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From President's Desk

This issue of GREASETECH INDIA *Vol. XIV, No.4* is a special issue. From this issue onwards GREASETECH INDIA will be available online on our website www.nlgi-india.org. It is in line with the current international trend of digital publication and need to save paper. The access to the journal on website will be password protected. It will be available free for NLGI India Chapter members and other interested readers can subscribe it online.

Research articles included in this issue of GREASETECH INDIA cover biodegradable gear oils, high performance grease and estimation of Boron from complex greases.

Any suggestion for betterment of GREASETECH INDIA technically or appearance wise is most welcomed. I earnestly request members to patronize GREASETECH INDIA and give suggestions to increase its circulation.

Dr. R. K. Malhotra
President,
NLGI-India Chapter

Biodegradable Lubricating Oils for Automotive Gears

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INTRODUCTION

In recent years pollution of environment (air, water, soil) has gained its voice. Lubricants and their decomposed products reach out to environment in greater or smaller way. Higher biodegradability and lesser aquatic toxicity of such products ensure safety of environment and can be termed as biodegradable and environmentally friendly lubricants. Vegetable oils and some synthetic oils i.e. synthetic esters have accepted biodegradability and toxicity and hence put themselves ahead as ideal base fluids for biodegradable lubricants formulations. Suitable legislation for lubricants to be more environment considerate as a social responsibility will promote biodegradable products.

In Lubricants, automotive gear oils play an important role as drive fluids for the automotive vehicles. Automotive gear oil must have anti-wear, extreme pressure, anti-oxidant, anti-foaming, low temperature properties for general working.

The main objective of this work is to evaluate and compare the various properties of two candidate synthetic ester based automotive gear oils, as biodegradable substitute, with two reference grades of 80W90 (GL 4) and 85W140 (GL 5) automotive gear oils based on mineral and synthetic PAO.

The purpose of evaluating ester based lubricants against mineral and synthetic PAO based lubricants is an attempt towards developing a biodegradable substitute that will have balance of better performance and cost as mineral oil based lubricants are cheaper whereas synthetic PAO based lubricants provide high performance though costly. The expected cost of the ester lubricants are lesser than synthetic PAO but costlier than mineral oil based lubricants.

VEGETABLE OILS AND SYNTHETIC ESTERS BASED ON VEGETABLE OILS

The first bio-based lubricants were unsaturated ester (triglycerides) oils of vegetable and animal origin. Most frequently used vegetable oils are rapeseed, soybeans and sunflower. Overall, vegetable oils have good lubricating properties, far superior to those of mineral oil. Vegetable oils also have a very high viscosity index as well as high flash/fire points.

Most important, vegetable oils have very high biodegradability around 90% - 100% and significantly lower carbon dioxide emissions. Additional environment benefits include low aquatic toxicity and low volatility.

But vegetable oils fall short on some important properties:

- Inferior oxidation and thermal stability

- Narrow viscosity range availability limits use in only some viscosity grades.

- High pour point

Vegetable oil-based formulated lubricants and greases have found their niche in many specialized markets, especially in lost-in-use applications.

With time, the concept crept in to design vegetable oil based synthetic esters as a better-performing alternative to vegetable oils and to overcome most of the shortcomings of the vegetable oils. Synthetic esters can be specifically tailored for their required application as they have many performance advantages over vegetable oils.

In simple terms, Esters are organic compounds formed from an organic acid and an alcohol. Numbers of esters are produced for various types of industrial applications. Esters are synthesized from relatively pure starting material hence avoid undesirable and unstable impurities common in conventional petroleum based oils.

The polarity in ester molecule improves volatility due to intermolecular attraction and enhances lubricity as polar molecules get attracted to charged metal surface thus facilitating better film formation. The ester linkage is also helpful to make ester biodegradable as it provides microorganism a vulnerable site.

Synthetic esters can be broadly categorized as on the basis of different types of acids and alcohols used:

- Monoesters
- Di-esters
- Complex esters
- Polyol esters
- Trimellitates

Synthetic esters exhibit certain physico-chemical advantages over vegetable oils as :

a) Higher thermal-oxidation stability

b) Lower pour point

c) Can be designed to required viscosity for application

Esters have many inherent properties useful for lubrication and provide advantage over other base fluids:

- High Viscosity index
- Relatively high lubricity
- Higher flash point
- Low volatility and lower rate of evaporation than most lubricants resulting in long service life.
- Good solvency and dispersibility that prevent deposits of varnish and sludge.

- High biodegradability
- Lower toxicity

The most common concern when formulating lubricants with ester basestocks is compatibility with elastomeric material used in the seals, as extra consideration must be taken for seal compatibility. Another disadvantage is hydrolytic stability or hydrolysis under certain conditions and also are expensive than mainstream lubricants.

BIODEGRADABILITY :

Definition:

(1) Biodegradation is defined as the chemical breakdown or transformation of a substance caused by organism or their enzymes.

(2)Primary biodegradation is defined as a modification of a substance by microorganisms that causes a change in some measurable property of the substance.

(3) Ultimate biodegradation is the degradation achieved when a substance is totally utilized by microorganism resulting in the production of carbon dioxide, methane, water, mineral salts, and new microbial cellular constituents.

Tests for Biodegradation

Following are the few established test methods for biodegradability:

- ASTM D-5864 Standard Test Method for Determining Aerobic Aquatic Biodegradation of lubricants. The method is used for testing non-volatile oils, which are not inhibitory to the inoculums micro-organisms.

- CEC-L-33-T-82 (now CEC-L-33-A-934) of the Coordinating European Council (CEC).

- OECD 301B, or Modified Strum Test of the Organization for Economic Cooperation and Development(OECD).
The method determines only ultimate biodegradability by measuring evolving carbon dioxide.

- EPA 560/6-82-003 or Shake Flask Test of the US Environmental Protection Agency (EPA).

The tests determine the rate of the biodegradation:

- Readily biodegradable - at least 60-70 % (depending on the test type) of the sample oil is degraded.
- Inherently biodegradable - 20-60 % of the sample oil is degraded.
- Persistent - less than 20% of the sample oil is degraded.

Biodegradability in general of different fluids

Sample Description	% Biodegradability 28 days OECD 301B	% Renewability content
Vegetable Oil	70 – 100	100
Mineral Oil	20 – 40	0
PAO	20 - 60	0
Alkyl Benzene	5 - 20	0
Diester	40 - 75	0 - 80
Aromatic Ester	5- 60	0
Polyol Ester	20 - 90	0 - 85
Complex Ester	20 - 90	0 - 85
Polyalkylene Glycol	10 - 70	0

EXPERIMENTAL :

Our Study has two parts. Firstly we have designed to synthesize suitable organic esters. Secondly we have carried out comparative studies of formulated biodegradable automotive lubricants using the said synthetic esters, with mineral oil and synthetic PAO based products.

Two tailor made esters, can be classified as diester and complex ester, were synthesized for automotive gear application as a biodegradable substitutes. Ester 1 has lower viscosity and Ester 2 being more viscous. The two varied viscosity synthesized esters give the option of preparing required viscosity lubricant by blending them. The ingredient for making both the esters were selected in such a way that they have maximum part of bio-based material which in turn, coupled with ester linkage, provides very good biodegradability.

Bio-based dibasic acids and alcohols / polyols were selected to make the required di-ester and complex ester in such a way that it will have good biodegradability, high VI, low pour point and excellent lubricity.

Physico-chemical properties of synthesized esters are given below :

A) Properties of Proprietary Esters :

PROPERTY	ESTER 1	ESTER 2
Viscosity @ 40 ^{0}C, CSt	103	977
Viscosity @ 100 ^{0}C, CST	14.5	83
Viscosity Index	145	166
Pour point, ^{0}C	- 42	- 6
Flash Point, ^{0}C	260	260
Acid value, mg KOH / gm,max	1.0	1.2

B) Products :

These formulated products use specially designed and synthesized suitable synthetic esters from harvestable resources. Additives play a major role in synthetic ester based lubricants. Selectively chosen additives have been used in the formulation to get balanced properties.

Combinations of various EP, Anti-wear, other additives were tried out to see the effect on extreme pressure, anti-wear and other properties as well as their solubility in esters selected and hence formulated with suitable ashless additives.

Synthetic PAO and mineral oil based lubricants are commercialized products and taken as reference for this study purpose.

C) Laboratory Evaluation Methodologies :

Kinematic Viscosity:

This tests were performed as per ASTM D 445.This test method specifies a procedure for determination of kinematic viscosity of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer.

Viscosity Index:

Standard practice for calculating viscosity index from kinematic viscosity at 40 and 100 ^{0}C was adopted as per ASTM D 2270. This practice covers the procedures for calculating the viscosity index of petroleum products, such as lubricating oils, and related materials.

Pour Point:

ASTM D 97 is standard test method for pour point of petroleum products : This test method is intended for use on any petroleum product.

Flash Point :

Flash point by Cleveland open cup tester was done as per ASTM D 92. This test method describes the determination of the flash point of petroleum products by a manual Cleveland open cup apparatus.

Copper Corrosion :

ASTM D 130 describes the standard test method for corrosiveness to copper from petroleum products by copper strip test.

Brookfield Viscosity :

ASTM D 2983 covers the standard test method for low-temperature viscosity of lubricants measured by Brookfield Viscometer.Brookfield viscometer and a low-temperature bath are used for the determination of the low-shear-rate viscosity of lubricants. The test may operate in the viscosity range of 500 to 1000 000 mPa.s (cP). The bath-controlled temperature is selected within the range of +5^0 to -54^{0}C.

Foam Stability :

Standard test method for foaming characteristics of lubricating oil is done as per ASTM D 892.This test method covers the determination of the foaming characteristics of lubricating oils at 24^{0}C and to 93.5^{0}C and then again at 24^{0}C .

Extreme Pressure Property :

ASTM 2783 covers the standard test method for measurement of extreme-pressure properties of lubricating fluids (Four-ball method). It is used to measure the load – carrying properties of lubricating fluids.

Wear Preventive Charateristic :

Standard test method for wear preventive characteristics of lubricating fluid (Four-ball method) comes under ASTM D 4172.

Biodegradability Test :

OECD 301B Modified Sturm was adopted to carry out the biodegradability. The modified Sturm test is adequate for soluble and insoluble organic, non-volatile materials. This test measures carbon dioxide evolved and therefore measures only “complete” oxidation; organic impurities will complicate the interpretation of carbon dioxide production data. Test material is introduced into a flask containing mineral substrate and a bacterial inoculum. After ultrasonic vibration, the flask contents are aerated with carbon dioxide-free air. A control without the test material is run in parallel. Any carbon dioxide released is absorbed in flasks containing barium hydroxide solution. Periodically, the amount of barium hydroxide solution used is determined by titration with hydrochloricacid. Biodegradation is expressed as a percentage of the total amount of carbon dioxide evolved during the test, (corrected for the control), against the theoretical carbon dioxide that the test material could have produced.

