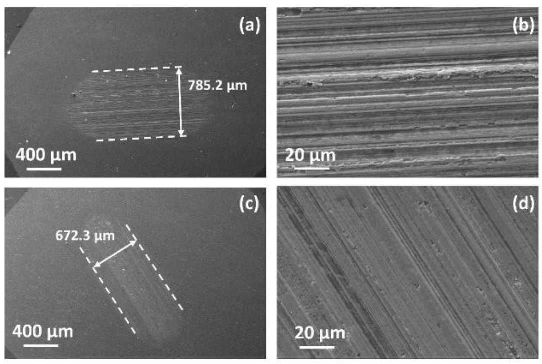

Fig. 4 Worn surfaces of disc lubricated with **(a-b)** basegrease **(c-d)** rGO grease

The typical SEM micrographs of worn-out tribo- surfaces of steel disc are shown in **Fig. 4**. Low- and high-resolution images of wear track width (WTW) lubricated with base grease is shown in **Figs. 4(a)-(b)**. The WTW was reached up to 785.2 µm. Breakdown in tribo-film leads to local seizure of asperities resulting in the removal of more material due to adhesion wear. Base grease-lubricated disc exhibited deep furrows and micro-pits on the worn surfaces, abrasive wear was dominated with more denser furrows. In the presence of rGO nano-sheets, the WTW was reduced significantly as compared to the base grease (**Figs. 4(c)-(d)**). The maximum reduction in WTW demonstrated by the optimized concentrationof rGO grease was about ~14.37%. The worn surfacesin the presence of rGO nanosheets appeared smootherthan that lubricated with base grease (**Fig. 4(d)**). Further, the severity of furrows and micro-pits was reduced significantly. It is evident that tribo-pairs lubricated with rGO grease are excellent in protectingthe contact surfaces.

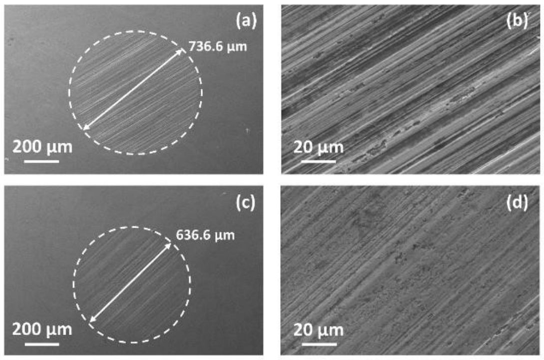

Fig. 5 Worn surfaces of ball lubricated with **(a-b)** base grease **(c-d)** rGO grease

SEM micrographs of worn-out steel balls are shown in **Fig. 5**. The worn surface lubricated with base grease showed maximum wear scar diameter (WSD; i.e., 736.6 µm), sharp scratches, and evidence of adhesion and abrasive wear (**Fig. 5(b)**). WSD was reduced significantly in the presence of rGO nanosheets in the grease. The maximum reduction in WSD was achieved with rGO grease ~13.5% at the optimized concentration. The adhesion wear phenomenon was reduced in the presence of rGO nano-sheets, and the severity of scratches were also reduced. The SEM micrographs confirmed the AW capability of rGO nano-sheets. This indicates that a little fraction of rGO nanosheets have significant potential to protect the tribo-pairs.

The Hertzian contact stress plays a crucial role in the establishment of a tribo-film between the interacting surfaces. The Hertzian contact stress between the ball and disc tribo-pair was estimated as 2.74 GPa. Under such high contact stress, the soap molecules are sheared and squeezed causes the liberation of base oil along with nano-sheets. Discharged base oil with nano-sheets lubricates the interacting surface and forms a beneficial tribo-film. The developed tribo-film due to the combination of thickener and base oil along with additives.[9,10] The base grease attains higher COF and MWV in contrast with the rGO grease. This affirmed that nano-sheets formed a protective tribo- film between the interacting surfaces. The rGO nano- sheets have lamellar structure as shown in **Fig. 1(a)**. It demonstrated the stacking of molecular lamellas which are interacted through wear surface by van der Waals forces. Hertzian contact stress of 2.74 GPa is significantly high and helps for ease shearing of lamellas. The lamellas of nano-sheets sheared and pressed on the track to form a protective layer through the absorption of rGO nano-sheets on the interacting surfaces.[11] This protective film reduced friction and protect the interacting surfaces against wear.

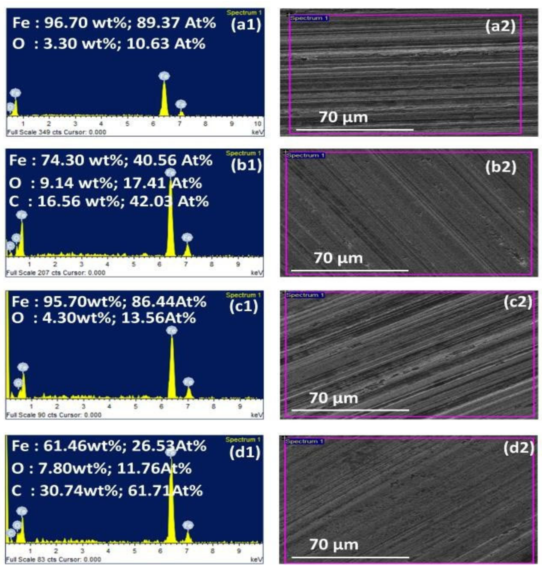

Fig. 6 EDS spectra of the worn surfaces of disc lubricated with **(a1-a2)** base grease **(b1-b2)** rGO grease and worn surfaces of ball lubricated with **(c1- c2)** base grease **(d1-d2)** rGO grease

The EDS analysis of steel discs and balls were carried out for elemental characterization. The SEM micrographs and the corresponding EDS spectra with the atomic% and weight% of an individual element on the worn area of discs and balls are explicitly illustrated in **Fig. 6**. The EDS spectrums of the steel disc and ball lubricated with base grease showed a peak of iron and oxygen (**Figs. 6(a1) and 6(c1)**). This confirms that the foreign particles/additives were not present in the base grease. The rGO greased worn surfaces (disc and ball) exhibited the presence of carbon (**Figs. 6(b1) and 6(d1)**). The presence of a high concentration of carbon on the worn surfaces confirms the deposition of carbon. The deposition of carbon formed a lubricious tribo-film. Thus, it shields the interacting surfaces. The oxygen peak appeared on all worn surfaces, and it may be due to oxidation of the worn surfaces.

Conclusions

The following conclusions have been drawn up from described work:

- There was no significant improvement observed in dropping point and consistency of rGO grease.
- The maximum reduction in COF and MWV was achieved ~18.15% and ~21.35% with the dispersion of 0.03% w/w of rGO nanosheets.
- Carbon traces was observed in the EDS spectrum, which confirms the deposition of nanosheets on the worn surfaces. Consequently, it formed a defensive tribo- film.

Acknowledgment

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Development of Extreme Pressure greases using Nano solid dispersion.

Dr. Somnath Chattopaddhyay, N. Parameswaran, Gouri Sankar Manna,
Dr. Mohan Lal Das & Sreejit Banerjee
Balmer Lawrie & Co Ltd, Applications Research Laboratory, Kolkata, India

Introduction:

Tribology is an inter-disciplinary subject involving mechanical, chemical and physical aspects of material science and engineering that deals with the interacting surfaces in relative motion.The principle application of tribology deals with friction, wear and lubrication. The term is ofGreek origin and in 1966 this word was used first by Peter Jost.

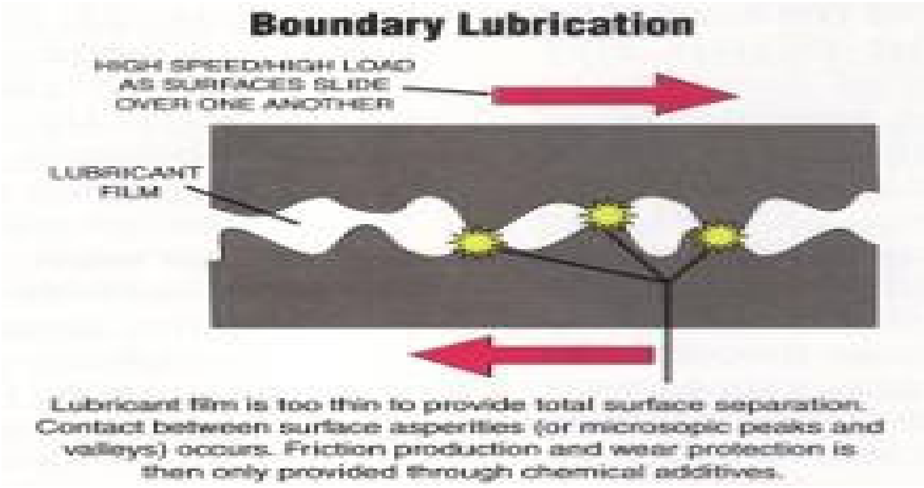
Friction causes material loss, energy loss and productivity loss in industrial machinery. Even-though friction cannot be completely removed and its presence to a lesser level is a requirementin many situations, it can be minimised to avoid the above-mentioned losses. The reduction in friction is achieved through lubrication which is nothing but proper selection and application of a substance called lubricant.

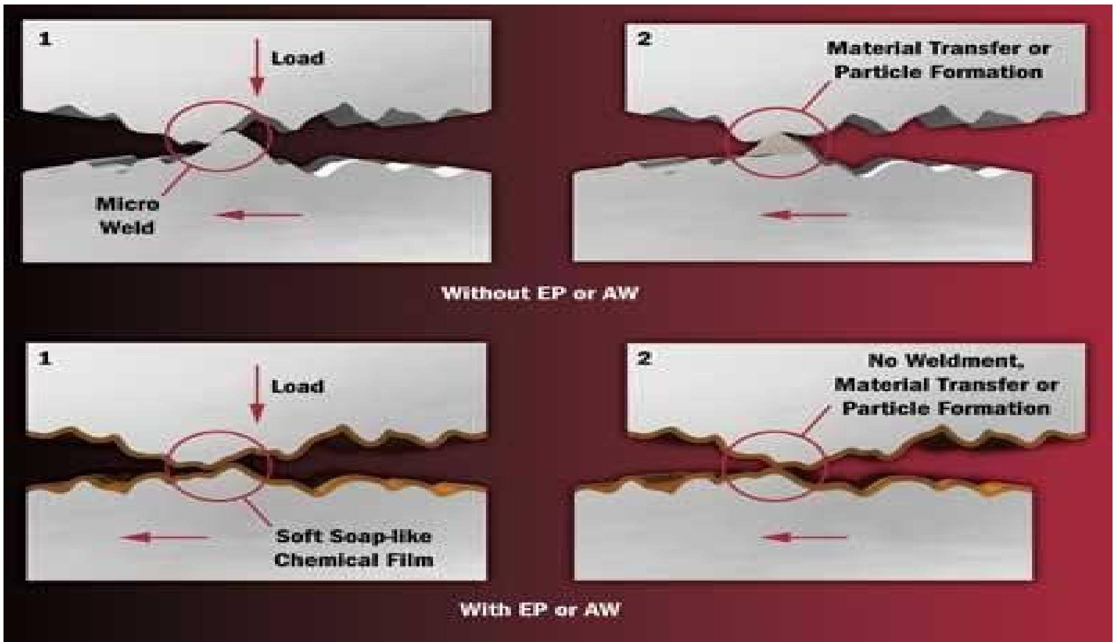
Lubricants are available in the form of liquid, semi solid, solid, gas etc. Grease is a semi solid to fluid substance made from thickener and base oils. To enhance the performance of the greases, chemicals namely additives are added which may be liquid, solid or solids dispersedin a medium. One of the additives added to the greases to improve the Extreme pressure, anti-wear performance of the greases are solids like Graphite, PTFE, Molybdenum di sulphide, Boron nitride etc. Liquid additives are the generally preferred to achieve better EP & AW properties.

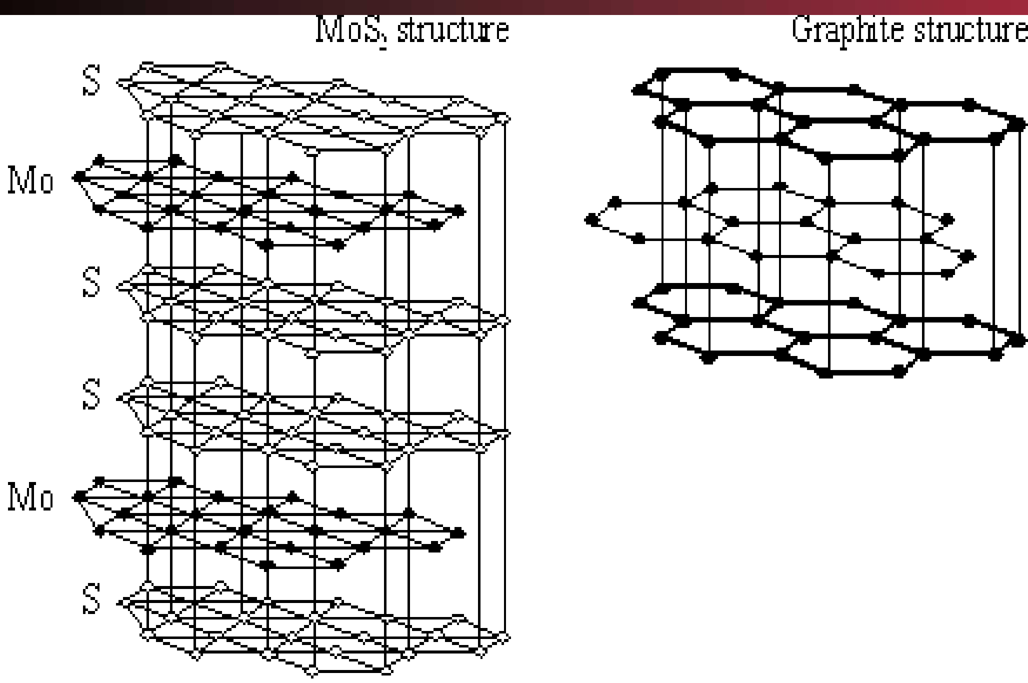
With the advent of modern technology, solid lubricants are now available in the form of Nanosolids and Nano solid dispersions. The effectiveness of the Nano solids has already been studied and they are getting established to be better over the conventional solids.

