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India Chapter
ISSN : 0972-2742

GREASETECH INDIA

A Quarterly Journal of NLGI-India Chapter

Vol. XXI, No. 1, July - Sept 18

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Vol. XXI, No. 1, July - Sept 18

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Testing of Lubricant Greases in the Static and Boundary Regimes

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Abstract:

The work presented here focuses on the issue of precise testing of friction of greases in the static and boundary lubrication regimes. Limiting friction is an important parameter in many applications wherein the force required to initiate macroscopic motion plays a crucial role. Such applications include, among others, seat regulators and window-pane mechanisms in automobiles, roller bearings in conveyers, O-rings, fishing gear, etc. In this current study, tribological behaviour of two fully formulated greases was studied at room temperature and at 80°C on an MCR Tribometer with a ball- on-three-plates test configuration, with the focus lying mainly on the novel test methodology. The obtained Stribeck curves and post-test surface characterization of the specimen showed that the additives chemistry of the grease can strongly influence the temperature dependence of the frictional behaviour, especially in the static and boundary regime.

Keywords: Boundary lubrication, static friction, limiting friction, tribofilms, ball on three plates test

1 Introduction

Lubricating greases find their use in various applications such as gears, bearings, chains, guides, etc. Selection of grease for a particular application depends upon various factors ranging from the contact pressure, lifetime, temperature, etc. With ever increasing demand for improvement in the efficiency of systems, selection criterions have also become quite stern. Under such conditions, having knowledge about the characteristics of the grease beforehand is highly beneficial in the selection process. This however is only possible for its inherent properties such as thixotropy, density, oxidation stability, rust protection, etc., and some specific tribological properties like extreme pressure properties, load ability, etc. There are of course various other parameters such as its resistance towards corrosion, long term stability, friction behaviour, etc., which need to be characterized individually for each given tribological system.

The current article deals with one such property, which is the break-away force of greases in a tribological system. Break-away force required to overcome static frictional resistance of the tribological system and set it into macroscopic motion. The value of coefficient of friction right before the onset of macroscopic motion is known as the limiting friction. Typical applications where this parameter could be of great significance are seat regulators, sliding guides, doors, locks, fishing gear, etc. While in most cases a low break-away force is wished for, it must also be noted that a certain amount of resistance is still required to inhibit involuntary movements. This parameter is also important in tribological systems with dynamic motion profiles involving start-stop events, which are often detrimental to the system.

In many applications, greases experience a range of temperatures and loads and it is of paramount importance that the performance of grease remains consistent over the entire range. In the current report, the performance of two greases has been evaluated at two different temperatures and loads. Herein, tribological characteristics such as limiting friction, wear resistance, and film forming ability of the grease are considered.

2 Experimental Setup

The tests were carried out on an MCR 502 from Anton-Paar, equipped with a Peltier heated tribology cell T-PTD200 in combination with a Peltier hood H-PTD 200 for precise temperature control. The test configuration used here, ball-on-three-plates, is shown below in Fig. 1.

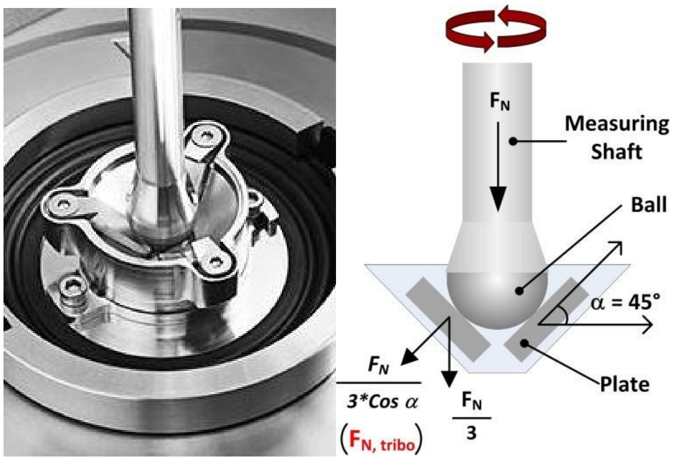

Fig. 1. Test Setup – Ball-on-Three-Plates

2.1 Test Profile

To study the influence of temperature and load on the system, tests were carried out at two different temperatures and loads, i.e., 23°C and 10 N, and 80°C and 50 N. The change in temperature from 23°C to 80°C, affects the elastic properties of the grease as well as the specimen. Taking this into account, the load was increased to 50 N in the test at 80°C to have similar contact conditions at both temperatures. During the test, the said load was applied to the contact and the system was allowed to stabilize for one minute (Interval I), see Fig. 2. This was followed by Interval II, wherein the speed was logarithmically increased from 10-5 to 500 rotations per minute (rpm) in a span of 6 minutes. This sequence is repeated three times for each set of specimen. The ball and the plates remained in contact during the entire test duration.