Normally, the test lasts for 28 days. Tests however may be ended before 28 days, i.e. as soon as the biodegradation curve has reached a plateau for at least three determinations. Tests may also be prolonged beyond 28 days when the curve shows that biodegradation has started but that the plateau has not been reached by day 28, but in such cases the chemical would not be classed as readily biodegradable.

FTIR Spectral Analysis :

All the samples were subjected to FTIR spectral analysis .

D) Results and Discussions :

The developed products were subjected to various testing related to automotive gear oil against mineral oil and synthetic PAO based products. Results of the study undertaken are given below in **Table 1** and **Table 2**

Table 1

TEST / PARAMETER	UNIT	TYPICAL RESULT 80 W 90 (API GL 4)			LIMIT
		Mineral	Synthetic	Ester	
Kinematic Viscosity @ 40 ^{0}C	cSt	145.10	113.2	120	
Kinematic Viscosity @ 100 ^{0}C	cSt	15.18	14.6	15.1	13.5– 18.5
Viscosity Index	-	106	132	130	-
Pour point	^{0}C	-30	-36	-39	-
Flash point (COC)	^{0}C	228	222	220	-
Copper Strip Corrosion at 120^{0}C,3 hrs.	-	2b	2b	1b	-
Acid number	mgKOH/gm	0.50	0.40	2.0	-
Brookfield Viscosity at -26 ^{0}C	cP	66,800	34500	20921	1,50,000 max.
Foam stability, Volume of foam after 10 mins. Test					
a) Seq. - I at 24 ^{0}C	ml	0/0	0/0	0/0	20/0
b) Seq. - ii at 93.5 ^{0}C	ml	0/0	25/0	35/0	50/0
c) Seq. - iii at 24 ^{0}C	ml	0/0	0/0	0/0	20/0
Four ball EP test Weld load	Kg	250	315	315	250
Four ball wear test, 75 ^{0}C, 1200 rpm, 20 Kg, 1 hr.	mm	0.361	0.326	0.335	-
Biodegradability	%	< 40	< 40	67	-

Table 2

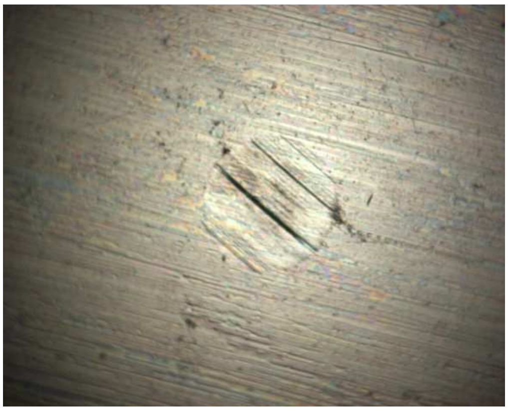
TEST / PARAMETER	UNIT	TYPICAL RESULT 85 W 140 (API GL 5)			LIMIT
		Mineral	Synthetic	Ester	
Kinematic Viscosity @ 40 ^{0}C	cSt	371.7	231.5	238.2	-
Kinematic Viscosity @ 100 ^{0}C	cSt	26.6	27.4	26.1	24.0 –32.5
Viscosity Index	-	96	153	141	-
Pour point	^{0}C	-12	-33	-24	-
Flash point (COC)	^{0}C	200	205	202	-
Copper Strip Corrosion at 120^{0}C,3 hrs.	-	2c	2c	1b	-
Acid number	mgKOH/gm	0.80	0.80	2.5	-
Brookfield Viscosity at -12 ^{0}C	cP	54888	7838	11800	1,50,000 max.
Foam stability, Volume of foam after 10 mins. Test					
a) Seq. - I at 24 ^{0}C	ml	0/0	0/0	0/0	20/0
b) Seq. - ii at 93.5 ^{0}C	ml	0/0	20/0	30/0	50/0
c) Seq. - iii at 24 ^{0}C	ml	0/0	0/0	0/0	20/0
Four ball EP test a) Weld load	Kgs	450	400	500	-
Four ball wear test, 75 ^{0}C, 1200 rpm, 20 Kg, 1 hr.	mm	0.369	0.333	0.346	-
Biodegradability	%	< 40	< 40	61	-

Higher viscosity index of synthetic esters provides more consistent lubricating film and lower pour point is also an added advantage over mineral based and similar to costlier synthetic based lubricant. Synthetic esters show clear edge over biodegradability as they are readily biodegradable while synthetic PAO and mineral based are inherent biodegradable.

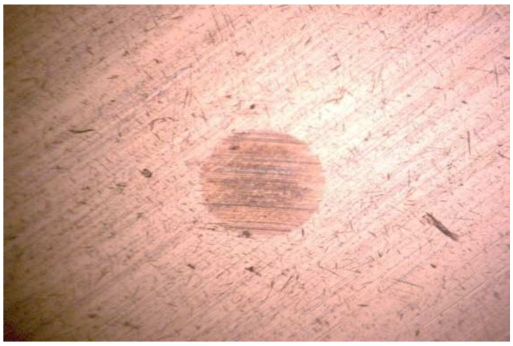
Synthetic Esters based lubricants show better anti-wear properties compare to mineral oil and comparable to synthetic PAO based lubricants. They have excellent 4-ball weld load, lesser wear scar diameter than mineral oil based lubricants on anti-wear test. Wear scar diameters are shown in **Figure. 1** and **Figure . 2** carried out as per ASTM D 4172.

ANTI-WEAR TEST : 80W90

Figure. 1



Synthetic ester based lubricant (0.335 mm)



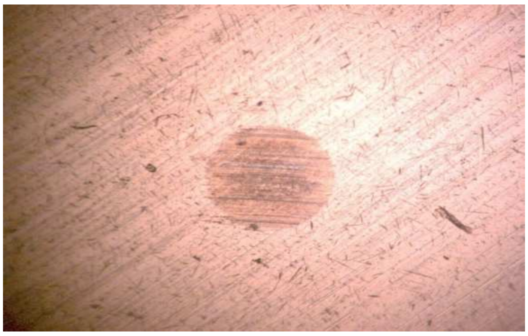
Synthetic PAO based lubricant (0.326 mm)

Mineral oil based lubricant (0.361 mm)

ANTI-WEAR TEST _: 85 W140

Figure . 2

Synthetic ester based lubricant (0.346 mm)



Synthetic PAO based lubricants (0.333 mm)

Mineral oil based lubricants (0.369 mm)

Thermo Gravimetric Analysis (TGA) :

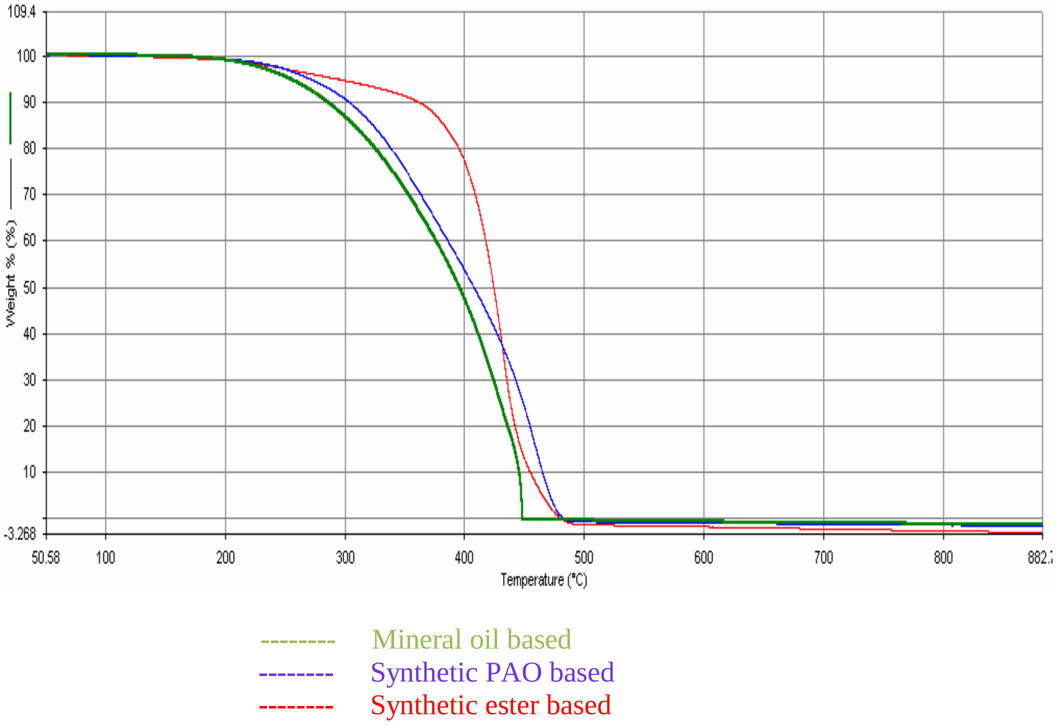
Thermo gravimetric Analyzer

TGA measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine their thermal stability at temperatures up to 1000°C and also to characterize materials behavior against temperature through weight loss or gain due to decomposition, oxidation, or dehydration.
This instrument was used to study the loss of mass with temperature of all the lubricants in order to determine the evaporation loss during operation.
Instrument used : PerkinElmer STA 6000 Thermo-gravimetric analyzer with DTA facility

TGA graphs have been shown in **Figure. 3** and **Figure . 4**.