These additives and solid lubricants are used alone or in combination with one another to effectively achieve the required extreme pressure & anti wear properties for the greases. The chemical additives mainly act by modifying the contacting surfaces with a film of reactive products generated at high working pressure and temperatures during elasto- hydrodynamic &boundary conditions. On the other hand, the solid lubricants like graphite and Molybdenum disulphide have hexagonal crystal structure and have lubricity mechanism that largely relies on the formation of very strong and flexible layers that slide over one another under stress. The effectiveness of these solid lubricants is greatly influenced by their purity, particle size and surface area.

Introducing nanoparticles in lubricants is a complicated task because size, shape, concentration and the materials itself are all very important factors to influence the lubrication performance of a specific system. Some nanoparticles are difficult to disperse in the liquid phase —the baseoil. For example, inorganic fullerenes are mineral particles with a spherical or cylindrical shape and a size having range between 50 and 150 nm. They do not present any affinity with oil and their dispersion is consequently difficult without surfactants. The hardness of nanoparticles isanother factor for consideration. Generally, nanoparticles greater than 100 nm tend to be veryhard, while those less than 10 nm tend to be soft, which results in significantly increased surface smoothness and lubrication behaviour. Initially, nanomaterials, specifically graphite, were only applied as dry lubricants in very harsh environments such as high temperature applications. Recent studies demonstrate a fine control over the size, shape, and surface functional groups of nanoparticles. The potential of nanoparticles in colloidal systems yields a high number of applications in all fields varying from lubrication to oil extraction, from biomedical applications to drug delivery systems. Addition of nanoparticles in lubricating oil / grease could significantly reduce the interfacial friction and improve the load-bearing capacity of the parts, which has been regarded as having great potential as lubricant additives. Different school of thoughts are there for the lubrication mechanism of nanoparticles, including the ball bearing effect, protective film, mending effect and polishing effect. Lee and colleagues categorized them based on: (i) the direct effect of nanoparticles on enhanced lubrication - the nanoparticles form a protective film between the two surfaces in contact; (ii) the presence of nanoparticles on surface enhancement — nanoparticles deposited on the surface that compensate for the loss of mass, whilst the roughness of the lubricating surfaces is reduced by the existence of nanoparticles.







There is a tremendous pressure on the grease formulators to develop cost effective and high performing products to meet the ever-increasing demand from the end users. The use of traditional and high-performance additives, while offering the required performance characteristics, may increase the cost of products. Many solid lubricants like MoS2, Boron nitride will be cost prohibitive and have availability issues.

Most of these additives and solid lubricants (except probably the Graphite) are environmentally very sensitive. The current and future requirements call for managing the maintenance cost of the machinery and the disposal cost of used lubricants within the acceptable and sustainable levels. This has led to grease formulators to look for alternative, cost effective, better or equally performing and environmentally safe/ benign chemicals or compounds for use as extreme pressure and anti-wear agents.

In this context our Company's Applications Research Laboratory has undertaken a study for the development of Extreme Pressure Greases based on Lithium and Lithium Complex thickener systems using Nano particle dispersion replacing the conventional liquid and or solid additives. In our study we have compared the effect of dispersed Nano particle in greases forExtreme Pressure and anti-wear properties viz. weld load, Scar dia. The antagonistic or synergistic effect of the solid dispersion on the drop point, Cu corrosion as well as consistency test was also demonstrated. Comparison is made on the EP and AW enhancing properties of Nano solid dispersion vis-a vis that of the conventional additives and presented in this paper. The results show Nano solid dispersion is an alternative choice for replacing the conventional additive systems with performance and commercial benefits in low dosages.

Experimental methods:

A. Materials and Methods:

Additives

To study the comparative effect between conventional additives and Nano dispersion the following additive groups were selected.

(A) EP additive Component (B) Anti wear (AW) additive (C) Molybdenum di sulphide (Moly)
(D) EP Additive package (E) Nano dispersion. All the additives were obtained from standard additive supplying companies.

Base Grease Preparation:

Simple Li grease and Li complex greases were prepared for testing the above-mentioned additive systems using mineral oil of viscosity 150 cSt @ 40 deg C for Li grease and with 220cSt at 40 deg C, for Li Complex grease using the conventional methods known for the manufacture of greases.

Sample Preparation:

Extreme Pressure & Anti-wear Greases were prepared for the study using the above mentionedliquid, solid and nano solid dispersion additives. Base grease has been taken without any additives.

The parameters related to EP properties viz. weld load (IP 239), Scar dia (ASTM D 2266) hasbeen checked. Additionally, other related parameters namely Drop point (ASTM D 2265), Cucorrosion (ASTM D 4048) as well as Consistency / Penetration test (ASTM D 217) was also done.

B. Evaluation of formulations:

In order to evaluate the tribological properties like wear, friction and load carrying ability the following experimental procedures were used.

1. Extreme Pressure property by four ball weld load tests:

One of the most widely used and accepted tests to characterize the extreme pressure or load carrying capacity of high-performance industrial greases is to evaluate the four-ball weld load. In the present study we have used this test to evaluate the four-ball weld load of all the greases. In this test one stainless steel ball kept in a spindle attached to a motor is rotated against three stationary balls kept immersed in the lubricant in a ball pot assembly. Load is applied on the three balls from below. Test is conducted as per IP 239 method. (Speed = 1470 rpm; Time = 10s) As the applied load is increased, at a particular load the four balls weld together when the lubricant loses its load carrying capacity. This load is declared as the weld load for the particular lubricant. The values obtained for all the greases are used to differentiate the extreme pressure property of the greases taken for the study.

2. Wear preventive characteristics of greases using four ball wear tests:

A well-known test to characterize the ability of the lubricant to prevent wear is to determine the wear scar diameter using a four-ball test machine. In this method one steel ball is rotated against three stationary balls kept immersed in the sample under study. We have conducted this test as par ASTM D 2266 method on all the grease samples using the following conditions.

1. Speed = 1200 RPM
2. Load = 40 Kg
3. Temperature = 75 deg C
4. Time = 1 hr

At the end of the test, diameter of the scar produced on all the three balls is measured. The average scar diameter obtained is a measure of wear preventive property of the grease.

The formulated greases with the chemical compound under investigation were also evaluated for Drop point (ASTM D 2265), Cu corrosion (ASTM D 4048) as well as Consistency / Penetration test (ASTM D 217) to understand the synergistic or antagonistic effects of the selected additive under investigation – IF any is there.

Results and discussions:

1. Comparative study on Weld load (IP 239) and Scar dia (ASTM D 2266).

With the target to achieve a simple lithium / lithium complex grease that can withstand a weldload above 280 kg the study began.

The samples made out of lithium grease for testing were prepared and named as –

Base Grease	Additive	Sample Name
Lithium grease 100%	None	A
Li grease 98%	EP Additive component 2%	B
Li grease 97%	EP Additive component 2%,AW additive 1% (standard pack)	C
Li grease 97%	MOLY 3%	D
Li grease 96%	MOLY 3%, AW additive 1%	E
Li grease 98.5%	EP Additive package 1.5%	F
Li grease 99.25%	Nano dispersion 0.75%	G
Li grease 98.25%	Nano dispersion 0.75%, AW additive 1%	H

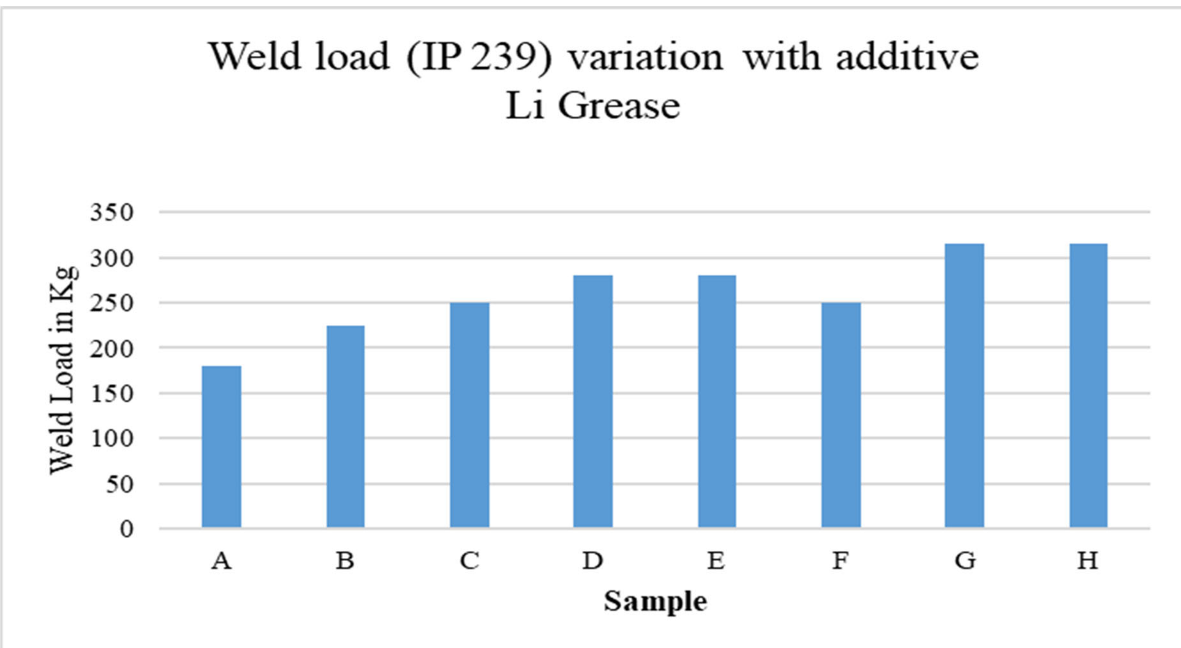
Table: 1 Weld load and Scar dia study in simple Li grease.

FORMULATION	Additive	Weld load IP 239	Wear scar ASTM D 2266
Li Grease	As such (A)	180 kg	0.786 mm
	EP Additive component 2% (B)	225 kg	0.670 mm
	EP Additive component 2%, AW additive 1% (standard pack) (C)	250 kg	0.590 mm
	MOLY 3% (D)	280 kg	0.678 mm
	MOLY 3%, AW additive 1% (E)	280 kg	0.562 mm
	EP Additive package 1.5% (F)	250 kg	0.688 mm
	Nano dispersion 0.75% (G)	315 kg	0.501 mm
	Nano dispersion 0.75%, AW additive 1% (H)	315 kg	0.496 mm

From the above study we can see that the addition of Nano dispersion is giving the best EP property in the grease with a very low treat level. Considering the weld load, where the base grease is giving 180 kg weld, the Nano added grease is giving a weld load of 315 kg. whereasthe Standard Pack (EP additive component (2%) + AW additive 1%) is giving only 250 kg weld load. Whereas addition of 3% Moly itself is giving up to 280 kg. An addition of 1% AWadditive with the other additives is not giving any extra advantage for weld load (except along with EP additive component), but it is having a significant effect on Scar dia.

A graphical representation may sight as:

Graph - 1

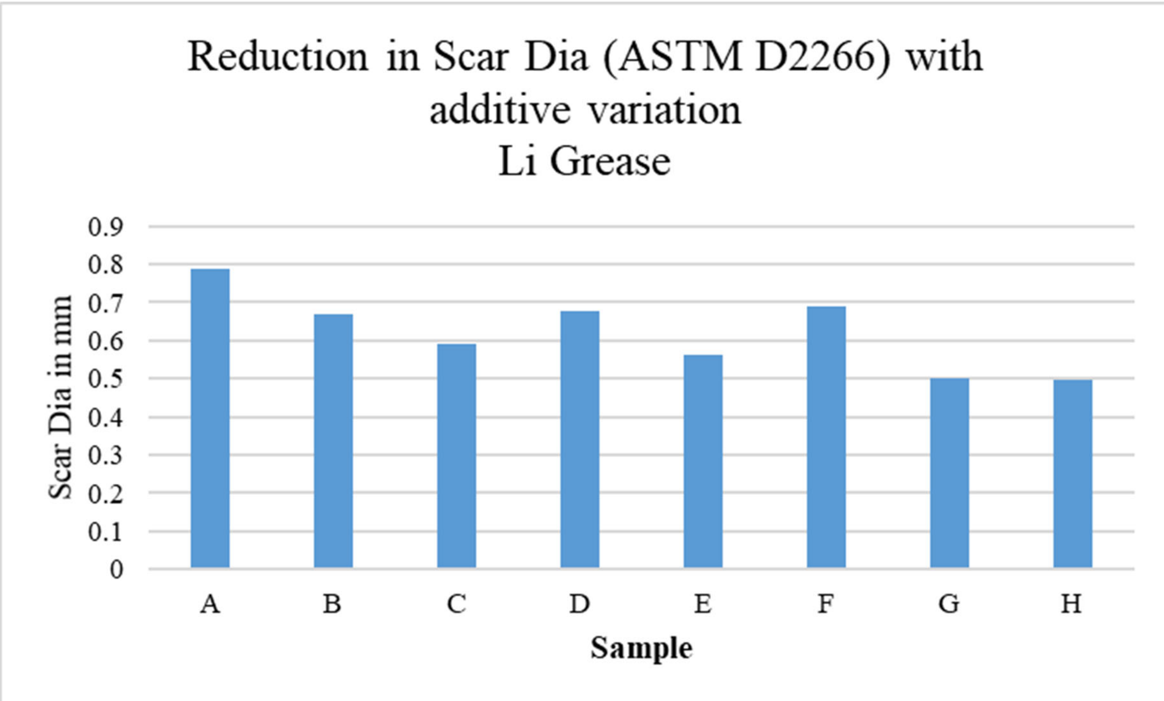


Where, A = As such, B = EP Additive component 2%, C = EP Additive component 2%, AW additive 1% (standard pack), D = MOLY 3%, E = Moly 3%, AW additive 1%, F = EP Additive package 1.5%, G = Nano dispersion 0.75% and H = Nano dispersion 0.75%, AW additive 1%.

Considering the comparative study of Scar dia for Nano dispersion and other EP additives, itis clear that Nano is having a very significant positive effect in reducing the scar dia. The simple lithium grease without any additive is showing an average scar dia of 0.786 mm, where Nano dispersed grease is of 0.501mm, 36.25% reduction in scar compare to base. Though the lowest scar dia is observed when Nano dispersed grease is treated along with 1% AW additive(0.496 mm, 36.89% reduction), with a marginal improvement. On the other hand, the recommended standard pack for EP enhancer additive is showing 0.590 mm dia (24.93% reduction in scar). 3% Moly treated grease here shows dia of 0.678 mm (13.74% reduction w.r.t. base grease). Again, addition of 1% AW additive along with 3% Moly shows a better average dia (0.562 mm, 28.49% reduction w.r.t. base grease). On the other hand, EP additive package shows 0.688 mm, 12.46% reduction in scar w.r.t. base grease, which is not good enough. All the additive systems showed higher wear scar dia compared to that for Nano dispersion-based formulation.