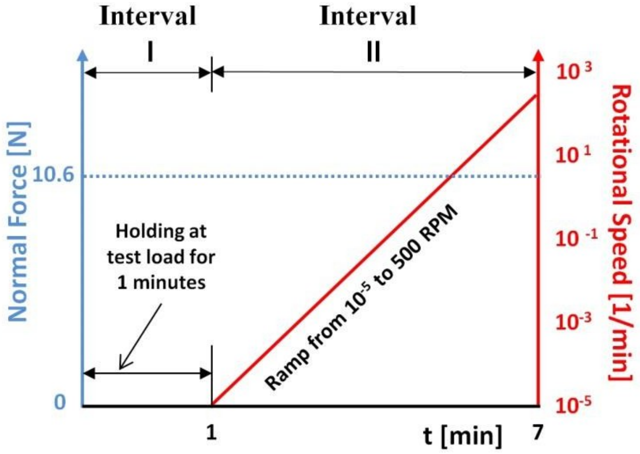

Fig. 2. Test profile showing logarithmic ramp of the rotational speed w.r.t. time.

2.2 Specimen

The balls, 12.7 mm in diameter, were manufactured out of Polyoxymethylene (*POM*). The plates, made out of brass, measured 6 mm in width, 15 mm in height, and 3 mm in thickness. The two greases considered for this study are commonly used greases with slight variation in their composition. They are referred to as *Grease 1* and *Grease 2*.

3 Results

The results section is divided into two parts. The first part deals with the tribometric data while the second showcases findings from electron microscopy of the wear tracks of the tested specimen.

3.1 Tribometric Data

This data is presented in form of Stribeck curves depicting changes in the coefficient of friction, μ, as a function of the rotational speed. As mentioned in Section 2.1, each test comprised of three loops or repetitions of the test profile. During the speed ramp of the first loop (*first run*), the contact experiences a breaking-in or running-in process. Herein, the surface asperities even out and the mating surfaces conform with each other to the extent possible. This is achieved either by wear of material(s), or through plastic deformation. The second and third loops (*reruns*) also help in characterizing the tribological properties of the greases.

3.1.1 First Runs

Tribometric data from the first runs from three tests with each of the two greases carried out at both temperatures is presented below in Fig. 3. The curves corresponding to *Grease 1* are plotted in red while those with *Grease 2* are in blue. The initial peaks in the curves represent the point where the system translates from a static state, into kinetic state of motion. The coefficient of friction at the vertex corresponds to the limiting friction of the system. From Fig. 3, it is clear that at 23°C, *Grease 1* shows a higher value of limiting friction compared to *Grease 2*. At 80°C though, there is no significant difference in the frictional behaviour between the two greases. At low temperature and low load, rheological properties of the grease play a pivotal role in dictating the tribological behaviour of the system. During the first run at 23°C, *Grease 1* forms a more effective film between the two mating surfaces. At higher temperature (80°C) and load (50 N), both greases are squeezed out of the contact and the frictional behaviour observed at lower sliding speeds in Fig. 3 (b) basically represents the frictional behaviour between solid-solid contact. At relatively higher speeds, there is a possibility of entrainment of grease at the contact interface. Under congenial conditions and presence of required additives in the grease, there is also a possibility formation of a protective film on the wear scar.