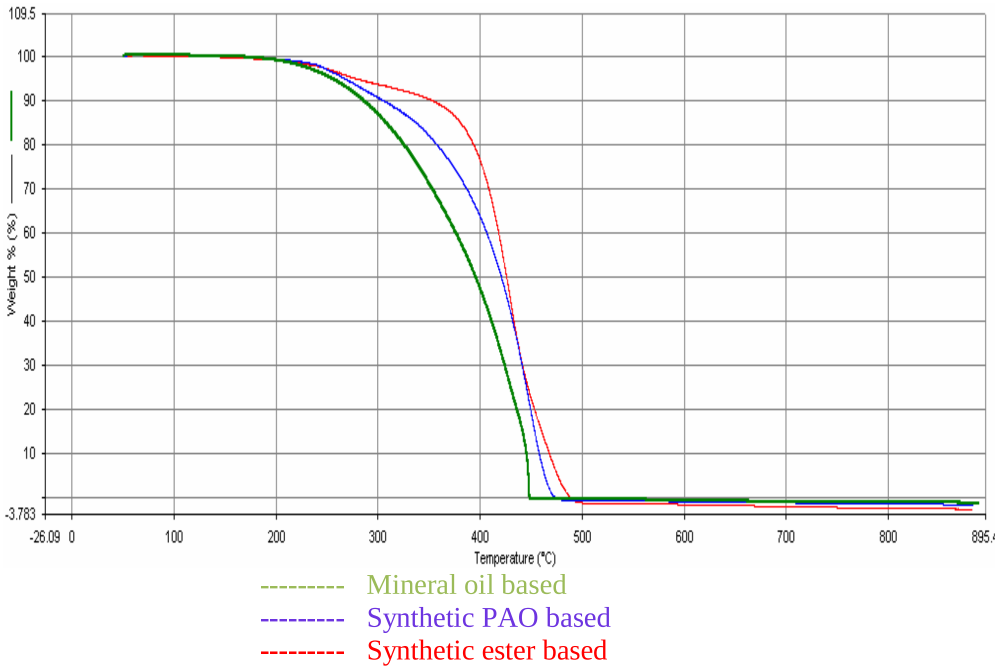
80 W 90

Figure. 3



85 W 140

Figure. 4



On the basis of TGA graphs Table 3 shows loss of mass in % of lubricants against temperature.

Table 3

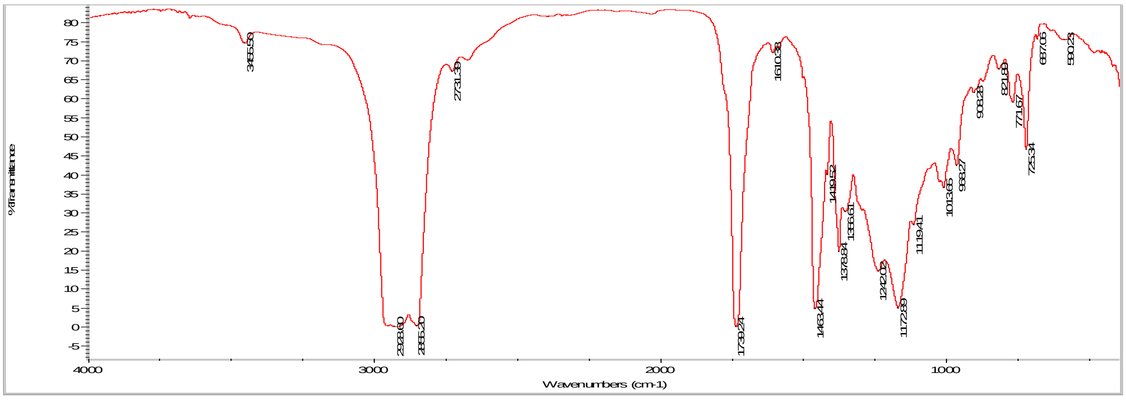
Loss in weight, %	80W90 (^{0}C)			85W140 (^{0}C)		
	Mineral	Synthetic PAO	Synthetic Ester	Mineral	Synthetic PAO	Synthetic Ester
Initiation	200	200	200	200	200	200
10%	285	300	360	290	302	352
20%	320	335	395	325	360	395
30%	345	355	410	350	385	410
50%	395	410	425	397	420	425
100%	450	475	480	450	475	490

Table 3 shows that synthetic esters based lubricants have lesser evaporation with temperature that results in lesser consumption of synthetic ester lubricants.

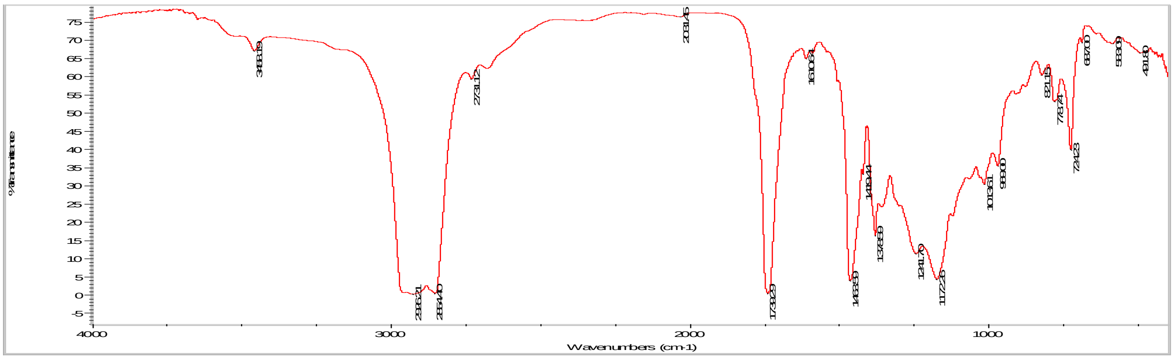
FTIR Spectral Analysis :

Fourier Transform Infrared Spectrum of each sample under study was recorded in Potassium Bromide cell windows in a demountable cell . The instrumental condition used were : Number of Scans – 32 , Resolution – 4 cm^{-1} and Scan Range - 4000 cm^{-1}- 400 cm^{-} The spectra are given in Figure.5, Figure. 6 and Figure. 7.

Figure . 5

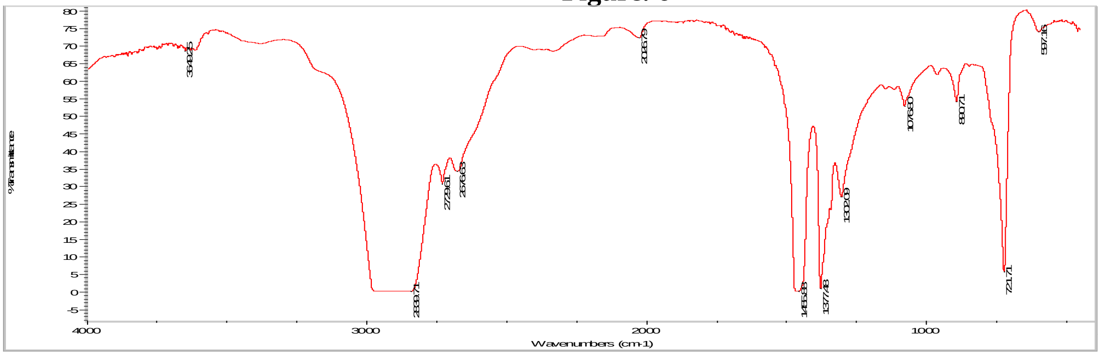


FTIR Spectrum of Sample Synthetic Ester based Gear Oil 80 W90



FTIR Spectrum of Sample Synthetic Ester based Gear Oil 85 W140

Figure. 6



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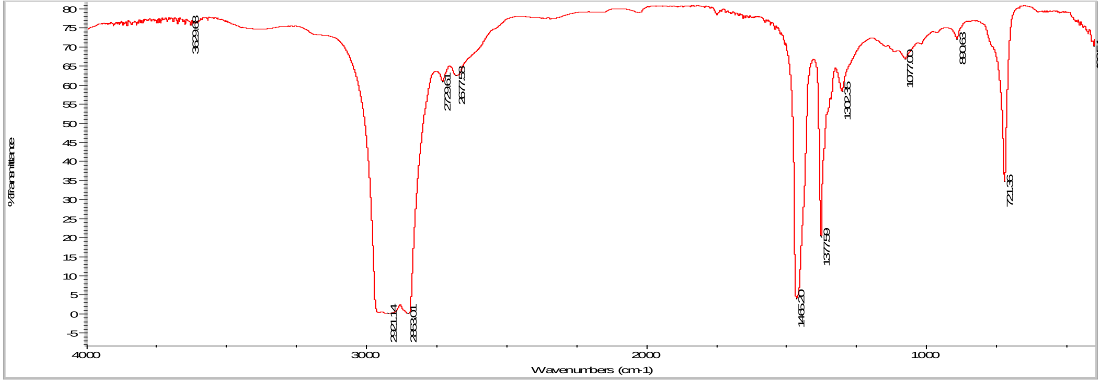
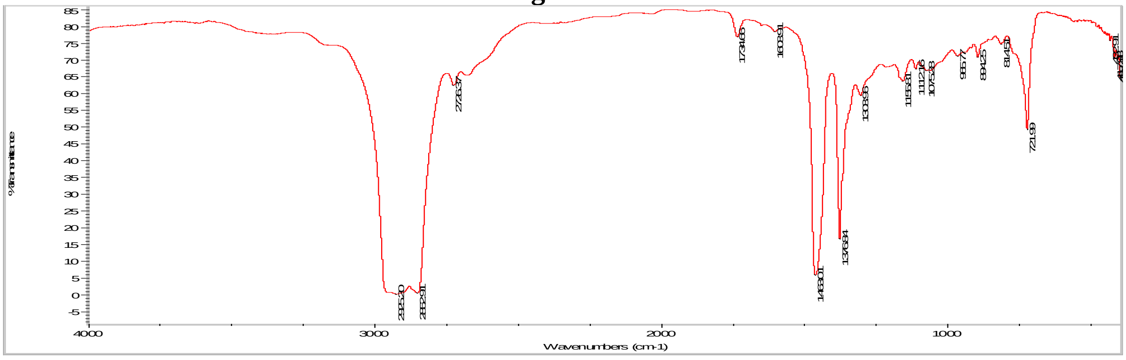
TIR Spectrum of Sample Synthetic PAO 85 W140