The graphical representation may sight as:

Graph - 2



Where, A = As such, B = EP Additive component 2%, C = EP Additive component 2%, AW additive 1% (standard pack), D = MOLY 3%, E = Moly 3%, AW additive 1%, F = EP Additive package 1.5%, G = Nano dispersion 0.75% and H = Nano dispersion 0.75%, AW additive 1%.

The above comparative study, clearly shows that Nano dispersion is having a good impact ina low dosage on Extreme pressure and anti-wear properties of simple lithium base grease.

The same effect studied on lithium complex grease also.

The samples made out of lithium complex grease for testing were prepared and named as –

Base Grease	Additive	Sample Name
Lithium complex grease 100%	None	P
Li complex grease 98%	EP Additive component 2%	Q
Li complex grease 97%	EP Additive component 2%,AW additive 1% (standard pack)	R
Li complex grease 97%	MOLY 3%	S
Li complex grease 96%	MOLY 3%, AW additive 1%	T
Li complex grease 98.5%	EP Additive package 1.5%	U
Li complex grease 99.25%	Nano dispersion 0.75%	V
Li complex grease 98.25%	Nano dispersion 0.75%, AW additive 1%	W

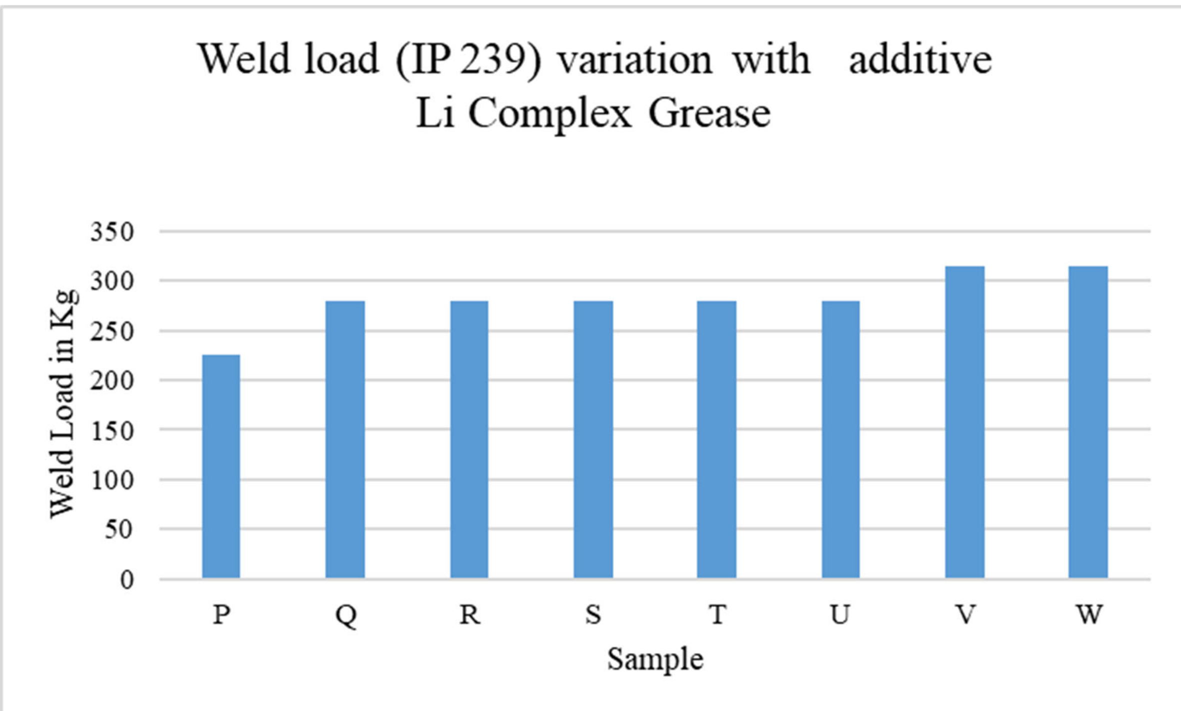
Table: 2 - Weld load and Scar dia study in Li complex grease.

FORMULATION	Additive	Weld load IP 239	Wear scar ASTM D 2266
Li Complex Grease	As such (P)	225 kg	0.621 mm
	EP Additive component 2% (Q)	280 kg	0.535 mm
	EP Additive component 2%, AW additive 1% (standard pack) (R)	280 kg	0.505 mm
	MOLY 3% (S)	280 kg	0.569 mm
	MOLY 3%, AW additive 1% (T)	280 kg	0.534 mm
	EP Additive package 1.5% (U)	280 kg	0.568 mm
	Nano dispersion 0.75% (V)	315 kg	0.480 mm
	Nano Dispersion 0.75%, AW additive 1% (W)	315 kg	0.477 mm

For lithium complex grease also, the comparative study for weld load property shows that using of Nano dispersion is giving the best result (315 kg weld load) with the targeted value of 280 kg at the dosage of 0.75% addition. Other additives are performing bellow the Nano dispersion. Here point to be noted that unlikely simple lithium grease, the complex grease is withstanding a better weld load with the other additives.

The graphical representation may sight as:

Graph – 3

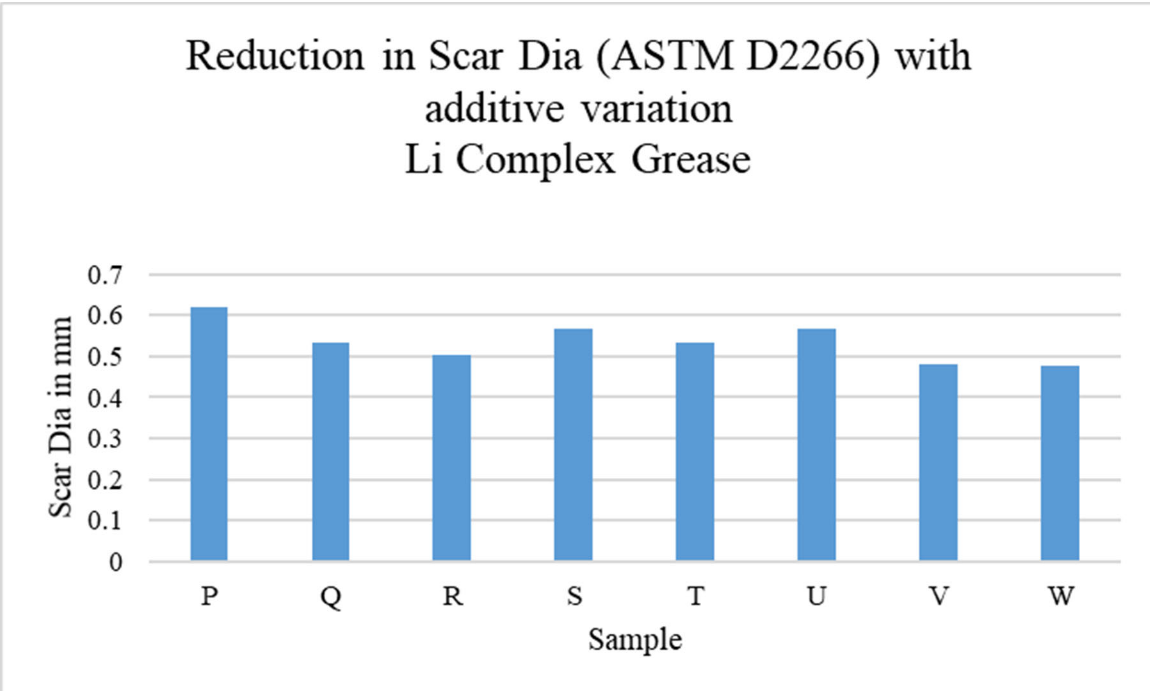


Where, P = As such, Q = EP Additive component 2%, R = EP Additive component 2%, AW additive 1% (standard pack), S = MOLY 3%, T = Moly 3%, AW additive 1%, U = EP Additive package 1.5%, V = Nano dispersion 0.75% and W = Nano dispersion 0.75%, AW additive 1%.

If we compare the scar dia, we will see that where the base grease is giving a scar dia of 0.621mm, the Nano dispersed one is giving 0.480 mm (22.7% reduction). More over addition of 1%AW additive along with the Nano dispersion is giving a further lower value of 0.477 mm (23.18% which is marginal improvement over the grease with only Nano dispersion. Standard Pack for EP additive is showing a good result (0.505 mm, 18.67% reduction in scar dia), followed by 1.5% EP additive package (0.568 mm, 8.53% reduction in scar dia). 3% Moly itself is showing (0.569 mm) at per with EP additive package, but 3% Moly along with 1% AW additive is showing a very good result (0.534 mm, 14% reduction in scar dia compare tobase grease).

The graphical representation may sight as:

Graph – 4



Where, P = As such, Q = EP Additive component 2%, R = EP Additive component 2%, AW additive 1% (standard pack), S = MOLY 3%, T = Moly 3%, AW additive 1%, U = EP Additive package 1.5%, V = Nano dispersion 0.75% and W = Nano dispersion 0.75%, AW additive 1%.

The above comparative study for lithium complex grease too, clearly shows that Nano dispersion is having a good impact in a low dosage on EP properties.

2. Comparative study for Drop point (ASTM D 2265).

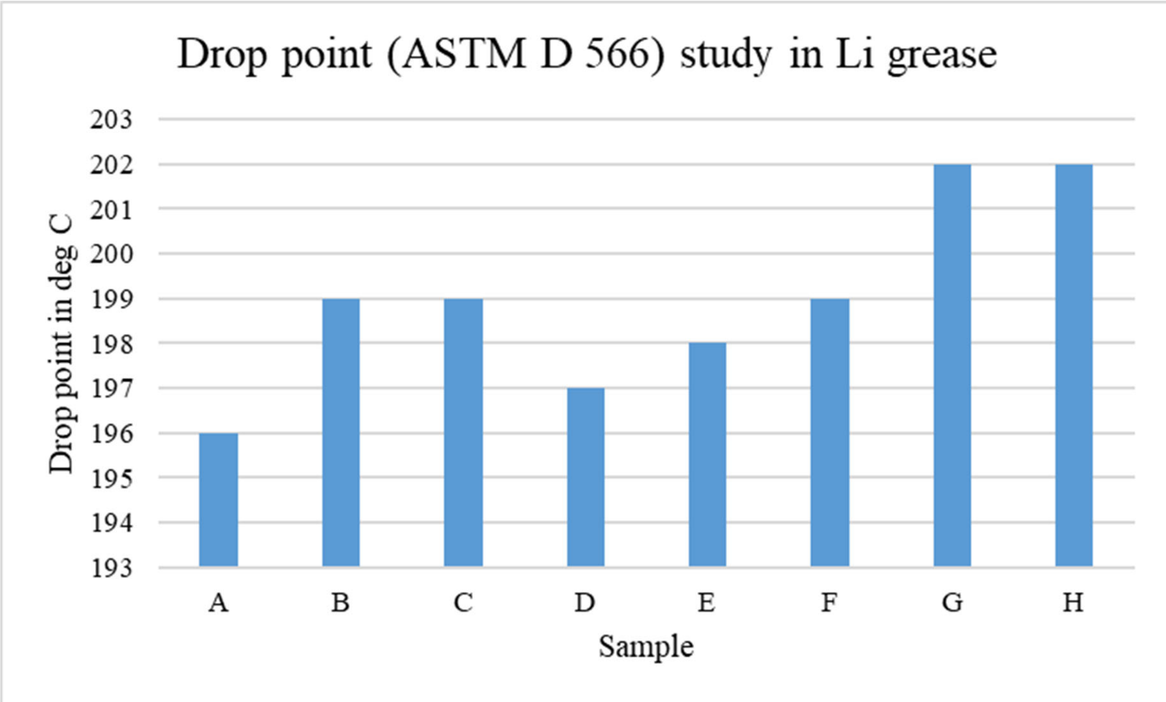
With the same set up of additive treated sample in both lithium grease and lithium complex grease the comparative study on drop point also done. It shows there is hardly any change in drop point caused by Nano dispersion and other EP additives for both the simple lithium and lithium complex greases. In case of simple lithium grease, Nano treated sample shows an enhance of 6 deg C in drop point (negligible), where as in case of lithium complex grease, it is only 5 deg C.

Table : 3 : Comparative study on drop point with EP effective additives on Li & Li Complex greases.

FORMULATION	Additive	DP pt, ASTM D 566
Li Grease	Lithium grease as such (A)	196 ^{0}C
	EP Additive component 2% (B)	199 ^{0}C
	EP Additive component 2%, AW additive 1% (standard pack) (C)	199 ^{0}C
	MOLY 3% (D)	197 ^{0}C
	MOLY 3%, AW additive 1% (E)	198 ^{0}C
	EP Additive package 1.5% (F)	199 ^{0}C
	Nano dispersion 0.75% (G)	202 ^{0}C
	Nano dispersion 0.75%, AW additive 1% (H)	202 ^{0}C
		ASTM D 2265
	Lithium complex grease as such (P)	264 ^{0}C
	EP Additive component 2% (Q)	268 ^{0}C
Li Complex Grease	EP Additive component 2%, AW additive 1% (standard pack) (R)	268 ^{0}C
	MOLY 3% (S)	267 ^{0}C
	MOLY 3%, AW additive 1% (T)	268 ^{0}C
	EP Additive package 1.5% (U)	267 ^{0}C
	Nano dispersion 0.75% (V)	269 ^{0}C
	Nano Dispersion 0.75%, AW additive 1% (W)	269 ^{0}C

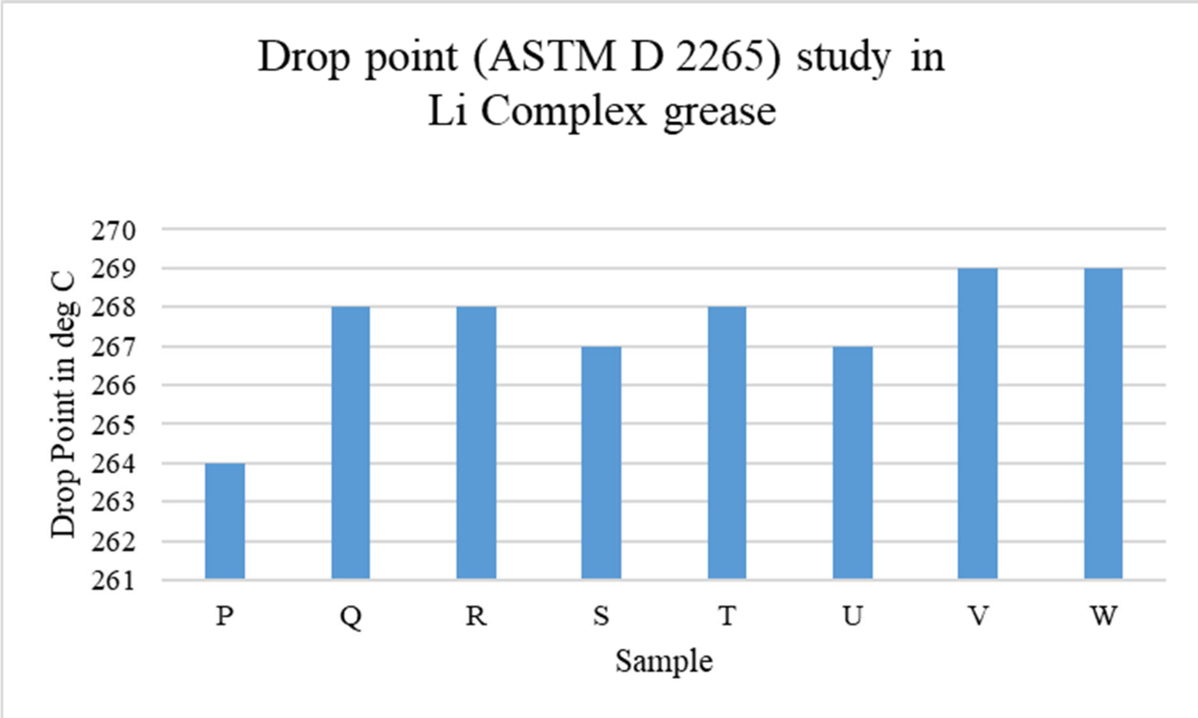
The graphical representation may sight as:

Graph – 5



Where, A = As such, B = EP Additive component 2%, C = EP Additive component 2%, AW additive 1% (standard pack), D = MOLY 3%, E = Moly 3%, AW additive 1%, F = EP Additive package 1.5%, G = Nano dispersion 0.75% and H = Nano dispersion 0.75%, AW additive 1%.