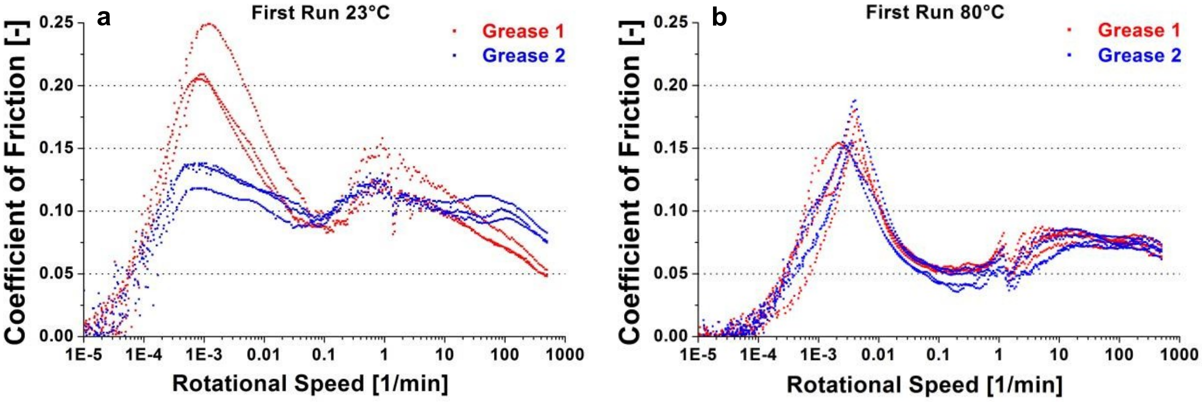

Fig. 3. Stribeck curves from the first loop of the tests carried out at 23°C (left) and 80°C (right).

3.1.2 Reruns

The condition of surfaces of the specimen at the mating interface during the reruns is significantly different as compared to that during the first run. The surfaces are more conformal and represent more or less the conditions present in a real life application. The Stribeck curves in Fig. 3 illustrate the tribological behaviour of the greases at the two test conditions after the initial running-in. The values of limiting friction and the overall frictional behaviour of *Grease 1* remain almost consistent under both test conditions. However, the same is not true for *Grease 2*. At 23°C and 10 N load, the limiting friction is at least three times higher than at 80°C and 50 N load. The black curve in the test at 80°C represents a rerun under dry condition wherein no lubricant was used. Although *Grease 2* shows a lower frictional resistance compared to Grease 1 at higher temperature and load, its lack of consistency over the temperature and load range makes it inferior to Grease 1. The reason for the difference in performance of the greases is explained below in the next section dealing with surface characterization.

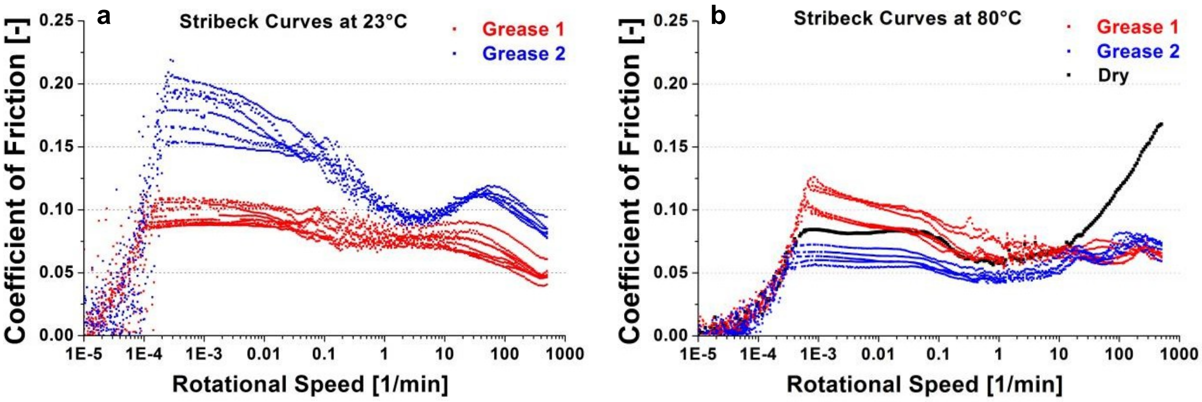

Fig. 4 Stribeck Curves from the second and third loops of the tests carried out at 23°C (left) and 80°C (right).

3.2 Surface Characterization

While the tribometric data provides an insight into the frictional and wear behaviour of a tribological system, surface characterization of the tested specimen in most cases offers an insight into what actually causes this behaviour. The analysis presented here was carried out on MA 15 scanning electron microscope (SEM) from Carl Zeiss, equipped with and energy dispersive X-ray spectroscope (EDX) for elemental analysis.