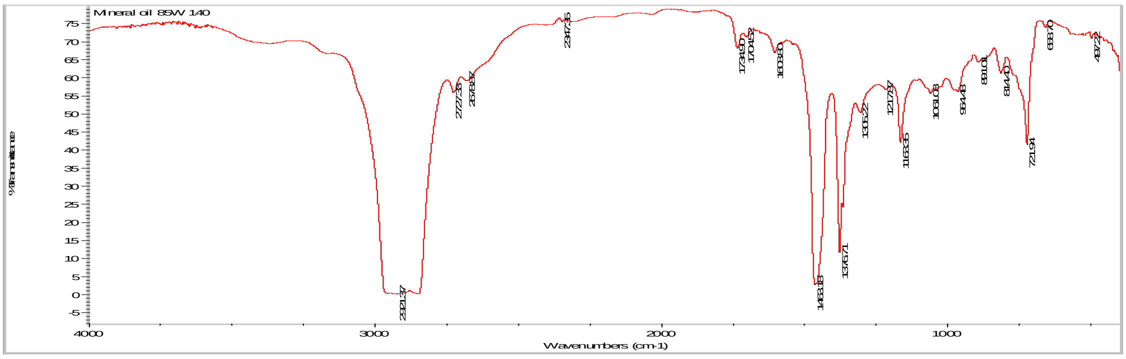


FTIR Spectrum of Sample Synthetic PAO 80 W 90

Figure . 7



FTIR Spectrum of Sample Mineral Oil 80 W 90



FTIR Spectrum of Sample Mineral Oil 85 W 140

It was observed from the infrared spectra of six samples, that there is a distinct difference in spectral patterns. Synthetic ester based Gear oils show characteristics peaks of ester functionality (1739 cm^{-1} & 1172 cm^{-1}) where as synthetic PAO based Gear oils show characteristics peaks of hydrocarbons (3000-2700 cm^{-1} , bifurcated peaks 1463 cm^{-1} & 1376 cm^{-1}, & 721.9 cm^{-1}) without peaks of aromatics -1603 cm^{-1}, 815 cm^{-1} in addition the peak at 890 cm^{-1}. Samples of mineral oil based lubricants do not show the characteristics peaks of ester (1740cm $^{-1}$ &1170 cm^{-1}) as observed in A & B and as well as PAO peak at 890 cm^{-1} as observed C & D but show only hydrocarbon based peaks 3000-2700 cm^{-1}, bifurcated peaks 1463 cm^{-1} & 1376 cm^{-1}, & 721.9 cm^{-1} including peaks of aromatics- 1603 cm^{-1}& 815 cm^{-1}.

CONCLUSION:

The study gives following conclusions:

a) The base fluids of the formulated products have biodegradability as well as renewability content of > 60 % and though not tested for the toxicity but expected to be very good as used esters are bio-based and biodegradable.

b) Low pour point and Brookfield viscosities at lower temperature suggest synthetic ester based products are excellent at lower temperature along with synthetic products.

c) The anti-wear and extreme pressure properties are very good in synthetic esters based lubricants.

d) Higher viscosity index in biodegradable products comparable with synthetic product results in lesser film variation with temperature.

e) From the results of lubrication properties, viscosity index, thermal gravimetric analysis, products would perform better than conventional mineral oil based lubricants and would be energy efficient with long drain interval in addition to environmental acceptance.

f) Synthetic PAO based lubricants also excel most of the properties but it would be costlier and lesser biodegradable and are derived from non-renewable sources.

g) Synthesis of proper esters and selection of additives give products that can match and excel most properties of automotive gear oils hence can be biodegradable and lesser toxic alternative of the conventional lubricants and high performance synthetic PAO based lubricants.

h) The candidate synthetic esters based automotive gear oils thus show a promising potential as an environmentally acceptable lubricants as it fulfills the performance, biodegradability and renewability criteria required for an environmentally acceptable lubricants and expected to meet eco-toxicity requirements also.

The revelation of drawbacks after longer field trials will open the scope of further work on these products.

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Acknowledgement

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DEVELOPMENT OF HIGH PERFORMANCE GREASE

Siddharth Perto Products

Nahid Parveen, Vijay Deshmukh and Sudhir Sachdeva

Conventionally, normal Calcium, Sodium & Lithium base greases are used for general lubrication in automotive & industrial applications. In certain applications, where high loads/shock loads are encountered EP greases are popular. With the advances in technology in process & engineering industries, the machines have to operate under higher loads, higher speeds & wider range of temperatures than previously prevailing. In some industries where operating conditions are severe, normal base greases do not function well and hence high performance complex greases like lithium complex, aluminum complex, calcium complex, or poly urea greases are preferred. These greases have better high temperature properties, high load carrying ability, good mechanical stability & water resistance.

However, with advances in lubricant technology and additive technology, it is now possible to further improve these greases which will enable them to withstand extreme operating conditions [1,2,3]. We have developed a high performance grease based on the latest additive technology, which has given better properties than conventional higher performance greases when tested in the laboratory. This paper compares the properties of this unique high performance grease with conventional high performance greases such as lithium complex, aluminum complex and poly urea greases.

Lithium Complex Grease (LCG)

These are the most popular greases because of their versatility. These are made with lithium hydroxide & fat such as hydrogenated castor oil or 12 hydroxy steric acid and complexing agents such as dibasic acids or boric acid [4,5]. Lithium Complex Greases are suitable for high temperature & high speed bearings and with appropriate EP additives can be used in high load applications.

Aluminum Complex Grease (ACG)

These are typically prepared using aluminum isopropoxide or its trimer by reacting with benzoic acid & stearic acid. The resultant greases have high drop point & good water resistance [6]. These greases also have very good flow properties which make them ideal greases in steel plant applications where centralized lubrication prevails.

Poly Urea Grease (PUG)

Poly urea greases are among the latest high performance greases to be developed. Polyurea grease thickeners are produced from the reaction of isocyanate and diamines to form polyureas. This class of greases were claimed to possess good high temperature capabilities. The longer life of poly urea greases may also be due to the fact that they contain no metal, retarding their oxidation at elevated temperatures [7,8].

Developed Grease (DG)

The Developed Grease has a very high drop point and can be used for high temperature applications with suitable base oils. It has excellent load carrying ability, excellent antiwear properties, good mechanical stability and water resistance. The other properties like oxidation stability, corrosion resistance are also comparable with other high performance greases.

Laboratory Evaluation and Comparison of Test data

We have selected three conventional high performance greases from the market for evaluation and comparison with our developed grease (DG). The three high performance greases selected for evaluation and comparison are Lithium Complex (LCG), Aluminum complex (ACG) and Poly urea greases (PUG). Table 1 summarises their basic characteristics.

.

TABLE 1

S. No.	Characteristics	DG	LCG	ACG	PUG
1.	Thickener Type	-	Lithium Complex	Aluminium Complex	Polyurea
2.	NLGI Grade	3	3	2	2
3.	Base Oil Type	Mineral Oil	Mineral Oil	Mineral oil	Mineral Oil
4.	Base Oil Viscosity, cSt @ 40 cSt	145	142	148	146

Test Results and Discussion

The main properties of a grease to perform satisfactory under severe operating conditions of loads, speeds and temperatures are their load carrying ability, mechanical stability and high temperature property. Other properties like rust and corrosion inhibition, water resistance, heat stability, etc. also play an important role in their satisfactory performance. So we have evaluated these four greases (DG, LCG, ACG and PUG) in the laboratory for some of these important tests. The tests and results are discussed below.

Load Carrying Ability

Four ball weld load test - ASTM D-2596.

Load carrying ability or extreme pressure property of grease is measured in terms of four ball weld load. In this test, the three steel balls are taken in a pot containing grease. The fourth ball is locked in a chuck and rotated around a vertical axis under load against three stationary balls. The rotating speed is 1770±60 rpm. A series of tests of 10 sec each runs are made at successively higher loads until welding of the balls occurs. The load at which the welding occurs is reported as weld load in Kg.

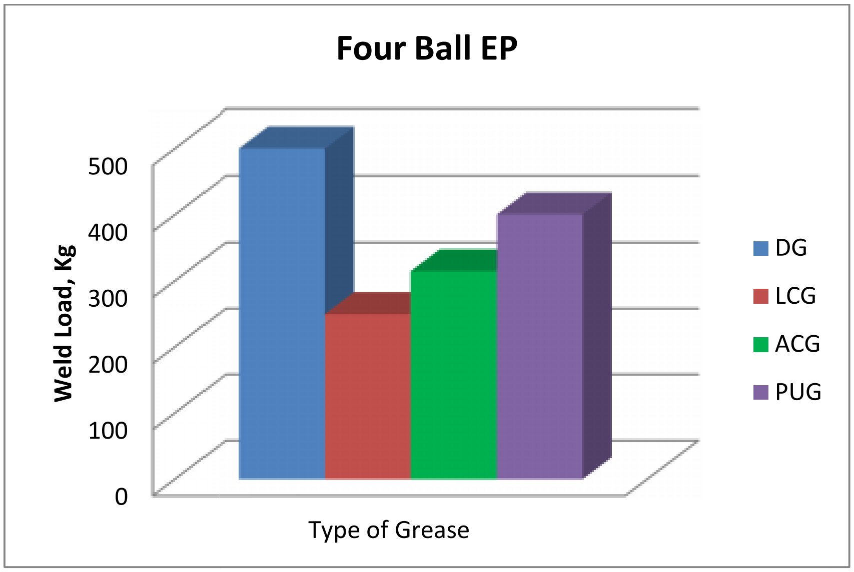

FIGURE 1

Figure 1 shows the comparison of weld load of developed grease and other high performance greases. From the chart it will be observed that developed grease gives higher weld load compared to the three high performance greases. Higher weld load of developed grease indicates that it has better load carrying ability than the other greases.

Antiwear Property

Four Ball Wear Test – ASTM D-2266

The antiwear property of greases is determined by Four Ball Wear Test. The apparatus is same as for four ball EP test. Here the test is run at constant load of 40 Kg, 75 ˚C, 1200 rpm for 60 minutes. After the test, the scar on the stationary balls is measured through a microscaope and average scar is reported as wear scar diameter in mm.

Figure 2 plots WSD values of greases as a function of antiwear properties. Under the identical test conditions, DG shows lowest wear scar diameter, indicating lowest wear. In the actual applications under severe operating conditions DG is expected to give low wear which will lead to enhance life of the machine components.

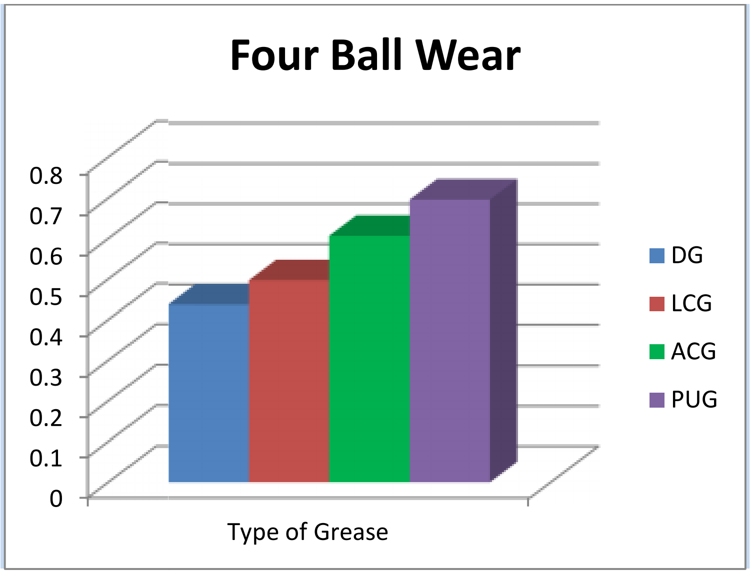

FIGURE 2

High Temperature Property

There are several rig tests that may predict with sufficient precision the suitability of a grease at elevated operating temperatures. The high Temperature rig test ASTM D-3336 or ASTM D-3527 for automotive applications are the most popular tests. However,in the laboratory, we have carried out the dropping point tests for all four greases.