Graph – 6



Where, P = As such, Q = EP Additive component 2%, R = EP Additive component 2%, AW additive 1% (standard pack), S = MOLY 3%, T = Moly 3%, AW additive 1%, U = EP Additive package 1.5%, V = Nano dispersion 0.75% and W = Nano dispersion 0.75%, AW additive 1%.

3. Comparative study for Cu corrosion (ASTM D 4048).

With the same set of treated samples for both lithium and lithium complex grease studied to observe the effect on cupper corrosion, which revels there is no effect of Nano dispersion (as well as the other EP enhancing additives also) on the same. The results are as bellow –

Table 4: comparative study on Cu corrosion caused by Nano dispersion and other EP additives

FORMULATION	Additive	Cu corrosion ASTMD 4048
Li Grease	Lithium grease As such	1a
	EP Additive component 2%	1b
	EP Additive component 2%, AW additive 1% (standard pack)	1b
	MOLY 3%	1a
	MOLY 3%, AW additive 1%	1b
	EP Additive package 1.5%	1b
	Nano dispersion 0.75%	1b
	Nano Dispersion 0.75%, AW additive 1%	1b

Li Complex Grease	Lithium complex grease assuch (A)	1b
	EP Additive component 2%	1b
	EP Additive component 2%, AW additive 1% (standard pack)	1b
	MOLY 3%	1b
	MOLY 3%, AW additive 1%	1b
	EP Additive package 1.5%	1b
	Nano dispersion 0.75%	1b
	Nano Dispersion 0.75%, AW additive 1%	1b

4. Comparative study for Consistency (ASTM D 217).

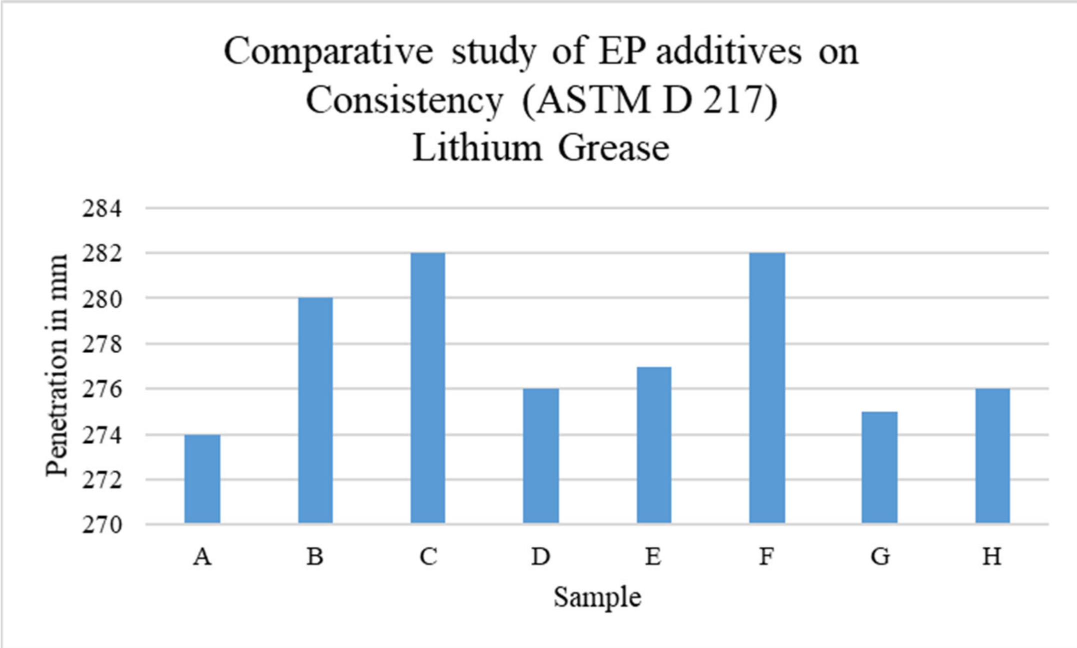
Further study has done to check the effect of Nano dispersion and the other EP additives on the consistency of the treated grease. This study also clearly shows that there is hardly any effect of Nano dispersion on both lithium and lithium complex grease in comparison to base grease. But, it with respect to the effect of other additives, it is having a protective effect on penetration. The results are as follows:

Table – 5: Comparative study on penetration for Nano dispersion and other EP additives in simple lithium grease.

Additive	Penetration in mm ASTM D 217
Lithium grease as such (A)	274
EP Additive component 2% (B)	280
EP Additive component 2%, AW additive 1% (standard pack) (C)	282
MOLY 3% (D)	276
MOLY 3%, AW additive 1% (E)	277
EP Additive package 1.5% (F)	282
Nano dispersion 0.75% (G)	275
Nano dispersion 0.75%, AW additive 1% (H)	276

The graphical representation may sight as:

Graph – 7



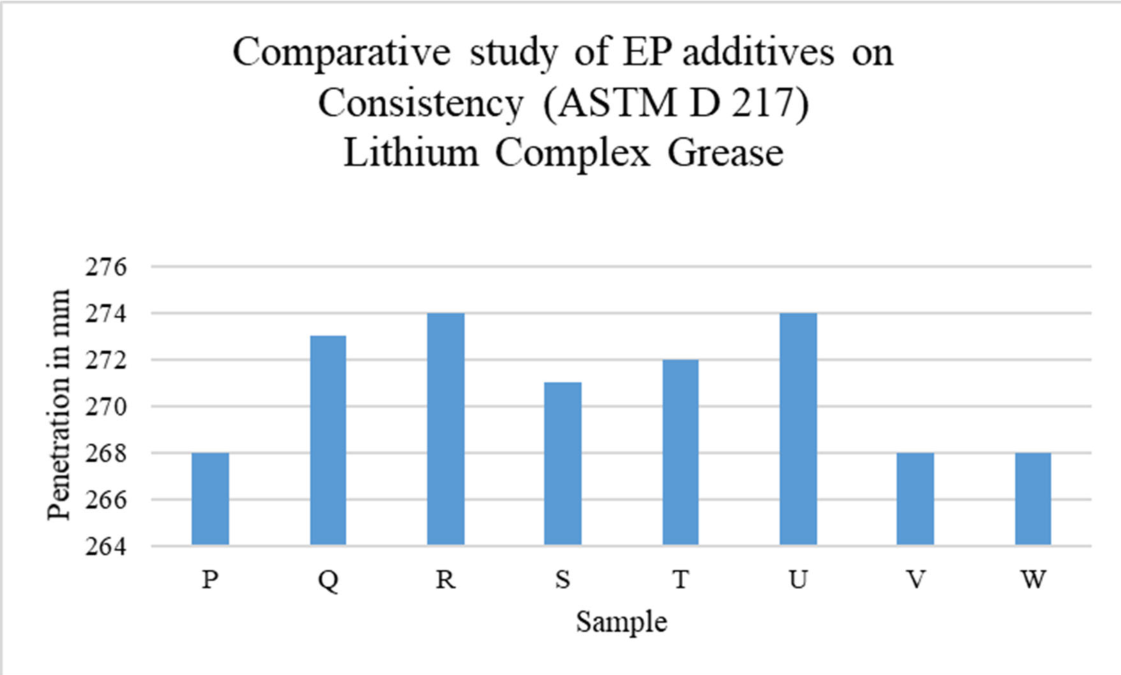
Where, A = As such, B = EP Additive component 2%, C = EP Additive component 2%, AW additive 1% (standard pack), D = MOLY 3%, E = Moly 3%, AW additive 1%, F = EP Additive package 1.5%, G = Nano dispersion 0.75% and H = Nano dispersion 0.75%, AW additive 1%.

Table – 6: Comparative study on penetration for Nano dispersion and other EP additives in lithium complex grease. Here also we can see that there is a protective effect on consistency by the Nano Dispersion in comparison to other additives.

Sample	Penetration in mm ASTM D 217
Lithium complex grease as such (P)	268
EP Additive component 2% (Q)	273
EP Additive component 2%, AW additive 1% (standard pack) (R)	274
MOLY 3% (S)	271
MOLY 3%, AW additive 1% (T)	272
EP Additive package 1.5% (U)	274
Nano dispersion 0.75% (V)	268
Nano Dispersion 0.75%, AW additive 1% (W)	268

The graphical representation may sight as:

Graph – 8



Where, P = As such, Q = EP Additive component 2%, R = EP Additive component 2%, AW additive 1% (standard pack), S = MOLY 3%, T = Moly 3%, AW additive 1%, U = EP Additive package 1.5%, V = Nano dispersion 0.75% and W = Nano dispersion 0.75%, AW additive 1%.

Conclusions:

1. A special Nano dispersion as an extreme pressure additive in formulating EP anti-wear grease in simple and complex type of Lithium greases is provided in this study.
2. The formulated greases with conventional types of other EP additives have shown acceptable characteristics, and there is no antagonistic effect on the performance of other additives like Drop point, anti-corrosion or in penetration.
3. The performance of the greases formulated with the Nano additive as well as with otherconventional EP additives are evaluated through well-known test for anti-wear and frictionreduction properties like Four ball weld load, Wear Scar Dia measurement by Four Ball Test machine.
4. The effectiveness of Nano dispersion in improving the EP and AW characteristics in Lithium and Lithium Complex greases is well established in comparison to the use of the conventional EP additives.
5. Considering the lowest nett additive treat cost, Nano dispersion qualifies as a promisingsubstitute for the currently available additive systems.

Acknowledgements:

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Comparative Study of Thermal and Oxidation behavior of Different Lubricating Greases used in Automotive Applications

S. Murali, A. K. Bhattacharya, G.S .Manna, S. Banerjee , Dr. M.L .Das & Sreejit Banerjee

Balmer Lawrie & Co.Ltd., Applications Research Laboratory,Kolkata, India.

Abstract :

In recent years, there is a ever growing demand of lubricants including lubricating greases in both Industrial and Automotive applications with variety of products available to end users. With the advent of newer technological development both in machinery as well as in end applications , many lubricants based on various combinations of Thickeners , additives & base oils are available to meet the stringent & extreme application conditions . Numerous variety of lubricating greases are available to users for major wheel bearing of all types vehicles trucks car , farm & mining equipment in automotive applications . Performance of the lubricating greases in the automotive applications requires to meet exceptional thermo-oxidative & structural stability, load bearing capacity and must provide protection against rusting & corrosion and to offer extended service life.

In the present study, comparative study on thermal and oxidative behavior of different lubricating greases available in the market used for automotive applications were attempted . Samples of different lubricating greases available from market were taken and subjected to characterization for the type of thickener, base fluid and additives for their composition .Samples were also subjected to the properties such as dropping point, penetration and thermal and oxidation characteristic behavior to study the difference in behavior pattern. Inductively Coupled Plasma Optical Emission Spectrometric (ICPOES) , Fourier Transform Infrared Spectrometric(FTIR) techniques & wet chemical methods were used for characterizing the different lubricating greases. Rotary Bomb Oxidation Stability (RBOT) Tester were used for studying the oxidative stability behavior of each of lubricating Greases . Effect of Oxidation was also observed before and after the RBOT test using FTIR spectral comparison analysis of lubricating greases . The thermal stability behavior pattern of each of the lubricating greases were studied using Thermogravimetric Analyzer (TGA) . Performance behavior of the lubricating greases were studied using standard Wheel bearing leakage tendency Test ASTM D 1263 (94).The information obtained from the above study will be useful in understanding the thermal and oxidation behavior pattern of different lubricating greases and their performance differences for suitability for use in given end automotive application .

Introduction

With advent of newer technology ,various changes in machinery & equipments were observed in both industrial and automotive applications. This has made significant requirements on various lubricants including lubricating greases. In recent years ,wide range of lubricating greases with varying performances are available to the end users on automotive applications. The thermal and oxidation stability of lubricating greases are important parameters for their performance towards end applications . Among the various lubricating greases, lithium based lubricating greases are most popular and widely used today. This is mainly attributed to better thermal & oxidation behavior with variety of type of lithium based lubricating greases from simple to mixed type and to complex type are available to users. The performance of the lubricating greases is mainly due to nature of base oil , thickener and performance additives used. Lubricating greases are designed to meet multipurpose requirements of end applications rather than specific one. The parameters such as high thermal & oxidation stability, minimum leakage tendency from wheel bearings, good water resistance properties, load bearing properties are few important parameters preferred by users for better performance for automotive applications.