3.2.1 Formation of Reaction Films

As we go from 23°C and 10 N of normal force to 80°C and 50 N, there is a decrease in the thickness of the grease film separating the mating surfaces owing to the decrease in viscosity and increase in pressure. Under such conditions, chemical properties of the grease largely dictate its tribological characteristics. Formation of protective tribofilms at the mating interface is one such instance. These tribofilms are chemically derived at the contact surface under suitable and synergetic conditions between additives, surface, and operational parameters such as temperature, contact pressure, etc.

Tribofilms can vary a lot in their elemental and physical characteristics. These characteristics can be tailored by tweaking the additive chemistry in the greases. In general, tribofilms have a much lower elastic modulus compared to steels or even bronze. They also shear much easier compared to metals. Hence, when formed at the mating interface, they act as sacrificial layers, thus, protecting the substrate underneath.

In the current investigations, tribofilms were predominantly observed on the wear scars of tests with Grease 1 at 80°C. This is shown in Fig. 5 which compares the wear scars on the plate specimen from tests run at 80°C with both greases. While the wear scar with Grease 1 is profusely covered with tribofilms, only traces of it are seen on the wear scar with Grease 2. Elemental analysis with the help of energy dispersive X-ray analysis (EDX) showed that the tribofilms comprised of calcium-based compounds.

Tribofilms are known to be beneficial even when they are formed on one of the mating surfaces. However, their formation might cause an increase in the coefficient of friction depending upon the material of the sliding counterpart [2]. Higher frictional resistance observed in the reruns of Grease 1 at 80°C in Error! Reference source not found. can be attributed to this phenomenon.

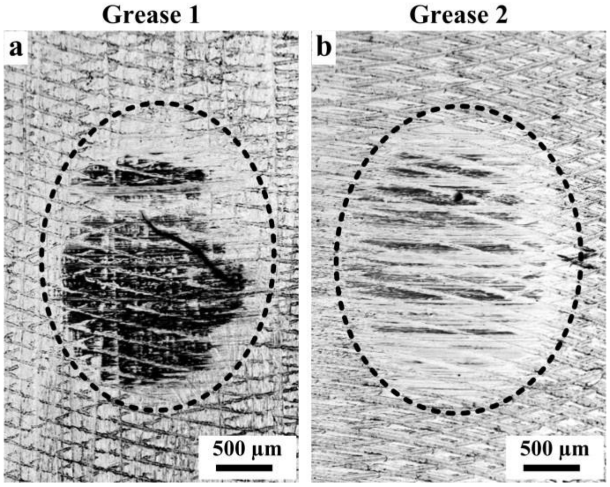

Fig. 5. SEM micrographs of specimen from tests with Grease 1 and 2 at 80°C, and 50 N normal force. The wear scar is highlighted with the dotted oval. The protective film (tribofilm) formed in the case of Grease 1 is the dark region within its wear scar.

These reaction films are only formed above a certain temperature, which in most cases falls around 70°C [1]. In the current investigations as well, tribofilms were only seen in tests with Grease 1 at 80°C. Tests with the same grease at 23°C did not yield any tribofilms as shown in Fig. 6. The surface of the wear scar on the left has no visible layers on it, and elemental analysis also confirmed the same.

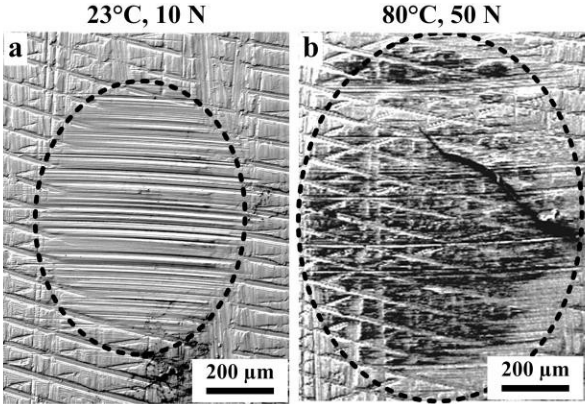

Fig. 6. SEM micrographs of specimen from tests with Grease 1 at (a) 23°C and 10 N normal force, and (b) 80°C and 50 N normal force. The wear scar is highlighted with the dotted oval. Tribofilms are only visible in the test carried out at 80°C.