Dropping Point

Dropping point Test-ASTM D-2265

It consists of preheating the aluminum block to a temperature which depends upon the expected dropping point of the grease sample. The test tube assembly is dropped into the hole in the block, and the cup is watched. At some temperature, a drop comes out of the cup and falls to the bottom of the tube. The sample temperature is read immediately. The dropping point is the sum of sample temperature and one third of difference between that and block temperature. The dropping point is far above the highest temperature at which we may use the given grease [9].

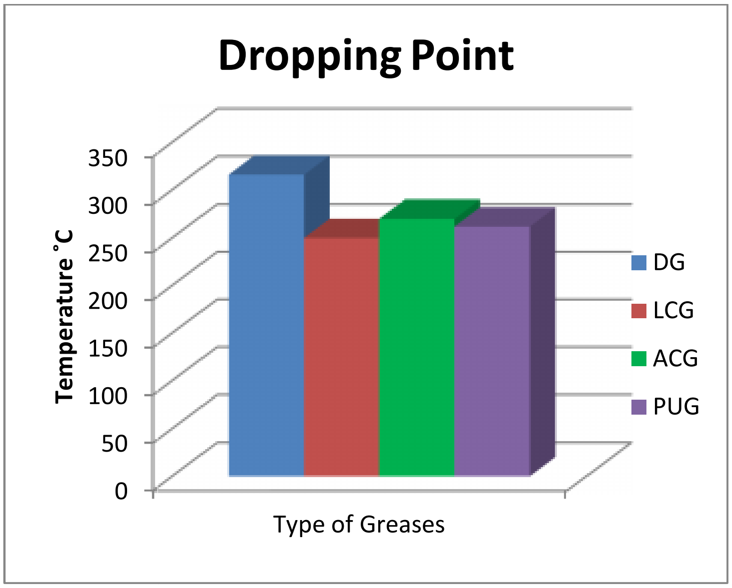

FIGURE 3

Figure 3 summarizes dropping point data of developed grease and other three high performance greases. The developed grease shows much higher dropping point than other greases. So it may work better at high temperatures compared to the other greases.

Oxidation Stability

Oxidation Stability Test-ASTM D-942

Besides heat degradation, the grease may be subjected to deterioration when it comes in contact with oxygen. The rate of oxidation enhances tremendously at high temperatures. The grease for high temperature applications should have good oxidation stability which can be improved by addition of suitable antioxidants.

The most common test used to determine the oxidation stability of greases is ASTM D-942 which is a static test. In this test, five glass dishes each one filled with 4 gm of grease and placed in small pressure bomb. The bomb is sealed and pressurized with oxygen. It is then placed in a bath at 99 ˚C. The initial pressure developed is noted. At the end of the test, after 100 hrs the pressure is noted and the drop in pressure is determined and reported.

In figure 5, comparative results of pressure drop of oxygen shows that the developed grease has lowest pressure drop. So results indicates the better ability of the developed grease to resist oxidation under test condition

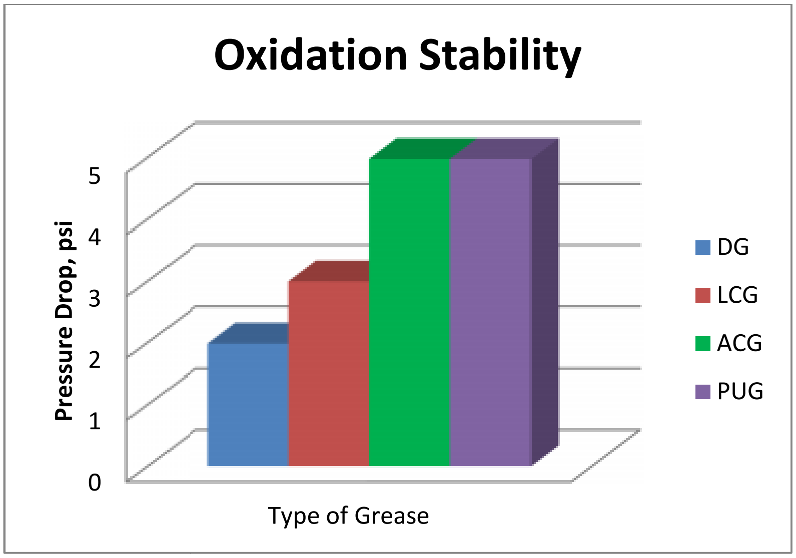

FIGURE 4

Mechanical Stability

Prolonged Worked Penetration Test- ASTM D-217

Mechanical stability is the ability of grease to resist changes in consistency when subjected to mechanical shearing. The most common laboratory tests used to evaluate mechanical stability are the prolonged worked penetration and roll stabilty.

The test consists of working the grease for 100,000 double strokes in a grease worker. Then the difference between the 60 strokes and 100,000 is noted which indicates the mechanical stability of the grease. Higher difference suggest poor mechanical stability.

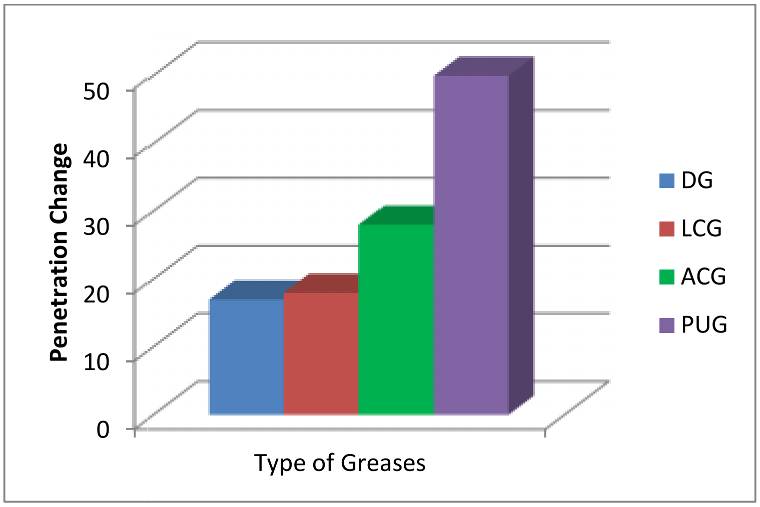

Figure 5

In figure 5 developed grease shows excellent mechanical stability. Mechanical stability of developed grease is comparable to lithium complex grease and much better than Al complex grease and poly urea grease. Thus it can give longer life than other greases.

Water Resistance

Ware Washout Test-ASTM D-1264

When grease comes in contact with water,the grease may undergo changes in its structure. It may become softer by water absorption and lose its structure. This will affect its ability to lubricate. There are many tests to determine the effect of water in grease. The most common being the water washout test as per ASTM D-1264.

Water Washout Test

In water washout test, we measure the amount of grease washed out of bearing under the conditions of test. A bearing is packed and mounted in a shielded housing. The bearing is rotated at 600 rpm under a jet of water at a given temperature for one hour. At the end of hour, the bearing is removed, dried and weighed. The amount of grease washed out is calculated by the weight loss which is reported.

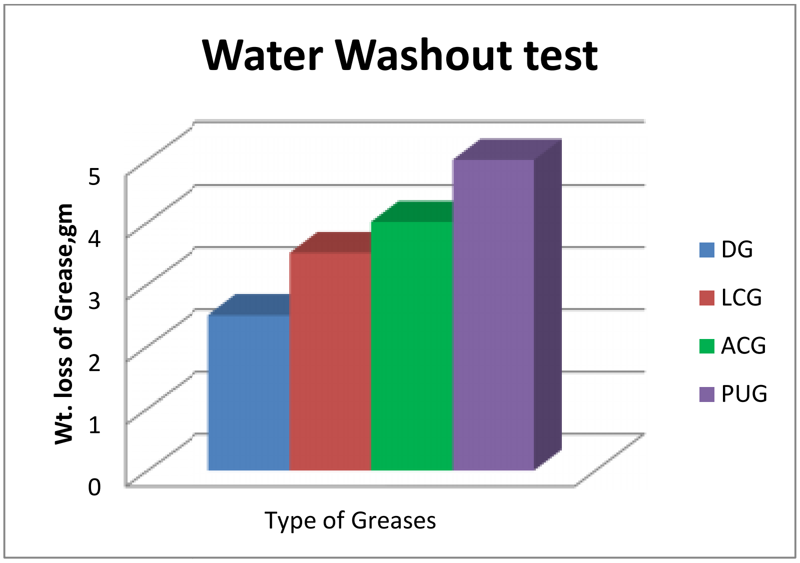

FIGURE 6

From the figure 6 it observed that developed grease gives lower weight loss in water washout test compared to other conventional high performance greases indicating it has better water washout resistance.

Corrosion Resistance

The greases, especially high performance greases are expacted to assure protection against rust and corrosion of bearings and lubricated parts.This property is improved by fortifying the greases with suitable rust and corrosion inhibitors.

Rust Test –ASTM D-1743

In this method, a tapered roller bearing is packed with 2 grams of the grease. The bearing is rotated under a given thrust load for 60 sec to distribute the grease uniformly. The bearing is then immersed in a container containing distilled water without breaking contact between rollers and races and stored at 52 C and 100% humidity for 48 hrs. At the end of 48 Hrs, the bearing is removed, cleaned and inspected for evidence of corrosion. A corrosion spot of 1.0 mm or longer is an indication of failure. Only pass or fail rating are used.

The results of rust test ASTM D-1743 are given in table 2 which indicate that the developed grease is comparable to other three greases.

Copper Corrosion

Copper corrosion Test-ASTM D-4048

The test consist of the immersion of a clean polished strip of copper in a grease sample at 100 C for 24 Hrs. At the end of the test, the strip is removed and cooled. The strip is then cleaned and inspected for staining. Corrosion may be qualitatively described or rated numerically by comparing with the standard. We observed that results of copper corrosion of developed grease are comparable to other three high performance greases.