Thermal degradation of lubricating greases were studied using Thermo gravimetric Analysis (TGA) and Differential Scanning (DSC) / Differential Thermal analysis (DTA). Grease oxidation resistance has always been an important aspect of its performance. However, because of its nature as a gelatinous colloidal dispersion in oil, understanding and improving the oxidation stability property of grease performance continues to be a technical challenge. Moreover, the wide range of components used to formulate the grease makes it difficult to devise bench tests that will accelerate grease response to oxidation conditions without loss of correlation with actual applications. In the present paper uses a combination of an advanced instrumental features that is precise control of test temperature and pressure with measurement of change in moderately high oxygen pressure on a test method ASTM D 942 that has been used for decades with conventional oil bath which is combined with infrared analysis of the grease before & after the test period of 100 hours run . The techniquehas expected to show significant differences among lubricating greases commonly used for lubrication.

In the present study, comparative study on thermal and oxidative behavior of different lubricating greases available in the market used for automotive applications were attempted . Samples of different lubricating greases available from market were taken for study and subjected to characterization for the type of thickener, base fluid and additives for their composition. Samples were also subjected to the properties such as dropping point, thermal and oxidation characteristic behavior to study the difference in behavior pattern. Inductively Coupled Plasma Optical Emission Spectrometric (ICPOES), Fourier Transform Infrared Spectrometric(FTIR) techniques & wet chemical methods were used for characterizing the different lubricating greases for composition . Rotary Bomb Oxidation Stability (RBOT) Tester were used for studying the oxidative stability behavior of each of the lubricating Greases . Effect of Oxidation was also observed before and after the RBOT test using FTIR spectral changes observed of lubricating greases . The thermal stability behavior pattern of each of the lubricating greases were studied using Thermogravimetric Analyzer (TGA) . Performance behavior of the lubricating greases were studied using standard Wheel bearing leakage tendency Test (ASTM D 1263 (94).The information obtained from the above study will be useful in understanding the thermal and oxidation behavior pattern of different lubricating greases and their performance differences for suitability for use in given end automotive application .

EXPERIMENTAL :

Chemicals & : All Chemical employed for the analysis are of Analytical Reagent grade and Standard glassware of Borosil make were used for analysis.

Gases : Nitrogen and Oxygen Gases Purity (99.99 %) for Instrumental Purpose

Instruments : ThermoNicolet Fourier Transform Infrared Spectrometer model iS10 (FTIR), Inductively Coupled Plasma Optical Emission Spectrometer(ICPOES) - Thermo Fisher Scientific make Model Thermal Analyser- Perkin Elmer Thermogravimetric Analyser -TGA with DTA facility model STA 6000, Semi Automatic Dropping Point Apparatus, Rotary Bomb Oxidation Stability Tester (RBOT) / Rotating Pressure Vessel Oxidation Tester (RPVOT) with fabricated stainless steel pressure chamber and a vertical rack for the five petri dishwhich can be fitted inside the pressure chamber. Tanas make model Quantum with two units were used for the test, Wheel Bearing Grease Tester/Apparatus, Stanhope Seta - Leakage Tendencies of Automotive Wheel Bearing Greases

PROCEDURE :

500 gms of ten samples of lubricating greases of consistency NLGI 2/3 collected from market for automotive application marked as '**A to J** '. Among the ten samples, Sample **D ,F ,H** ARE NLGI consistency 2 greases . The samples were subjected to above study by adopting the following procedures :

A. Fourier Transform Infrared Spectral Analysis of Lubricating Greases :
Infrared spectra of each of the market samples were recorded directly as such in Potassium Bromide cell windows in a IR Demountable cell. The instrumental conditions covering spectral range 4000cm-1 to 400 cm-1, 32 number of scans and resolution of 4 cm-1. The type of thickener , type of base fluid used , presence of additives including polymeric additives are qualitatively identified . In addition, IR spectrum of each of the samples before and after the RBOT oxidation test were also recorded to identify the IR spectral changes if any which will indicate oxidation resistivity/ stability of the lubricating greases .

B. Inductively Coupled Plasma Optical Emission Spectrometric (ICP OES) analysis of Lubricating Greases :

Each of the lubricating grease samples were subjected to ashing at 775^0C for two hours and ash obtained was dissolved in mineral acid using Concentrated hydrochloric acid and suitable dilute stock solution was made distilled water (250ml) which was subjected to elemental composition for elements (calcium , lithium ,sodium, potassium , magnesium, aluminium, iron and boron) Elemental composition (metals) will provide information of nature of thickener, filler if any present in the greases. Boron presence will indicate the type of complex thickener present and their levelindicate whether it is boric acid based or borated ester based .Presence and level ofzinc willindicate from additive or from filler like zinc oxide.

C. Separation of Thickener and Oil from Lubricating Greases using Soxhlet Extraction M Method :

Each of the lubricating grease samples were subjected to Soxhlet extraction method to extract the oil from grease. About 25 grams grease was taken in previously weighed thimble made from filter paper which is placed in Soxhlet extraction apparatus and solvent hexane was used to eluate out the oil from grease under reflux condition for 8 hours. Soap Thickener is retained in the thimble and weighed. Thickener content in the grease is determined from difference in weight of the thimble divided by weight of the sample taken into 100 . Transferred the Eluted content containing extracted oil with solvent into previously weighed 500 ml beaker and solvent hexane was removed from the extract over a hot plate and extracted oil obtained was dried in a oven set 100^0C for overnight. Oil obtained from grease was subjected to viscosity measurement at 40^0C , 100^0C and VI (Calculated) as per ASTM D 445 method.

D. Dropping Point determination of Lubricating greases : The standard procedure adopted for grease sample as per ASTM D 566 & D2265 were used using semi automatic dropping point apparatus. The dropping point of grease is a very important parameter of the grease which defines the temperature up to which grease is able to retain the semisolid structure beyond which the soap melts leading to fluid state.

E. Thermal Analysis (TGA) of Lubricating Greases :The sample preparation procedure is given below :

The instrument was calibrated with known standard before analyzing the samples. Initially, tared the weight of blank ceramic cup followed by weighing about 40-60 mg of each of grease sample in the ceramic sample cup and placing it in a sample chamber in a furnace .The sample was heated at a heating rate of 10 ^{0}C / minute from 50 ^{0}C to 900 ^{0}C and the mass loss was recorded against temperature in the form of thermogram (TGA graph) of the sample. Any variation due to type of base oil (major constituent) used in the grease as well as soap composition is reflected in the inflexions / plateau in the thermogram. All the samples were subjected to analysis by adopting above procedure. Recorded simultaneously Differential Thermal Analysis **(DTA)** study of Lubricating Greases temperature was obtained in the form of DTA graph for each sample of lubricating grease under similar conditions.

F. Rotary Bomb Oxidation Stability Test (RBOT) of Lubricating Greases :

20 grams each of the sample were taken for this study (5x 4 grams) of each grease sample were taken in previously weighed small circular standard glass dishes and each of the 4 grams were filled in the five racket inside the stainless steel rack. Placed the rack carefully with sample of grease in a petri dish inside a pressure vessel as shown in Fig 1.the pressure vessel with 20gms ofgrease was kept in a sample chamber of RBOT unit as shown in Fig .1(a & b)

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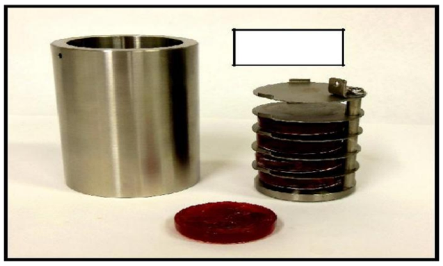


Fig.1a

Fig.1b

Fig. 1 (a &b). shows Stainless Steel cylindrical pressure vessel in which a Stainless Steel rack with provision of grease sample taken in glass petri dish

The combined stack of grease-filled dishes are then inserted into a cylindrical pressure chamber and then placed on a stainless steel rotating base and entire vessel with rotating base inserted into the unit with sealing gasket which is bolted with three nuts slowly so that no leakage is observed. The oxygen of purity 99.9% was introduced into the pressure chamber with pressure set at an initial pressure of around 95 - 100 pounds per square inch (PSI = 690 kPa) and room temperature which is then increased to 99 ±0.5°C. Under this increased temperature, the oxygen pressure is carefully released through a vent available in the unit to maintain pressure inside the chamber in running condition not more than 110 ±2 PSI). The unit was rotated at a standard rpm required for the test. The test continued for 100 hours . The pressure PSI at regular intervals of 12 hours were taken for study although the instrument has provision of continuously recording pressure change with time. After 100 hours completion of the test , the final pressure displayed was noted and pressure vessel was cooled to room temperature with rotation stopped with rotational controller in the unit and with the help of vent the oxygen was released from the pressure vessel. Nuts were opened and the pressure vessel with tray filled with grease was taken out. The grease after the test was drawn , collected and subjected to FTIR Spectral analysis. Repeated the procedure for each of the grease samples in a above similar conditions.

G. Leakage Tendencies of Automotive Wheel Bearing Greases :
The standard procedure adopted for testing the each grease sample as per ASTM D 1263 usingWheel Bearing Grease Tester/Apparatus. Brief procedure of test is the grease is distributed in a modified front-wheel hub and spindle assembly. The hub is rotated at a speed of 660 +/- 30 rpm for 6 hr +/- 5 min, at a spindle temperature which is raised to and then maintained at 105.6 +/- 1.2°C (220 +/- 2.5°F). Leakage of grease or oil, or both, is measured, and the condition of the bearing surface is noted at the end of the test Significant of the test - the test method provides a screening device that permits differentiation among products having distinctly different leakage characteristics. study is intended to distinguish between wheel bearing greases showing different leakage tendencies. Performed the test on each lubricating grease samples & report the total amount of leakage of grease or oil, or both, into the collector and into the hub cap.

Results and Discussions :

A) Fourier Transform Infrared Spectral Analysis of Lubricating Greases : Table 1 shows inferences drawn from Infrared spectrum of each of the samples recorded in Potassium Bromide cell windows regarding type of thickener , base oil & additives including polymeric additive

Table 1

S.No.	Sample Description	Type of Thickener Used	Remarks
1	A	Lithium 12-Hydroxystearte baseThickener	**Base Oil** - Mineral Oil - 3000cm-1-2700cm-1, 1602cm-1, 1463cm-1, 1376cm-1,1303cm-1,1155cm-1, 1111.9cm-1, 1032cm-1, 892cm-1, 865 cm-1, 814cm-1 , 722 cm-1) . **Thickener Peaks** :3338 cm-1, Bifurcated peaks at 1580cm-1 & 1560cm-1 , 1160cm-1 ,1032cm-1 & 722cm-1**Additive :** Absence of peak due to Polybutene (1231cm-1). Presence of ZDDP additive Besides it has also shown P-S based additive- (966cm-1) & 671cm-1.Antioxidant additive peak at 650cm-1
2	B	Lithium 12-Hydroxystearte base Thickener	**Base Oil** - Mineral Oil - 3000cm-1-2700cm-1, 1603cm-1, 1461cm-1, 1376cm-1,1305cm-1,1132cm-1, 1113cm-1, 1076cm-1, 892cm-1, 861 cm-1, 814cm-1 , 721 cm-1) . **Thickener Peaks** :3333 cm-1, ifurcated peaks at 1579cm-1 & 1559cm-1 , 1132cm-1 ,1032cm-1 & 722cm-1**Additive :** Absence of peak due to Polybutene (1231cm-1). Absence of ZDDP additive But it has also shown P-S based dditive- (968cm-1) Antioxidant additive peak at 3630cm-1
3	C	Lithium 12-Hydroxystearte base Thickener	**Base Oil** - Mineral Oil - 3000cm-1-2700cm-1, 1602cm-1, 1461cm-1, 1376cm-1,1307cm-1,1155cm-1, 1113cm-1, 1030cm-1, 890cm-1, 866 cm-1, 816cm-1 , 722 cm-1) . **Thickener Peaks** :3338 cm-1, Bifurcated peaks at 1580cm-1 & 1560cm-1 , 1160cm-1 ,1032cm-1 & 722cm-1**Additive :** Absence of peak due to Polybutene (1231cm-1). Presence of ZDDP additive Besides it has also shown P-S based additive- (1003cm-1) & 671cm-1.Antioxidant additive peak at 3632cm-1
4	D	Lithium Complex Base Thickener	**Base Oil** - Mineral Oil - 3000cm-1-2700cm-1, 1602cm-1, 1462cm-1, 1376cm-1,1305cm-1,1156cm-1, 1032cm-1, 890cm-1, 867 cm-1, 812cm-1 , 722 cm-1) . **Complex Thickener Peaks is difficult to differentiate by IR same peaks for Thickener will be indicated** :3338 cm-1, Bifurcated peaks at 1580cm-1 & 1560cm-1 , 1160cm-1 ,1032cm-1 & 722cm- 1.**Additive :**Presence of peak due to **Polybutene (1231cm-1).**Absence of ZDDP additive Besides it has also shown P-S based additive- (966cm-1) Antioxidant additive peak at 3630cm-1 .
5	E	Lithium 12-HydroxyStearate base Thickener plus Filler Silicate)	**Base Oil** - Mineral Oil - 3000cm-1-2700cm-1, 1601cm-1, 1463cm-1, 1376cm-1,1305cm-1,1156cm-1, 1112cm-1, 1030cm-1, 892cm-1, 866 cm-1, 811cm-1 , 722 cm-1) . **Thickener Peaks** :3338 cm-1, Bifurcated peaks at 1579cm-1 & 1560cm-1 , 1160cm-1 ,1032cm-1 & 722cm-1**Filler** Silicate/clays peaks at 3691cm-1 , 1070 cm-1(broad peak) & 669cm-1 **Additive :** Absence of peak due to Polybutene (1231cm-1Absence of