4 Summary

The two greases studied here differed slightly in their additive chemistry, which led to differences in the frictional behaviour of the tribological system, especially in the boundary friction regime. The differences can be attributed to formation of tribofilms at the mating interface at elevated temperatures, which helped in maintaining uniform friction behaviour of the grease over the temperature range by forming protective tribofilms at the surface. This study presents a unique test methodology which offers the possibility of studying the frictional behaviour of lubricants in general, and greases in particular, with high degree of accuracy, especially in their boundary friction regime.

5 References

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Characterisation of Synthetic Ester Base Fluids used in Synthetic Lubricants

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Abstract :

In recent years, there is a ever growing demand of lubricants 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 end applications , many lubricants based on mineral oils from group I to group III as well as synthetics are available for application requiring stringent & extreme conditions. Synthetic base fluids mainly are used by the lubricant manufacturers are hydrocarbons, esters and polymeric glycols which have certain inherent properties such as better thermal and oxidation stability as compared to conventional mineral oil base fluids. Among the synthetics available, synthetic poly alpha olefin (PAO) & polyalkylene glycols(PAG)are technology driven and have limited manufacturers globally as compared synthetic ester fluids manufacturers. Ester based fluids are widely used in fire resistant hydraulic fluids, biodegradable lubricants, metal working fluids , bio fuels etc. Synthetic esters are derived from reaction of alcohol with organic acid and can be tailormade by varying the alcohols & the organic acids derived from vegetable oil origin.

In the present study , an attempt has been made to study some ester based fluid for their composition and their properties such as thermal and oxidation characteristic behavior . Few selected ester fluids were characterized for composition using FTIR ,Gas Liquid Chromatographic (GLC), Gel Permeation Chromatographic (GPC) techniques and Wet Chemical methods. Samples of synthetic ester formulated with and without antioxidant were subjected to oxidation stability test using Rotary Bomb Oxidation Stability (RBOT) Tester and their thermal behavior were studied using Thermo gravimetric Analyser (TGA) for their performance. Effect of Oxidation was also observed before and after the test using FTIR spectral analysis. Effect of Antioxidants - both phenolic type and aminic type on the ester fluids were also studied using RBOT test. The information obtained from the above study will be useful in understanding the thermal and oxidation behavior pattern of different esters for suitability for use in given applications .

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 to meet the conventional to stringent, extreme and specialized applications. In order to meet the above challenging conditions , wide range of base fluids are available ranging from conventional hydrocarbon base to tailor made synthetics hydrocarbons, to synthetic esters & polymeric glycols are available to the manufacturers.

Base oil is one of the most important and major component of lubricants are available in various grades with trend shifting from mineral oil origin to synthetics. Synthetic base fluids mainly are used by the lubricant manufacturers when requirements demands a certain inherent properties such as better thermal and oxidation stability as compared to conventional mineral oil base fluids. Among the synthetics available, synthetic poly alpha olefin (PAO) & polyalkylene glycols(PAG) are technology driven and have limited manufacturers globally as compared Synthetic Ester Fluids Manufacturers. Synthetic Ester based fluids are derived from reaction of alcohol with organic acid and can be tailor made by varying the alcohols & the organic acids derived from vegetable oil origin to suit the end applications. In recent years , increase in environment regulations imposed on manufacture lubricants based on environment friendly, less toxic and biodegradable fluid, synthetic ester based fluid forms best option available to Lubricant manufacturers. Considering the numerous ester based fluids available ,there is not many standard methods available or reported in literature to characterize these ester based fluids.

In the present study, an attempt has been made to study some ester based fluid for their composition and their properties such as thermal and oxidation characteristic behavior . Few selected ester based fluids were characterized for composition using FTIR ,Gas Liquid Chromatographic (GLC), Gel Permeation Chromatographic (GPC) techniques and Wet Chemical methods. Samples of synthetic ester blended with and without antioxidant were subjected to oxidation stability test using Rotary Bomb Oxidation Stability (RBOT) Tester and their thermal behavior were studied using Thermo gravimetric Analyser (TGA) for their performance. Effect of Oxidation was also observed before and after the test using FTIR spectral analysis. Effect of Antioxidants both phenolic type and aminic type on the ester fluids were also studied using RBOT test.The information obtained from the above study will be useful in understanding the thermal and oxidation behavior pattern of different esters for suitability for use in given applications .