Table 2: Performance Data of Developed Grease and other High Performance Greases

S. No.	Performance test	Test Method	High Performances Greases			
			DG	LCG	ACG	PUG
1.	Thickner Type		-	Li Complex	Al Complex	Polyurea
2.	Worked Penetration	ASTM D-217	242	237	285	281
3.	Mechanical Stability, 10^5strokes, Penetration change	ASTM D-217	17	18	27	50
4.	Four Ball EP,kg	ASTM D-2596	500	250	315	400
5.	Four Ball Wear	ASTM D-2266	0.44	0.50	0.61	0.70
6.	Drop Point,˚C	ASTM D-2265	>300	257	270	262
7.	Water Washout	ASTM D-1264	2.0	3.5	4.0	6.0
8.	Oxidation Stability,	ASTM D-942	2	3	5	5

	psi drop					
9.	Copper Corrosion	ASTM D-4048	1b	1b	1b	1b
10.	Rust Test, Distilled water	ASTM D- 1743	pass	pass	pass	pass

Conclusions

The laboratory evaluation of the developed grease and the comparison of its data with other high performance greases show the superiority of the developed grease. There are many desirable performance attributes associated to this developed grease to work as high performance grease such as high drop point, high mechanical strength (shear stability), better antiwear and load carrying capability for extreme pressure conditions, very good water resistance, rust and corrosion resistance and oxidation stability. The developed grease has good potential to work as a excellent high performance grease specially in steel plants.

In the next phase of our studies, we are planning to carry out extensive field trials of this unique high performance grease under most severe operating conditions. This will further prove the suitability of this grease as new improved high performance grease.

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Quantitative Estimation of Boron based Complexing Compounds used in Lithium Complex Greases

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Introduction

In recent years, there is a growing demand for lubricants including lubricating greases with advent of newer type of highly efficient equipments and machineries operating in wide range of extreme application conditions such as temperature, load, etc. In order to meet the such demands, initially, simple multipurpose lubricating greases and non soap lubricating greases were used which had limitations at extreme conditions. This was overcome by use of complex soap thickener based lubricating greases. A wide variety of lithium complex greases along with simple lithium greases are being extensively used for both industrial and automotive applications. In general, complex soap thickener are derived as the salts (soap) formed of high molecular weight fatty acids and salts of short organic or inorganic acids. The combination of these two units exhibit strong interactions which increases the dropping point of such greases. The complexing agent presently being used in lithium complex greases are either based on boron inorganic type - Boric acid or boron in combined organic form as borated esters . Besides few organic dicarboxylic acid namely Azelic acid, Sebacic acid are also widely being used in recent times .

Use of Boric acid has a inherant problem of grit formation , inconsistent dropping point and tedious manufacturing process which was overcome by use of Organo Boron compound which also provides much ease to grease manufacturing processes .The main advantage of complex soap thickener over simple conventional soap thickener based greases are their capablity of maintaining an excellent stability at high temperature besides other enhanced performance properties such as load bearing , shear stability, water resistance,rust protection etc.. Not many methods are known and reported to separate these ingredient complexing agent from these complex soap thickener based lubricating greases . The methods reported are very few in literature to identify and quantitatively estimate the complexing agents used in the lubricating greases available in the market.

In the present study , an attempt has been made through an analytical approach to identify , separate & quantitatively estimate the complexing agent in a few market samples of lubricating greases used for both industrial and automotive applications. In the proposed approach, lithium complex lubricating grease samples have been subjected to separation, identification and quantitative estimation of the complexing agent. Dropping Point ,Thermogravimetric and Fourier Transform Infrared Spectrometric (FTIR) techniques were used along with suitable wet chemical analytical procedure. The information obtained from the study will be very useful in understanding of the products with different types of complexing agent used in lithium lubricating greases for a given application .

EXPERIMENTAL :

Chemicals : All chemicals employed for analysis were of Analytical Reagent Grade : Methanol , Hexane , Chloroform, Anhydrous Sodium Sulphate, Sodium Hydroxide , Concentrated Hydrochloric acid, Concentrated Sulphuric acid , DL- Mannitol , Phenolphthalein & Methyl Orange indicators.

Labware : Standard glasswares of Borosil make were used for analysis. Standard Soxhlet Extraction Apparatus, Whatman 40 (12.5 cm) Filter paper , Heating mantle, Oven ,Vacuum Dessicator, Separating flask 1000ml, Beaker 250ml & 500ml capacity ,Gooch crucible G4 , Heating Mantle.

Instruments : Thermofisher Fourier Transform Infrared Spectrometer model Magna 560 ESP (FTIR) , PerkinElmer STA 6000 Thermogravimetric Analyser(TGA)with provision differential thermal analysis (DTA) and Koehler Instruments Inc. make Semi Automatic Point Apparatus.

PROCEDURE :

500 gms of seven market samples of lubricating greases constituting lithium complex (NLGI consistency 2 & 3) based soap thickener for both industrial & automotive applications marked as (A to G) were collected and subjected to above study by adopting the following procedures. The Lithium complex soap greases expected to be based on boric acid / borated esters / Organic dicarboxylic acid as a complexing agent.

A Dropping Point determination of Lubricating greases :

The standard procedure adopted for lubricating grease samples (A to G) as per ASTM D 566 was used . Dropping Point was determined by 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. A type of lubricating greases is simple or complex soap thickener based is known from the dropping point of the said greases .

B FTIR Spectral analysis :

Infrared spectrum of each of above samples of lubricating greases were recorded in Potassium Bromide cell windows without spacer in a IR demountable cell. The Infrared spectral range used was $4000cm^{-1}$- 400 cm^{-1}. Number of Scans : 32, Resolution : $4cm^{-1}$

Thermofisher Fourier Transform Infrared Spectrometer model Magna 560 ESP (FTIR) was used for study .Infrared Spectral analysis provides information on the nature of complex soap thickener being used in the lubricating greases.

C Soap Thickener Content by Soxhlet Extraction Procedure :

The soap thickener content in the samples were estimated by soxhlet extraction method. About 10 - 20 grams of each sample was taken in previously weight thimble made of filter paper and placed in Soxhlet Extraction apparatus in which 250 ml hexane was taken to extract the oil under reflux condition for 8 hours through repetitive re- circulation of solvent through the sample Separated oil was obtained after removal of solvent hexane over a water bath and kept in a vacuum desiccators to remove completely any entrapped solvent hexane. Quantitatively estimated the separated oil content from the weight of separated oil. Similarly, quantitatively estimated the separated hexane insoluble portion containing soap after drying through weight of the separated solid . The separated oil from the sample obtained above method were subjected to FTIR spectral analysis to know the clear separation of soap from greases .

D Separation and Quantitative estimation of complexing agent in Lubricating Complex Grease :

Weighed about 5-10 grams of lubricating grease sample in a previously weighed 250 ml beaker, treated with 150 ml (1:2) dilute hydrochloric acid solution to split the complex soap thickener .Boiled the contents in beaker over a hot plate until entire solid soap splits into flowable liquid on the surface of solution . The solution was to cool down . Transferred carefully the content into separating flask (1litre) and extracted out the organic portion with one to two (50 ml) proportion of solvent Diethyl Ether .The separated out carefully the aqueous layer into a 500 ml beaker along with aqueous washing of ether layer . In the case of lithium based complex greases with use of different complexing agent – boric acid , borated esters, the aqueous solution with washings need to be carefully separate out and collected .A suitable stock solution(250ml) was made further estimation of boric acid content by Boric acid (DL) Mannitol method as given below **(I).**

The separated ether layer with washings obtained from above was evaporated over a water bath. The semi - solid gel like with base oil residue obtained was subjected to FTIR spectral analysis, Thermogravimetric (TGA) analysis with differential thermal analysis provision . The residue from ether layer will be useful for analysis of lithium complex greases with commonly used organic based complexing agent - di carboxylic acid such as Sebacic acid / Azelaic acid or any . Generally, the residue obtained from ether extraction contains mixture of fatty acid 12Hydroxystearic acid with organic acid – mono / di carboxylic acid along with base oil **(II).**

(a) Estimation of Boric acid content by(DL) Mannitol titrimetric method (from I) :

25 to 50 ml of stock solution was taken in 250 ml conical flask and titrated with added 10% sodium hydroxide solution using drops of phenolphthalein indicator to neutralize excess acid to just faint pink solution . Added few drops of 0.1 N hydrochloric acid solution until pink color just disappears. Added few drops of methyl orange indicator and boiled the solution for 1-3 minutes to expel carbon dioxide over a hot plate and continued the titration carefully with 0.1 standardized sodium hydroxide solution taken in burette to yellow color solution . 2 grams of

(DL) Mannitol. Continued the titration with 0.1 N standardised sodium hydroxide solution further until pink color appears with no further disappearance. From the volume of 0.1 N sodium hydroxide consumed , boric acid content (in mg) was estimated using relation : 1ml of 0.1 N Sodium Hydroxide = 6.183 mg boric acid. From the dilution factor and weight of the grease sample taken, boric acid content (%) was estimated.

(b) FTIR Spectral analysis of separated residue obtained from ether extraction (semisolid gel like residue - from II) :

30mg of each of the residue sample was smeared between the potassium bromide cell windows in a demountable IR cell .IR spectrum of the each of the residue sample was recorded under recorded under similar instrumental conditions. Infrared spectral range used was 4000cm^{-1}- 400 cm^{-1}. Number of Scans : 32,Resolution : 4cm^{-1} .Thermofisher make Fourier Transform Infrared Spectrometer model Magna 560 ESP (FTIR) was used for study .

(c) Thermogravimetric (TGA) analysis (with differential thermal analysis provision) of separated residue obtained from Ether extraction (semisolid gel like residue - from II) :

30-60 mg of each of the residue sample was taken in a mini crucible and placed the crucible into TGA sample compartment and covered with a lid . The instrumental condition used :
programmed heating rate between temperature 50 to 300 deg. C at 5 deg. C / minute and between between 301 to 900 deg. C at a heating rate of 20 deg.C/minute. Nitrogen gas was used with a flow rate a flow rate of 5ml / minute . Differential thermogram was also recorded simultaneously under similar condition along with thermogram for each of the samples. Besides above each of the grease sample were also recorded under similar condition. PerkinElmer STA 6000 TGA instrument was used for the study.

Results and Discussions :

A Dropping Point determination of Lubricating Complex Greases :

Table 1 shows the results of dropping point of samples of Lithium complex lubricating greases. It was observed that different samples shows different dropping point .It is also observed from the Table that lithium complex lubricating greases shows different dropping point though it may contain complex soap thickener based lubricating greases .