			ZDDP additive Besides it has also shown P-S based additive- (966cm-1) .Antioxidant additive peak at 3632cm-1
6	**F**	Lithium Complex Base Thickener	**Base Oil** - Mineral Oil - 3000cm-1-2700cm-1, 1594cm-1, 1463cm-1, 1376cm-1,1309cm-1, 1156cm-1, 1030cm-1, 887cm-1, 858 cm-1, 809cm-1 , 722 cm-1) . **Complex Thickener Peaks is difficult to differentiate by IR same peaks for Thickener will be indicated** :3338 cm-1, Bifurcated peaks at 1579cm-1 & 1558cm-1 , 1160cm-1 ,1032cm-1 & 722cm- 1.**Additive :** Absence of peak due to Polybutene (1231cm-1). Absence of ZDDP additive Besides it has also shown P-S based additive- (966cm-1) Antioxidant additive peak at 3650cm-1 .,1189cm-1,1160cm-1, 932 cm-1,(Phenolic antioxidant)
7	**G**	Lithium 12-Hydroxystearte base Thickener	**Base Oil** - Mineral Oil - 3000cm-1-2700cm-1, 1604cm-1, 1461cm-1, 1376cm-1,1309cm-1, 1156cm-1, 1030cm-1, 892cm-1, 866 cm-1, 812cm-1 , 722 cm-1) . Thickener Peaks :3330 cm-1, Bifurcated peaks at 1579cm-1 & 1560cm-1 , 1076cm-1 ,1032cm-1 & 722cm- 1.**Additive** : Absence of peak due to Polybutene (1231cm-1). Absence of ZDDP additive Besides it has also shown P-S based additive- (966cm-1) ,Antioxidant additive peak at 3617cm-1 in addition shows peak at 1260cm-1 ,1207 cm-1 ,699cm-1may be small amount chlorinated hydrocarbon.
8	**H**	Lithium 12-Hydroxystearte base Thickener	**Base Oil -** Mineral Oil - 3000cm-1-2700cm-1, 1603cm-1, 1462cm-1, 1376cm-1,1304cm-1, 1155cm-1, 1090cm-1,1030cm-1, 892cm-1, 869 cm-1, 807cm-1 , 722 cm-1) . Thickener Peaks :3338 cm-1, Bifurcated peaks at 1580cm-1 & 1560cm-1 , 1160cm-1 ,1032cm-1 & 722cm-1 in addition, additional peak 1740cm-1 was also observed (Ester functionality)) . **Additive** : Absence of peak due to Polybutene (1231cm-1). Presence of ZDDP additive Besides it has also shown P-S based additive- (965cm-1) & 660cm-1.Antioxidant additive peak at 3615cm-1 Antioxidant additive peak at 3617cm-1 in addition shows peak at 1260cm-1 ,1207 cm-1 ,669cm-1may be small amount chlorinated hydrocarbon,
9	**I**	Lithium 12-Hydroxystearte base Thickener	**Base Oil** - Mineral Oil - 3000cm-1-2700cm-1, 1606cm-1, 1461cm-1, 1376cm-1,1306cm-1, 1167cm-1, 1031cm-1, 892cm-1, 866 cm-1, 815cm-1 , 723 cm-1) .Besides it shows addition peak at 1746cm-1 & 1167cm-1 due to ester functionality. Thickener Peaks :3330 cm-1, Bifurcated peaks at 1579cm-1 & 1560cm-1 , 1160cm-1 ,1030cm-1 & 722cm-1**Additive** : Absence of peak due to Polybutene (1231cm-1). Absence of ZDDP additive Besides it has also shown P-S based additive- (966cm-1) Antioxidant additive peak at 3619cm-1
10	**J**	Lithium Complex Base Thickener	**Base Oil -** Mineral Oil - 3000cm-1-2700cm-1, 1604cm-1, 1456cm-1, 1376cm-1,1340cm-1, 1132cm-1, , 1030cm-1, 889cm-1, 866 cm-1, 814cm-1 , 722cm-1) . **Complex Thickener Peaks** is difficult to differentiate by IR same peaks for Thickener will be indicated :3328 cm-1, Bifurcated peaks at 1579cm-1 & 1560cm-1 , 1132cm-1 ,1032cm-1 & 722cm-1**Additive** : Absence of peak due to Polybutene (1231cm-1). Absence of ZDDP additive Besides it has also shown P-S based additive- (966cm-1) Antioxidant additive peak at 3652cm- 1.Inaddition,shows small amount ester (1734cm-1) & 1703 cm-1 due to unreacted fat and

B Inductively Coupled Plasma Optical Emission Spectrometric (ICPOES) analysis ofLubricating Greases :

Table 2 shows elemental composition of all samples of lubricating greases under study which gives information regarding the types of thickener used in the greases whether it is purely lithiumbased or lithium calcium based, complex type based on boron based complexing agent, mixture soap and non soap thickener clay/silicate based or purely non soap clay based.

Table 2

S.No.	Sample Description	% Boron	% Calcium	% Magnesium	% Sodium	% Zinc	% Lithium	% Aluminium	% Silicon
1.	**A**	0.011	0.027	0.003	0.030	0.039	0.263	--	--
2.	**B**	---	0.022	---	---	---	0.337	--	--
3.	**C**	----	0.025	0.0034	---	0.051	0.290	--	--
4.	**D**	0.35	0.039	0.0032	0.021	---	0.410	--	--
5.	**E**	--	0.120	0.28	---	---	0.171	0.0049	high
6.	**F**	0.14	0.039	---	---	0.063	0.445	--	--
7.	**G**	--	0.097	0.007	---	---	0.179	--	--
8.	**H**	--	0.148	0.011	---	---	0.210	--	--
9.	**I**	---	0.640	0.037	0.006	0.14	0.320	--	--
10.	**J**	0.14	0.0350	----	----	0.66	0.315	--	--

From the above table, it was observed that complex greases - Sample **D, F and J** have shown presence of boron which are in varying amount indicates boron based complexing agent is used. Higher amount of boron in sample **D** indicates boric acid is used as a complexing agent and sampleF and J may have used borated ester as a complexing agent. Sample **I** has shown high calcium besides lithium indicating mixed calcium lithium soap thickener based. Besides, Sample **E** has shown different elemental composition with mixture of lithium and clay based with aluminium magnesium, silicon as observed. From the above study, it was observed that variation in elemental composition is mainly attributes to varying amount of thickener content and types of thickener used .

C Separation of Thickener and Oil from Lubricating Greases using Soxhlet Extraction Method

Table 3 shows separated solid as thickener content along with separated oil content of each of the samples of greases under study by Soxhlet Extraction Method using Hexane as a eluant.

Table 3

S.No	Sample Description	Separated Thickener(wt %) from Grease	Separated Oil (wt%) from Grease	Kinematic Viscosity at 40^0C	Kinematic Viscosity at 100^0C	Viscosity Index VI (Calculated)	Type of Oil Used Viscosity Data & FTIR Spectral Analysis
1	**A**	13.40	86.20	116.75	12.23	+94.2	Paraffinic oil
2	**B**	15.14	84.42	108.60	10.05	+80.1	Mixture of Paraffinic& Naphthenic Oil
3	**C**	14.49	84.20	173.83	15.27	+ 86.8	Mixture of Paraffinic& Naphthenic Oil
4	**D**	11.17	88.46	182.99	16.91	+ 97.7	Paraffinic oil
5	**E**	15.95	13.85	181.94	14.22	+ 67.2	Mixture of Paraffinic& Aromatic Oil
6	**F**	11.53	88.10	234.82 .	22.08	+113.7	Group II Paraffinic Oil
7	**G**	12.38	87.21	147.05	14.193	+ 93.2	Paraffinic Oil
8	**H**	11.13	88.64	171.29	15.048	+ 85.9	Mixture of Paraffinic& Naphthenic Oil
9	**I**	14.27	85.42	144.68	13.269	+83.0	Mixture of Paraffinic & Naphthenic Oil
10	**J**	14.55	85.20	168.21	14.028	+74.8	Mixture of Paraffinic& Naphthenic Oil

From the table , it was observed that there is a distinct variation in thickener and oil content in grease samples under study. From the viscosity data and FTIR spectra of each of the separated oil from greases indicated the type of oil used . All the separated oil samples were checked for the presence of any polymeric additive such as polybutene (PIB)and olefinic copolymer (OCP)commonly used in greases. Among the samples , Samples-**A, B,C & D** have shown a very small amount of OCP type presence.

D Dropping Point determination of Lubricating greases :

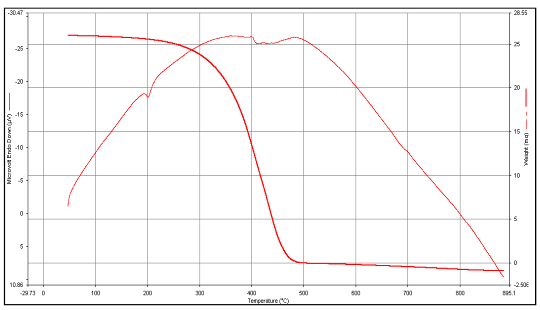
Table 4 shows the results of dropping point of the greases under study as per standard test method ASTM D 566 / ASTM D 2265 methods .

From Table 4, it was observed that different samples have different dropping points . As observed , out of ten grease samples in study , five samples**(A,B,C, G & H)** were simple lithium 12-Hydroxystearate thickener based , three (**D, F & J**)of them were lithium complex samples(no dropping point around 300 deg. C) and one sample **(E)** mixed lithium 12-Hydroxystearate thickener plus filler and one sample **(I)** mixed type lithium 12-Hydroxystearate thickener plus calcium 12-Hydroxystearate. This is important observation that lubricating greases considered for the study have different dropping point due to different thickener based used .

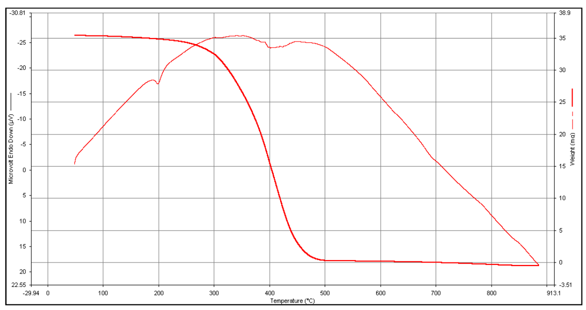
Table 4

S.No.	**Sample Descripition**	**Type of Thickener**	**Dropping Point ^{0}C as per ASTM D 566 / * ASTM D 2265 method**
1.	**A**	Lithium 12-Hydroxystearte Base	200
2.	**B**	Lithium 12-Hydroxystearte Base	195
3.	**C**	Lithium 12-Hydroxystearte Base	200
4.	**D**	Lithium Complex Base	* 300 Without Drop
5.	**E**	Lithium 12-HydroxyStearate Base plus Filler Silicate)	200
6.	**F**	Lithium Complex Base	* 298
7.	**G**	Lithium 12-Hydroxystearte Base	200
8.	**H**	Lithium 12-Hydroxystearte Base	195
9.	**I**	Lithium 12-Hydroxystearte Base	193
10	**J**	Lithium Complex Base	*262

E Thermal Gravimetric Analysis (TGA) of Lubricating Greases :
Thermogravimetric Analysis (TGA) with DTA Analysis : Thermogravimetric analysis of all the grease samples under study were carried out between 40 ^{0}C to 900 ^{0}C at a heating rate of 10 ^{0}C / minute. Thermogram (TGA) and its differential thermogram (DTA) of each of the samples under study were recorded and analyzed for their thermal behavior pattern as shown in Figure 2 .



A



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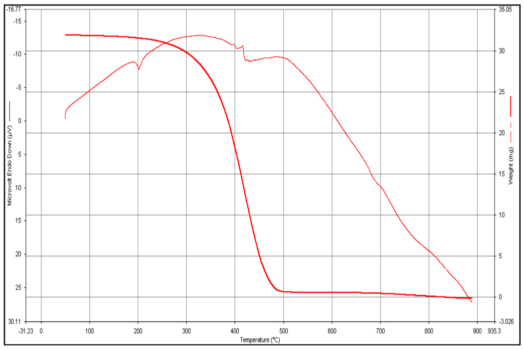

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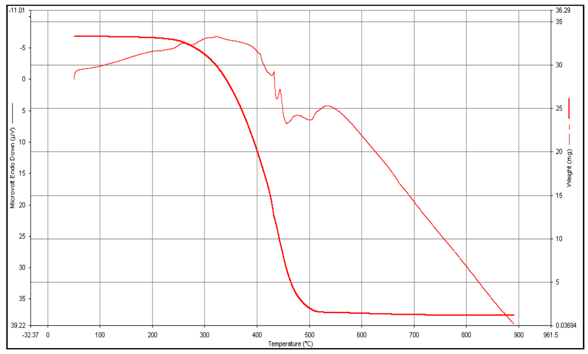

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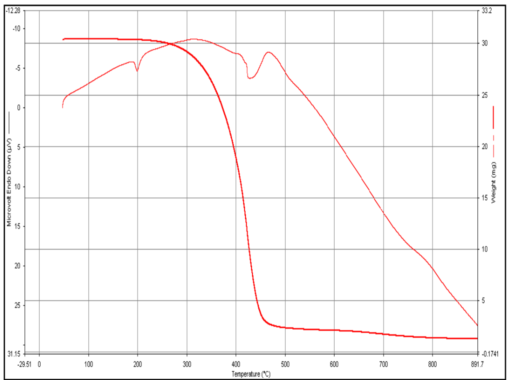

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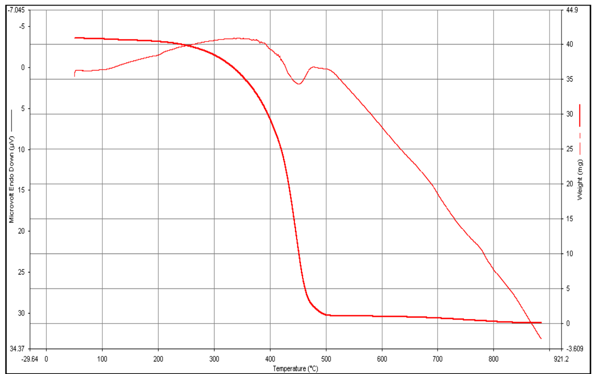

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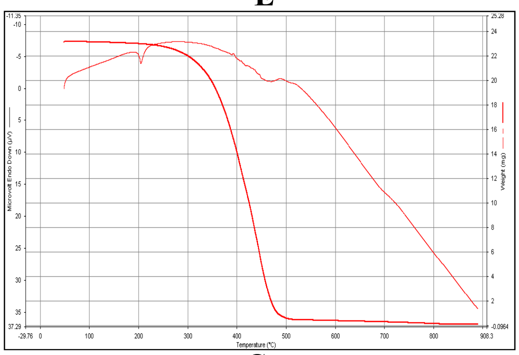

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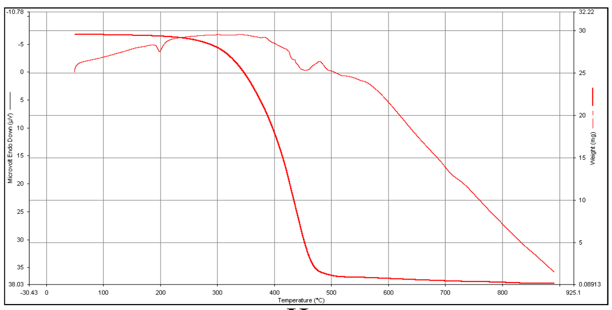