EXPERIMENTAL :

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

Gases : Nitrogen , Oxygen ,Zero Air, Hydrogen Gases Purity (99.99 %) for Instrumental Purpose

Instruments : Thermo Nicolet Fourier Transform Infrared Spectrometer model iS10(FTIR), Thermal Analyser – Perkin Elmer Thermogravimetric Analyser TGA with DTA model STA 6000, Thermo make Gas Liquid Chromatograph (GLC) model GC 1310, Waters Make HPLC with GPC option. Tannas make- Rotary Bomb Oxidation Tester ((RBOT) / Rotating Pressure Vessel Oxidation Tester (RPVOT).

PROCEDURE :

500 ml of six known samples of readily available Synthetic Ester based fluids used in synthetic lubricants marked as ‘A to F ’ were collected .These samples were subjected to above study by adopting the following procedures :

1. Fourier Transform Infrared (FTIR) Spectral Analysis :

Infrared spectrum of each of above samples along with its separated constituents obtained after splitting with alkali 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 : 1cm-1 Thermo Nicolet Fourier Transform Infrared Spectrometer model Is 10 (FTIR) was used for the study. Infrared Spectral analysis provides information on the nature of ester under study.

2. Gas Liquid Chromatographic (GLC) Analysis of the samples under study :

2 gms of ester sample was taken in 250 ml conical flask to which added 15gms of NaOH solution made with 50ml of water diluted with 50 ml of methanol. The solution was stirred and connected with water condenser. The solution was refluxed for 3 to 4 hours until saponification reaction is completed. Cool the solution to room temperature . Acidify the solution with concentrated hydrochloric acid with cooling until entire alkali is neutralized .Transfer the entire content to separating flask (1L) and extracted out the organic residue (fatty acid plus organic alcohol) using solvent ether .Filtered off the aqueous acid layer and wash the solvent ether content with plenty of water to remove any adhering free inorganic acid. The organic solvent layer is collected in a 250ml beaker after passing through anhydrous sodium sulphate to remove any adhering water . The beaker with content was kept over a water bath to remove the solvent. The organic residue obtained was subjected to methyl ester conversion for GLC analysis.The procedure for methyl ester conversion as given below:

Residue obtained from sample was taken in a 250 ml conical flask with standard joint, added 100 ml of methylating agent (Methanol 3 : Benzene 1: Sulfuric acid 0.1) .Conical flask with above content was attached to the water condenser and kept on a heating mantle & refluxed the solution for four hours cooled the solution and carefully transferred into a separating flask (1L).Added 2 x 100 ml distilled water to wash the condenser. Extracted out the organic acid including the fatty acid as methyl ester into 2x100 ml diethyl ether. Separated out the lower aqueous layer. Washing of extracted ether layer with 2x100ml distilled water was carried out to remove any free mineral acid. The ether layer was collected in a 250 ml beaker and solvent was removed by keeping the extracted solution in beaker over a boiling water bath. The residue obtained was dissolved in chloroform and transferred to 50ml volumetric flask and stopperred.

For GLC analysis : Isothermal condition was used with oven temperature - 180 deg.C , Flame Ionisation Detector(FID) - 210 deg.C & Injector temperature 210 deg.C. were used. Packed Column (2 meter long , Diethylene Glycol Succinate Ester (DEGS) liquid coated on solid Chromosorb AW ,1/8 O.D Stainless Steel with adaptor) was used for analysis .Nitrogen flow rate : 30ml per minute was used. 2 to5 microliter of sample solution in chloroform was injected into the column for chromatographic separation. From the GC chromatogram , the percentage fatty acid distribution from percentage area was obtained.

3. Gel Permeation Chromatographic (GPC) analysis of Sample under study :

Gel permeation chromatogram of each of Ester sample was recorded using Refractive Index Detector (model 2414, Attenuation x4) . Molecular weight and its distribution of each Ester sample was obtained using calibration curve prepared using retention time of each known Polyethylene glycol standards with peak molecular weights of the standards covering 200 to 3400 . Breeze 2 Software was used for calibration and estimating molecular weight & its distribution of the subjected ester sample . Waters make modular HPLC system with GPC option was used for the analysis , 200 -400 microliter of samples solution made in THF solvent was injected into Universal Injector U6K.Three Standard Ultrastyragel colums packed in Tetrahydrofuran (THF) of pore size 100 , 1000 & 10000 angstrom were connected in series were used characterizing the polymeric additives in samples of gear oil . Binary HPLC pump model 1525 was used to pump at flow rate 1ml /minute of solvent(THF).