Table 1

S.No	Sample code	Sample Details	Dropping Point ^{0}C
1.	**A**	Industrial Grease NLGI 3	202
2.	**B**	Industrial Grease NLGI 2	260
3.	**C**	Industrial Grease NLGI 2	255
4.	**D**	Industrial Grease NLGI 2	272
5.	**E**	Industrial Grease NLGI 2	280
6.	**F**	Automotive Grease NLGI 3	226
7.	**G**	Industrial Grease NLGI 3	246

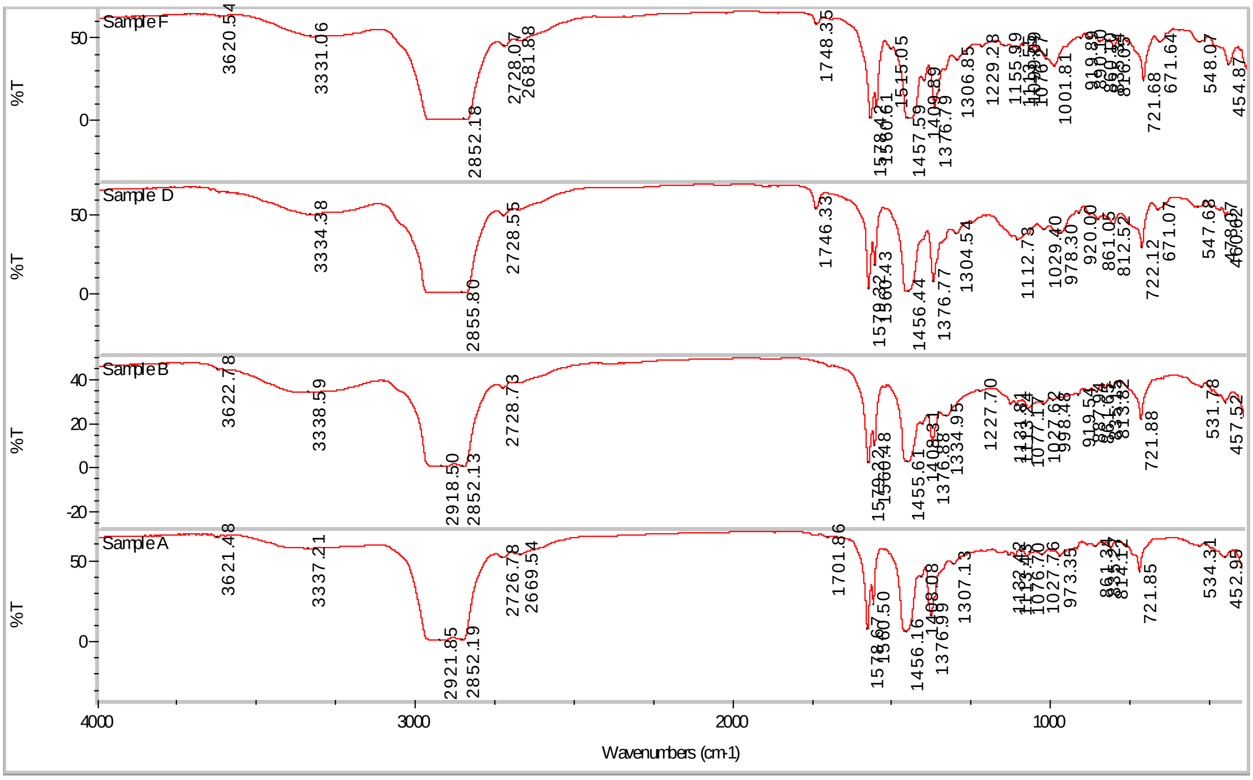
B Fourier Transform Infrared Spectral Analysis of Lubricating Greases :

The lubricating grease samples (A to G) were smeared between potassium bromide cell windows and IR spectra of each of the sample were recorded . IR spectrum recorded between 4 000cm^{-1} -400cm^{-1} with number of scan 32 and resolution of 4 cm^{-1} instrumental conditions.
Table 2 indicates that nature of the soap thickener present in different lubricating greases. The characteristics peaks of complex soap thickener indicates the type of greases that for a given applications.

Table 2

S.No	Sample Code	Sample Details	Characteristic peaks of Soap thickener by FTIR Analysis
1.	**A** **Industrial**	Lithium Grease Soap NLGI 3	3325(-OH) cm^{-1} , bifurcated peaks 1579& 1560 cm^{-1} , 721 cm^{-1}.
2.	**B** **Industrial**	Lithium Complex Soap Grease NLGI 2	3335cm^{-1}(-OH),Bifurcated Peaks-1579&1560cm^{-1}, relatively broad peak 1460 cm^{-1}(-B-O –C-),721 cm^{-1}. * The region boric acid /borated ester complexing agent peak appears overlap with peak methylene group absorption of hydrocarbon base fluid in the grease
3	**C** **Industrial**	Lithium Complex Soap Grease NLGI 2	3335cm^{-1}(-OH), Bifurcated Peaks -1579 & 1560 cm^{-1}, relatively broad peak 1460 cm^{-1}(-B-O –C-), 721 cm^{-1}. * The region boric acid /borated ester complexing agent peaks appears overlap with peak methylene group absorption of hydrocarbon base fluid in the grease .
4	**D** **Industrial**	Lithium Complex Soap based Grease NLGI 2	3334cm^{-1}(-OH),Bifurcated Peaks-1579 & 1560 cm^{-1} carbonyl group of soap thickener,relatively broad peak 1460 cm^{-1}(- B-O –C-), 721 cm^{-1}.* The region boric acid /borated ester complexing agent peaks appears overlap with peak methylene group absorption of hydrocarbon base fluid.
5	**E** **Industrial**	Lithium Complex Soap based Grease NLGI 2	3330cm^{-1}(-OH), Bifurcated Peaks -1579 & 1558 cm^{-1}, relatively broad peak 1460 cm^{-1}(- B-O –C-),721 cm^{-1}.
6	**F** **Automotive**	Lithium Complex Soap based Grease NLGI 3	3334cm^{-1}(-OH),Bifurcated Peaks -1579 &1558 cm^{-1} carbonyl group of soap thickener, 721 cm^{-1}.
7	**G** **Industrial**	Lithium Complex Soap Grease NLGI 3	3331(-OH) cm^{-1} , bifurcated peaks 1578 & 1560cm^{-1} carbonyl group of soap thickener , 721 cm^{-1}.

Figure 1 shows typical IR Spectra of four different lithium complex greases:



From **Table 2** as well as from **Figure 1**, it was observed that FTIR spectral analysis was not able to clearly differentiate lithium complex greases complexed with different complexing agent (from observed in A to G) including sample A (without complexation). The region boric acid /borated ester complexing agent peaks(-B-O-C) appears overlap with peak methylene group absorption of hydrocarbon in the grease.

C Soap Thickener Content by Soxhlet Extraction Procedure :

Table 3 shows the results of separated soap from lithium complex greases under study.

Table 3

S.No	Sample Description	Sample Details	Separated Soap content (wt%)	Separated (Oil with additives) content (wt%)
1	**A**	Lithium Grease NLGI 3	9.7	90.3
2	**B**	Lithium Complex Grease NLGI 2	15.9	84.1
3	**C**	Lithium Complex Grease NLGI 2	16.7	83.3
4	**D**	Lithium Complex Grease NLGI 2	8.4	91.6
5	**E**	Lithium Complex Grease NLGI 2	7.3	92.7
6	**F**	Lithium Complex Grease NLGI 3	11.6	88.4
7	**G**	Lithium Complex Grease NLGI 3	8.9	91.1

From **Table 3**, it was observed that different samples have different soap contents(A toG).As expected sample with lower consistency have shown lower soap contents with exception of sample F . It was also observed that boric acid based lithium complex grease has shown more soap content as compared borated esters as well as organic dicarboxylic acid for given consistency (B, D & F) .

D Separation,identification and quantitative estimation of complexing agent in Lubricating Complex Greases :

a) Estimation of Boric acid content by(DL) Mannitol Titrimetric method (from **I**) :

Table 4

S.No	Sample code	Sample Details	Boric acid content (wt%)
1.	**A**	Industrial Grease NLGI 2	----
2.	**B**	Industrial Grease NLGI 3	2.75
3.	**C**	Industrial Grease NLGI 3	2.63
4.	**D**	Industrial Grease NLGI 2	0.60
5.	**E**	Industrial Grease NLGI 2	0.97
6.	**F**	Automotive Grease NLGI 2	---
7.	**G**	Industrial Grease NLGI 3	---

From the above **Table 4,** it was observed that out of the samples under study, four(B, C, D ,& E) of the samples were based on either boric acid or based on borated ester as a complexing agent. It was also observed that boric acid content in two of the samples (D & E) were lower than the samples (B & C) indicating borated ester type of complexing agent used where as in samples(B &C) simply boric acid being used .

Boron in the form of boric acid and borated ester will provide boric acid which can be estimated by using this mannitol method. From the content of boric acid obtained, it can be inferred that type of boron based complexing agent being used . Incase boric acid content found to be negligible, it is expected that the complexing agent used be organic dicarboxylic acid based.In the lithium complex greases , there is a different options available to manufacturers using different complexing agent to market their products for a given application.

b) FTIR Spectral analysis of separated residue obtained from Solvent ether extraction(semisolid gel like residue - from II) :

Sample with boric acid / borated ester based complexing agent on acid splitting gave a residue mainly 12 -Hydroxy Stearic acid along with basefluid . The peak observed mainly are bifurcated peaks at 3200cm^{-1}(-OH group) , 1697cm^{-1} (-C=O of -COOH),919 cm^{-1}(COOH) whereas sample with organic dicarboxylic acid as a complexing agent will provide combined form of both peaks of 12-Hydroxy Stearic acid as well as above organic dicarboxylic acid which is observed mainly around 1710 cm^{-1}& 935 cm^{-1}.The intensity of 935 cm^{-1}is not very strong as compared peak at 1700cm^{-1}.