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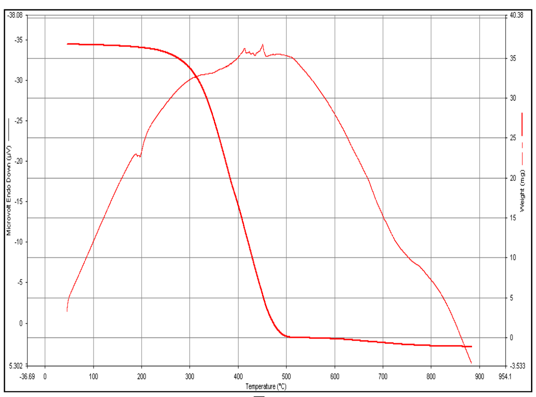
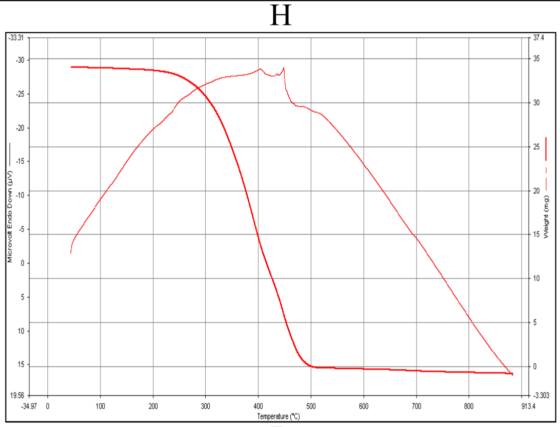


I



J

Fig. 2 typical TGA with DTA curves of samples of lubricating greases (A to J)under Study

It is also observed that the samples of complex soap thickener based lubricating greases such as **''D' , 'F'** and **'J'** have shown no distinct characteristics peaks of complex soap melting but appear as humps in spread out pattern at high temperatures beyond 260^0C onwards but also shows small peak around 200^0C. This observation is quite different from simple soap thickener based greases which indicates small sharp peak at around 195 to 205^0C (sample -**'A'**, **'B ','C', 'G','H').** Sample **'E'** and Sample **'I'** also have shown similar pattern as that of simple soap thickener based greases although they are different sample **E** with filler clay and Sample **I** mixed soap with calcium& lithium based. Type of oil portion of the grease used contributes to thermal decomposition patternat high temperatures beyond 350^0C.

F Rotary Bomb Oxidation Stability Test (RBOT) of Lubricating Greases Samples understudy :

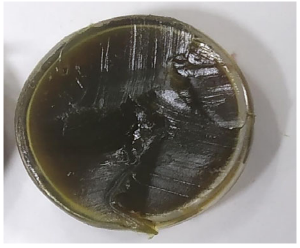
Table 5 shows the recorded pressure in PSI of oxidation chamber at mentioned regular time intervals of lubricating greases being tested by RBOT Test . Initial pressure of oxidation chamber of all the lubricating greases under study was around 96 PSI .

Table 5

S.No.	Sample Description	12 hours Pressure PSI	24 hours Pressure PSI	36 hours Pressure PSI	48 hours Pressure PSI	60 hours Pressure PSI	72 hours Pressure PSI	84 hours Pressure PSI	100 hours Pressure PSI
1	**A**	**110.1**	**112.8**	**120.2**	**120.1**	**119.9**	**119.2**	**117.3**	**115.8**
2	**B**	**109.2**	**112.6**	**121.9**	**119.7**	**118.6**	**117.1**	**115.8**	**114.9**
3	C	107.2	115.6	118.9	118.2	116.4	110.6.1	105.2	102.1
4	**D**	**110.6**	**114.2**	**121.5**	**120.4**	**119.6**	**118.1**	**117.6**	**115.2**
5	E	109.2	111.1	120.1	119.2	110.8	106.4	103.1	99.8
6	**F**	**112.6**	**119.8**	**120.9**	**120.8**	**120.3**	**119.8**	**119.4**	**116.5**
7	G	109.6	115.6	119.1	118.2	116.4	110.6	109.2	105.1
8	H	108.3	115.6	118.9	118.2	114.4	109.3	103.8	99.2
9	**I**	**108.9**	**112.6**	**119.2**	**114.1**	**109.8**	**102.1**	**98.9**	**90.9**
10	**J**	**112.6**	**118.2**	**122.5**	**120.8**	**120.6**	**119.8**	**118.6**	**117.8**

It was observed that sample **'I '** 'as shown lowest pressure PSI after 100 hours test followed by sample under study **- ' 'E'** and sample **'G' followed by 'A', 'B' 'D', 'F' &''** has shown highest pressure PSI with **less pressure drop** among the lubricating greases under study which indicates higher oxidation stability of these greases . Among the three remaining simple lithium based lubricating greases **'C', 'G'& 'H'** also shown relatively good oxidation stability among lubricating greases under study on comparison .

Infrared spectra of each of the samples before and after the oxidation test were recorded directly as such in Potassium Bromide cell windows in a IR Demountable cell and compared for any spectral changes .



Fresh Grease Sample E before RBOT Test

Grease Sample E after RBOT Test

Fresh Grease Sample I before RBOT Test　　　　Grease Sample I after RBOT Test

Fig. 3 shows visual appearance of Grease sample after the Oxidation Test carried out for 100 Hours :

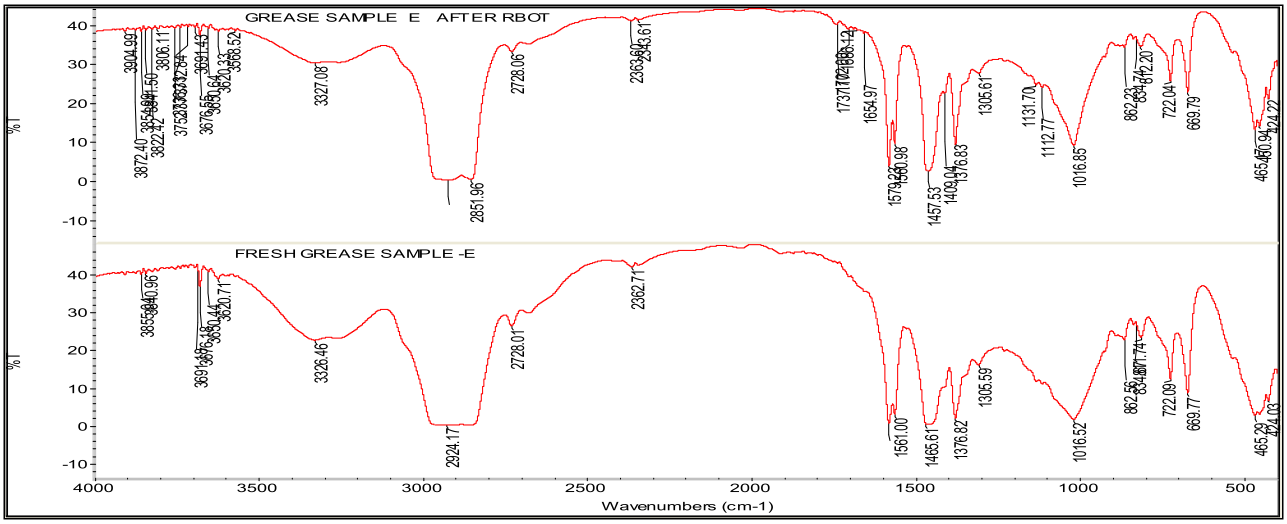


Fig.4 FTIR Spectral comparison of Grease sample E Before and After RBOT Test

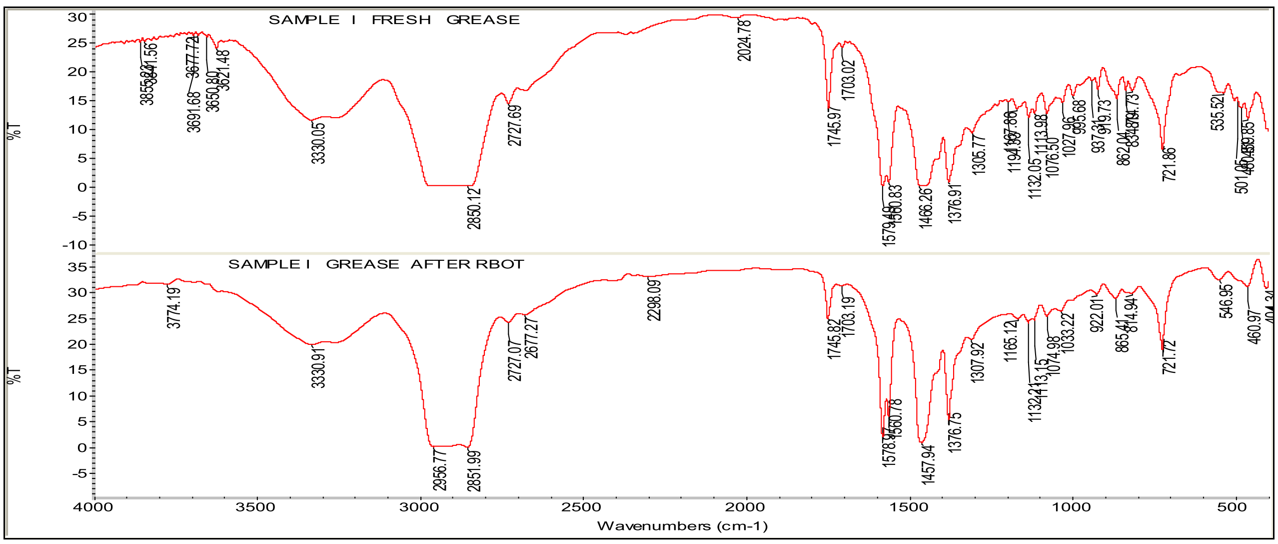


Fig.5 FTIR Spectral comparison of Grease sample I Before and After RBOT Test

The changes if any in the IR Spectra will indicate oxidation resistivity/ stability of the lubricating greases .The base oil in the lubricating greases is prone for oxidation of hydrocarbon with formation of carboxylic acid indicated by the presence peak at 1710 cm-1.The intensity of this characteristic peaks indicative of oxidation stability of the grease . Higher the intensity less the oxidation stability of lubricating grease and vice versa. Besides , depletion of peak at 3650cm-1 will also give information of depletion of antioxidant additive .

G Wheel Bearing Leakage Tendency Test of Different Lubricating Greases under Study :

The standard procedure adopted for testing the each grease sample as per ASTM D 1263 using wheel bearing grease tester/apparatus. The results of Wheel Bearing Leakage Tendencies of each of the greases are given in Table 6.

Table 6

Sl. No	Sample Description	Leakage by mass in gram (5.0 gram Max)	Deposits in Wheel Bearing races of rollers	Evidence of abnormal changes in consistency or structure
1	**A**	**1.20**	Free from deposits	No Changes
2	**B**	**1.41**	Free from deposits	No Changes
3	**C**	**1.33**	Free from deposits	No Changes
4	**D**	**0.87**	Free from deposits	No Changes
5	**E**	**2.12**	Free from deposits	No Changes
6	**F**	**5.20**	Heavy Deposits on roller	Soft thin mass is coming out from Hubs
7	**G**	**1.46**	Free from deposits	No Changes
8	**H**	**1.10**	Free from deposits	No Changes
9	**I**	**5.24**	Heavy Deposits on roller	Soft thin mass is coming out from Hubs
10	**J**	**0.20**	Free from deposits	No Changes

Among the lubricating grease samples under study , Sample **,'F'** and **,'I'** have shown higher wheel bearing leakage tendencies as compared to remaining eight lubricating greases This may be also due to their performance. Among the three lithium complex greases ,'**D'** **,'F ', and 'J** ' , sample **'J'** has shown the least leakage tendencies followed by sample **'D'** . The abnormal high leakage tendency behavior shown by sample, '**F** ' despite being complex grease its performance. It is also observed from the table that samples of lithium complex thickener grease have shown much lower leakage tendency than simple soap thickener based greases.

Conclusions :

In the present work , attempt has made to use of FTIR ,Soxhlet extraction technique for separation of solid thickener & oil from greases and dropping point apparatus for identifying the types of lubricating greases available in the market for same given end automotive wheel bearing applications. Viscosity data of extracted oil from each of the lubricating grease provides useful information about types of oil /combination of oil being used in the lubrication greases.

The information on thermal properties / stability characteristics of each of the lubricating greases were provided by use of Thermogravimetric analyzer (TGA) with DTA facility. The oxidation resistivity /stability for each of the lubricating greases were provided by use by RBOT / RPVOT tester using fabricated sampling vessel and performed ASTM D942 Method using dry heating facility instead of using oil bath. Infrared spectra of each of the samples before and after the oxidation test were recorded and compared for any IR spectral changes in terms of depletion of antioxidantadditives and appearance of oxidized peak of hydrocarbon from base oil (peak at 1710cm-1).The intensity of this characteristic peaks indicative of oxidation stability of the lubricating grease .

Leakage Tendencies Test of Automotive Wheel Bearing Greases as Performance test was adoptedfor testing the each grease sample as per ASTM D 1263 using wheel bearing grease tester/apparatus. Type of lubricating grease-simple or complex type ,consistency of grease and composition willdetermine the performance behavior of lubricating greases in this test.

Among the lubricating samples under study, samples –'**A, D, H and J '** have shown much better Thermo oxidative property with minimum wheel bearing leakage tendencies. Sample '**F'** has shown much better thermo oxidative property however wheel bearing leakage tendencies is abnormal high despite being complex thickener base grease . Sample grease **I** has shown poor oxidative property as and has shown high wheel bearing leakage tendency . Remaining grease samples **'B, C, E & G'** have good thermo oxidative property with leakage tendencies within the limits **.**

The information obtained from the performance test can differentiate different market samples of lubricating greases and best performing greases can be correlated to the respective composition of lubricating grease.

The information obtained from the above study will be useful in understanding the composition , thermal and oxidation behavior pattern of different greases, performance test for suitability for use in given end applications .Correlation of performance of the greases with composition of greases above study can provide very useful information.

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Oil Bleed Characteristics of Greases under Centrifugal Forces

Virender Kumar, Naveen K Pokhriyal, Manohar Vennampalli,
Veena R Bansal and Deepak Saxena
Indian Oil Corporation Limited, R&D

Abstract

The oil liberated from within the thickening grease matrix due to mechanical or thermal stress provides lubrication during applications. Hence, dynamic oil bleed characteristics of grease have more significance in comparison to static oil bleed especially in high speed applications. This study deals with effects of time, temperature, speed, base oil viscosity and thickeners matrix in dynamic oil separation under centrifugal forces. Results indicate that dynamic bleed can be controlled with suitable selection of grease matrix and base oils.