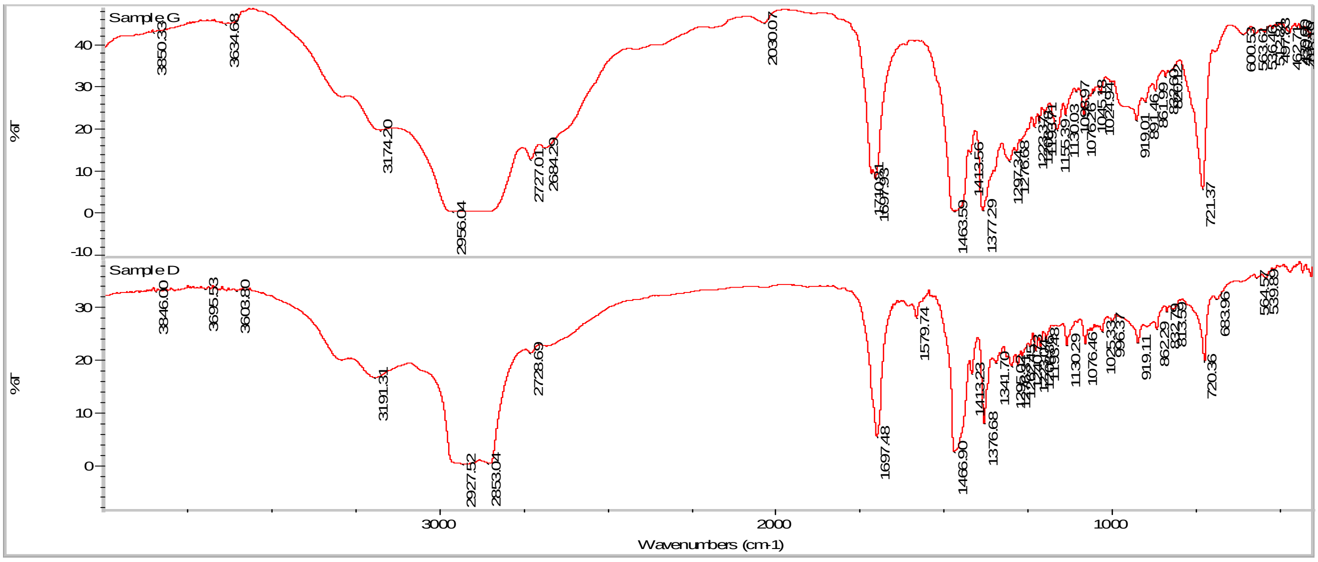
Table 5 shows results above observations of samples under study

Table 5

S.No	**Sample Code**	Sample Details	Characteristic peaks of Residue obtained after acid splitting by FTIR Analysis
1.	**A** **Industrial**	Lithium Grease NLGI 3	Bifurcated 3200 (-OH) cm^{-1}, 1697 cm^{-1}, 721 cm^{-1}(12-Hydroxy stearic acid) along base fluid peaks
2.	**B** **Industrial**	Lithium Complex Grease NLGI 2	Bifurcated 3200(-OH) cm^{-1} , 1697 cm^{-1}, 919cm^{-1}, 721 cm^{-1} (12-Hydroxy stearic acid) along base fluid peaks
3	**C** **Industrial**	Lithium Complex Grease NLGI 2	Bifurcated 3200(-OH) cm^{-1},1697 cm^{-1}, 721 cm^{-1}(12-Hydroxy stearic acid) along base fluid peaks
4	**D** **Industrial**	Lithium Complex Grease NLGI 2	Bifurcated 3200 (-OH) cm^{-1} , 1697 cm^{-1}, 919cm^{-1} 721 cm^{-1}(12-Hydroxy stearic acid) along base fluid peaks
5	**E** **Industrial**	Lithium Complex Grease NLGI 2	3200 (-OH) cm^{-1} , 1697 cm^{-1}, 919cm^{-1} 721 cm^{-1}(12-Hydroxy stearic acid) along base fluid peak s
6	**F** **Automotive**	Lithium Complex Grease NLGI 3	3200 cm^{-1}(-OH), Bifurcated broad Peaks -1709 cm^{-1}& 1695 cm^{-1}, 930cm^{-1} ,721 cm^{-1} along with base fluid.Peak at 1709cm^{-1} is mainly attributed from organic dicarboxylic acid which is used as a complexing agent.
7	**G** **Industrial**	Lithium Complex Grease NLGI 3	3200 cm^{-1}(-OH), Bifurcated broad Peaks -1709 cm^{-1}& 1695 cm^{-1}, 935cm^{-1} , 721 cm^{-1} along with base fluid.Peak at 1709cm^{-1} is mainly attributed from organic dicarboxylic acid which is used as a complexing agent.

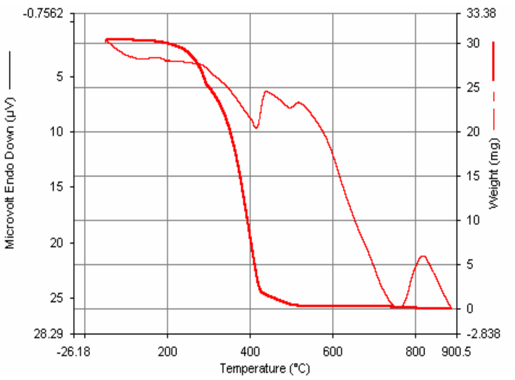
From the **Table 5 ,** it was observed that samples (B,C,D & E) boron based complexing agent (boric acid as well as borated ester) can be differentiated from the samples containing organic dicarboxylic acid based(F & G) .

Figure 2 show a Typical FTIR spectra indicating above observations

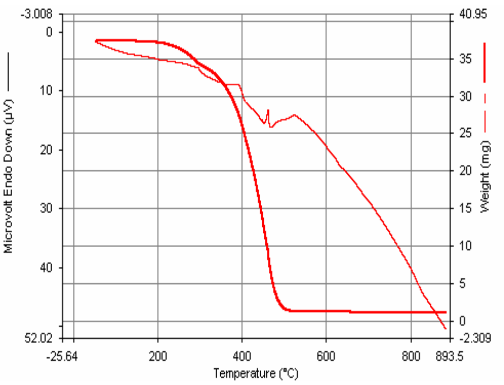


(c) Thermogravimetric (TGA) Analysis (with Differential Thermal Analysis provision) of separated residue obtained from Ether extraction (semisolid gel like residue - from II) :

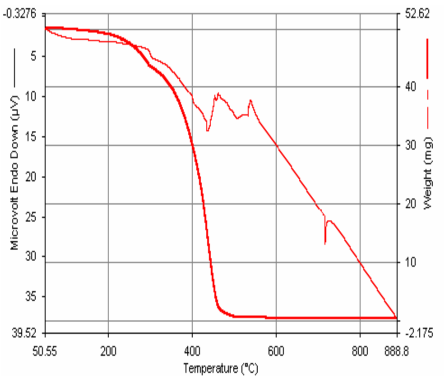
Thermogravimetric analysis of all the samples under similar instrumental conditions were carried out under nitrogen atmospheric condition.Differential thermogram(DTA) were recorded parallel along with the TGA thermogram .



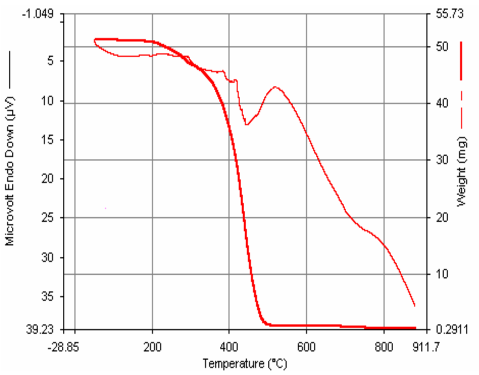
Sample A



Sample B



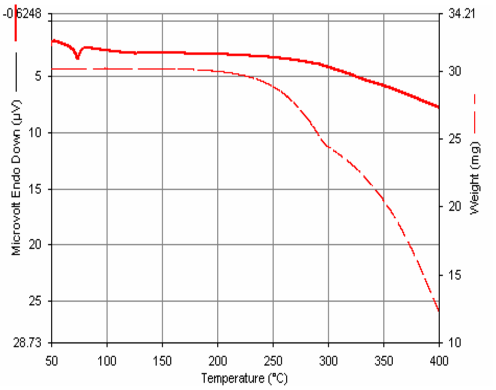
Sample E



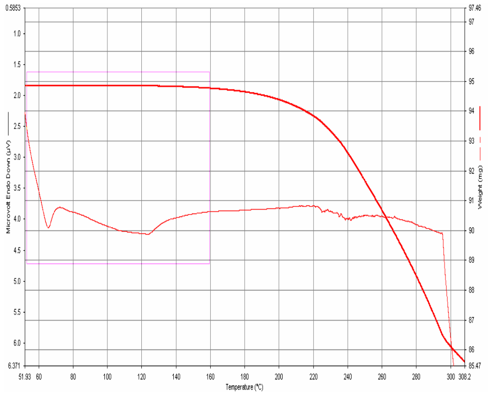
Sample G

It was observed from the thermograms of the complex samples (B ,E & G) when compared with sample A (uncomplexed) there is a distinct difference in the pattern of degradation with increase temperature. It is also observed in differential thermogram of each of the grease samples including uncomplexed grease a lithium 12HSA soap at 198- 200 ^{0}C (a melting point of soap) and a multiple humps at melting of complex soap (not defined peak).

The fatty acid residue in basefluid obtained from each of the grease samples through acid splitting followed by extraction using solvent ether was subjected to differential thermal analysis. It was observed that boric acid / borated ester based samples (A, B, C, D & E) have shown peak characteristics of melting point of 12-Hydroxy Stearic acid (65-68 ^{0}C) whereas organic dicarboxylic acid based complex grease have shown two peaks one due to melting point of 12-Hydroxy Stearic acid (65-68 ^{0}C) as well as relatively broader peak with less intensity due to organic dicarboxylic acid (124-132 deg.C) as observed in sample (E & F) . A typical differential thermograms have shown to depict above observation.



(FA in A, B , C & D)



(FA in F & G)

Conclusions :

1. Based on the above analytical study , attempt has been made to separate , identify and quantitatively boron based complexing agent used in lithium complex greases available in the market for both automotive and industrial applications. The study also included simple uncomplexed lithium grease as well as organic dicarboxylic acid complexing agent based lithium complex greases to differentiate the greases by identifying the type of complexing agent used .
2. Both FTIR spectral analysis and Thermogravimetric with differential thermal analysis is able to identify and differentiate various type of lithium complex greases.
3. From the boric acid content, it was able to differentiate the among boron based complexing agent whether it is boric acid based or borated esters based .
4. Dropping point of lubricating greases is very valuable and important tool to indicate whether grease is complexed or simple type and was able to guide above study .
5. It was concluded that there is a distinct variation in complexing agent used in different greases available in the market for a given application. More prominent & widely used lithium complex greases , different type of complexing agents are available which are being used in varying amount by different Manufacturers.
6. The method is easily adoptable in the laboratory, the results are reproducible and does not does not require very expensive chemicals and labwares.

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