Key words: Greases, Dynamic oil bleed, Static oil bleed, Centrifugal forces.

1. Introduction

Greases are made by thickening lubricating oils with thickeners and their performance mainly depends upon the selection of thickeners and fluids. In soap based greases, thickeners form grid like structure of fibers in which oil is dispersed similar to oil in sponge. On the other hand, non-soap thickeners are generally smaller having colloidal, spheroidal or sheet structure in greases Thickener matrix holds the lubricating oil and gradually releases the oil during storage or operation. During operation, oil is released due to mechanical and thermal stress. Hence, controlled oil release is required depending upon the end applications.

Oil release from greases occurs in two distinct modes: 1. Static Bleed 2. Dynamic Bleed

1.1 Static Bleed

Static bleed is the release of the oil from the thickener grid in the storage container or in a non-moving system. Oil puddling can also be referred as a static bleed and it mainly depends upon grease composition and environmental conditions such as the temperature. Static bleeding is more pronounced in softer greases and/or if the grease's base oil viscosity is low. ASTM D 1742 and D 6184 are test methods used to determine static bleed.

ASTM D 1742: This static bleed test method is used to determine the tendency of lubricating greases to separate oil when stored at 25°C at an applied air pressure of 0.25 psi. It gives an indication of the oil retention characteristics of lubricating greases stored in both normally-filled and partially-filled containers stored at room temperature. This test is not suitable for use with greases softer than NLGI grade 1.

ASTM D 6184: In this static test method, a 10-g sample of grease is placed in a 60-mesh wire cone, which is then suspended in a covered beaker and placed in an oven at 100°C for 30 hours. The amount of oil that bleeds from the grease collects in the beaker and it is weighed, and the percentage of separated oil is calculated.

1.2 Dynamic bleed

Dynamic bleed is more important and actual release of oils and additives in the application during use due to temperature or mechanical stresses. Dynamic bleed conditions can also be caused or aggravated by over-greasing, misalignment, excess load and starvation, Contamination, mixing of incompatible grease, vibrations and centrifugal forces.

For high speed applications, oil bleed can be excessive due centrifugal forces. Excessive oil release can cause hardening of grease structure which eventually affects performance. On the other hand, in low speed applications oil bleed can be deficient leading to excessive wear and noise. Hence, grease composition should be designed carefully to have optimum oil bleed under both high and low centrifugal forces. ASTM D 4425 is the test method used to determine oil bleed under centrifugal forces.

ASTM D 4425: This is a dynamic bleed procedure for determining the tendency of lubricating grease to separate oil when subjected to high centrifugal forces. The grease samples are subjected to a centrifugal force equivalent to a G-value of 36000 at 50°C. The normal test duration is 24 hours, but it can be extended to 48 or 96 hours. At these specified time intervals, the centrifuge is stopped, and the amount of separated oil is measured and the volume percent calculated.

Present study attempts to assess the dynamic oil bleed behavior of lithium greases under centrifugal forces. The main focus of present study is to study effect of base oil viscosities on dynamic oil bleed time while keeping other aspects of formulation constant. Test variables like temperature, time and centrifugal forces were also varied.

2. Experimental

2.1 Manufacturing of Test Samples

A grease kettle for small batch production, consisting of a reactor connected to a heating and cooling system, was used to manufacture greases. The same general recipe, including the actual quantity of ingredients, and manufacturing protocol, were used for all the greases. Since the focus of this work is to study the influence of centrifugal forces on oil bleed, all the greases were prepared using the same amount of 9.0 w/w% thickener. Thickener was produced by saponification reaction between 12-hydroxystearic acid (12-HSA) and lithium hydroxide monohydrate in specific base oils chosen for the given grease batch. Common batch process was followed and greases were finished using colloid mill The list of custom greases and their technical data are presented in Table 1.

Table 1: List of greases tested in the present study

Greas e name	Base oil	Thickener	Oil viscosity @ 40 °C (cSt)	Additive/ Polymer	NLGI Grade
LG1	Mineral	Lithium -12 HSA	50	None	2
LG2	Mineral	Lithium -12 HSA	100	None	2
LG3	Mineral	Lithium -12 HSA	150	None	2
LG4	Mineral	Lithium -12 HSA	220	None	2
LG5	Mineral	Lithium -12 HSA	410	None	2
LG6	Mineral	Lithium -12 HSA	580	None	2.5
LG7	Mineral	Lithium -12 HSA	970	None	2.5
LG8	PAO	Lithium -12 HSA	100	None	2

2.2 Experimental Equipment and Procedure

A high speed refrigerated/heated bench top centrifuge having maximum speed upto 30,000 rpm and relative centrifugal forces (RCF) up to more than 65,000 g was used in present studies. For all studies, 15 gm grease samples were taken in polypropylene co-polymer centrifuge tubes with suitable cap/lid and placed in fixed angle rotor for fixed test durations. After end of test run, separated oil was weighed. To obtain consistent result, same acceleration/de-acceleration profile was used in all tests run.

3. Results and Discussions

3.1 Effect of oil viscosities and centrifugal forces

Test results indicate that centrifugal oil bleed mainly depends upon following parameters - base oil viscosity, temperature and centrifugal force.

In lithium greases, soap thickener has a grid like structure as confirmed by scanning electron microscopy (**Figure-1).** Thickener grid holds the dissolved oil like sponge (**Figure-2)** and releases oil due to thermal and mechanical stress.

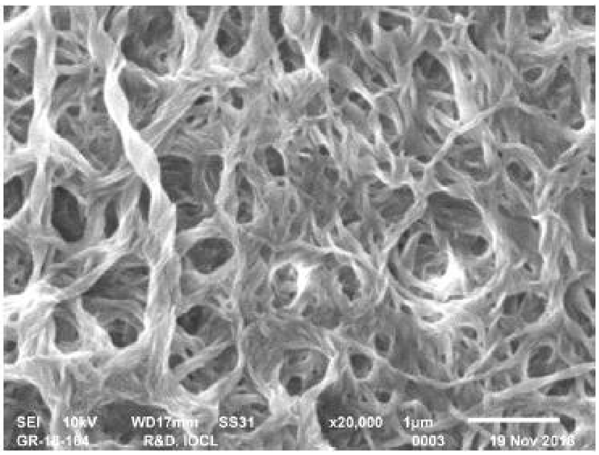

Figure-1: SEM image of Lithium Grease in Mineral Oil

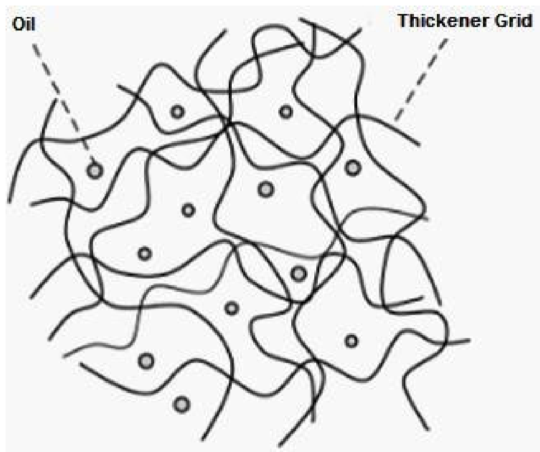

Figure-2: Thickener Grid with Dissolved Oil

For every customized lithium grease having certain thickener and base oil viscosity, there is a certain RCF at a given temperature below which there is no or minimal oil bleed. This can be called "Cut-Off RCF-value".

Mathematical equation of Darcy's law explains the dynamic oil bleed behavior of greases under centrifugal fields. This behavior is similar to groundwater flowing in aquifers. As per this equation, oil bleed velocity can be calculated where - ΔP is the pressure gradient applied at grease interface and K is the permeability tensor of the thickener matrix and η is the dynamic viscosity of oil.

$$Vb = K \, x \, \frac{\Delta P}{\eta}$$

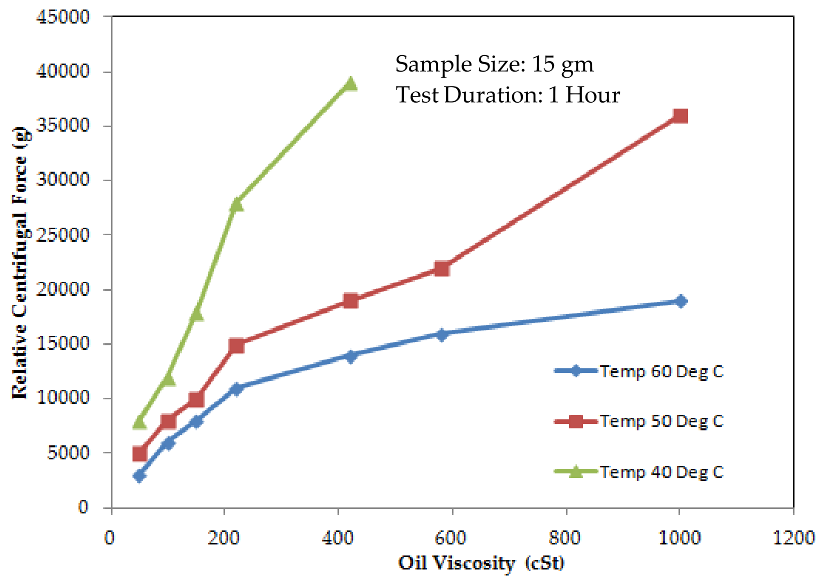

Figure-3: RCF versus Oil Viscosity at Different Temperatures

Figure-3 shows the effect of base oil viscosities on "Cut-Off g-value" at different temperatures. Results indicate that "Cut-Off g-value" increases with increasing base oil viscosities. "Cut-Off g-value" deceases with increase in temperature and this is more significant at higher temperatureas shown in **Figure-3**. During application, oil viscosity decreases due to increased temperature produced by bearing friction. In general, lower the viscosity and higher the temperature, easierthe dynamic oil bleeds from grease matrix. Experiment indicates that oil bleed can fails if base oil viscosity is very high and this will lead to starved lubrication.

3.2 Dynamic bleed behavior with time.

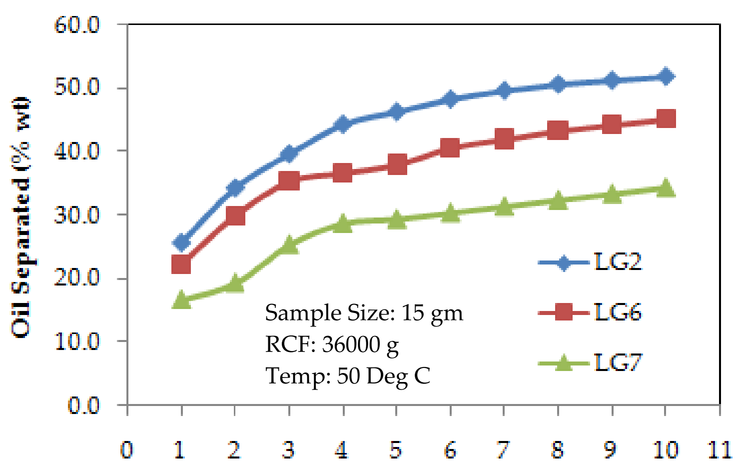

Figure-4: Oil Bleed Behavior wrt Time

Figure-4 shows oil bleed characteristics of greases with respect to time at a given centrifugal field and temperature. Results indicate that rate of oil bleed increases initially and then decease gradually. Results indicate that only 40-60% of total oil in lithium grease is available for bleed in studied temperature range. Time taken to reach this level of oil bleed depends upon the centrifugal force, temperature and oil viscosity. This study confirms that all the oil in grease matrix is not available for bleed and oil bleed rate strongly depends upon the residual oil left in grease matrix. Time taken to reach this level at a certain temperature and centrifugal forces can be correlated to actual bearing life of grease. Higher the centrifugal forces and temperatures, faster the oil bleed velocities. Slower bleed rates were observed for higher viscosity oils in comparison to lighter oils. Results also indicate the bleed oil characterizes such as viscosity, density, viscosity-gravity constant (VGC) and mean molecular mass remain consistent throughout the oil bleed time.

3.3 Effect of Base oil Composition

Molecular compositions do not have significant effect on bleed velocities of lithium greases as shown in **Figure-5.** LG7 grease shows almost similar oil bleed velocities to LG2 grease in spite of having fully paraffinic oil. Hence oil bleed velocities mostly depend upon the base oil viscosity.

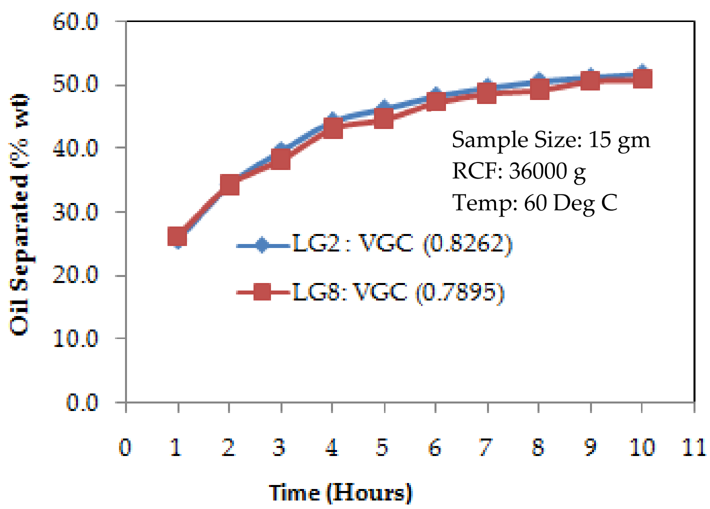

Figure-5: Effect of Oil Composition on Oil Bleed

4. Conclusions

In this article, oil bleed characteristics of lithium greases under centrifugal forces were discussed, and the following observations can be concluded:

- For every lithium grease made in certain viscosity oil, there is a minimum RCF value at a given temperature below which there will be no or minimal oil bleed. This minimum RCF increases with oil viscosity and decreases with temperature.
- Oil bleed behavior at given RCF and temperature is not linear and significantly depends upon the remaining oil in grease thickener matrix.
- All the oil in grease matrix is not available for release under centrifugal field and oil bleed can decrease significantly or even stop after certain oil bleed.
- In present study, it was found that molecular compositions of oils have minimal effects on oil bleed behavior.

5. Acknowledgement

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