4. Thermal Analysis (TGA) of Ester Samples under study: – The sample Preparation procedure is given below :

The instrument was calibrated with known standard before analysing the samples. Initially, tared the weight of blank ceramic cup followed by weighing about 40-60 mg of each of ester 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 0C / minute from 50 0C to 900 0C and the mass loss was recorded against temperature in the form of thermogram (TGA graph) of the sample.The study conducted under Nitrogen gas atmosphere(40ml/min. flow rate). Any variation due to type of ester sample is reflected as a inflexions / plateau in the TGA thermogram. All the samples were subjected to analysis by adopting above procedure. Recorded simultaneously Differential Thermal Analysis (DTA) study of Ester sample .The temperature was obtained in the form of DTA graph for each sample of ester fluid under similar conditions.

5. Rotary Bomb Oxidation Stability Test (RBOT) of Ester samples Under Studyas per modified ASTM D 2272 method :

50gms each of the Ester sample was taken in a sample glass vessel for this study.

Figure1 shows sample glass pressure vessel. with sample holder in which a sample under study was taken

Figure 2 shows RBOT/RPVOT unit

To the sample pressure vessel containing 50gm sample of ester, placed 55gm of copper as a catalyst and added 5ml of distilled water. Mixed the solution thoroughly and placed vessel inside the stainless steel rotating base sample holder which grips sample vessel strongly when it is rotated inside the sample chamber. Placed the pressure vessel with sample inside the sample chamber of instrument 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 90 pounds per square inch (PSI = 690 kPa) and room temperature which is then increased to 99 ±0.5°C. The unit was rotated at a standard rpm required for the test. The test continued until the pressure drops below 65 PSI although the instrument has provision of continuously recording pressure change with time. After completion of the test 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. The ester sample after the test was drawn& dissolved in removed water by passing through anhydrous, collected and subjected to FTIR Spectral analysis. The surface of copper ring was also observed. Repeated the procedure for each of the ester samples in a above similar conditions.

Effect of Antioxidants on the ester samples were also studied on RBOT test rig with selection of one phenolic type and one aminic antioxidant type taken for study on three ester samples. Dosage about 1% level in the ester samples were kept for the study and their performance was observed on the RBOT test. 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. The changes if any in the IR Spectra fresh ester sample with antioxidant additive against used sample after oxidation test will indicate oxidation resistivity/ stability of the ester fluids.

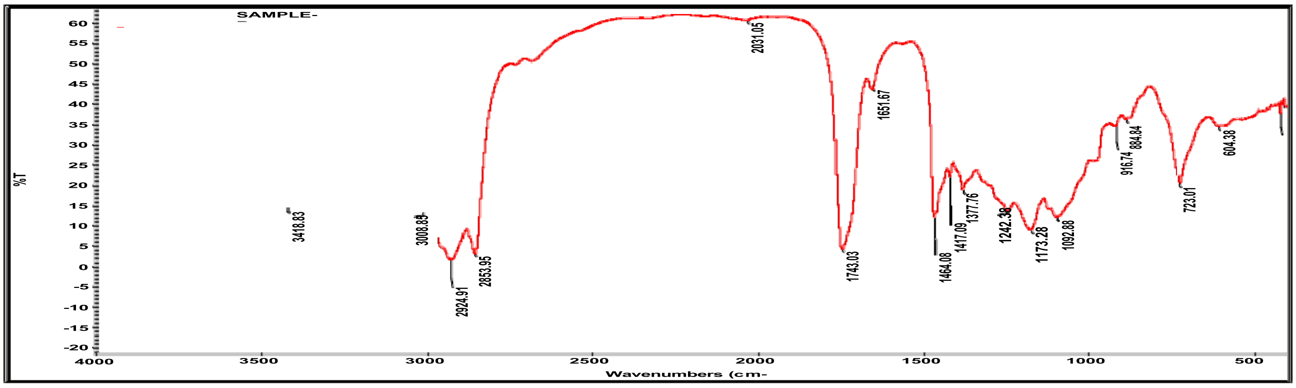
Results and Discussions :

1.Fourier Transform Infrared (FTIR) Spectral Analysis : Table 1 shows the results of FTIR Spectral analysis of Ester samples under study. It was observed from the IR Spectral analysis that there is a distinct difference in IR spectral features of Sample **'A'**, Sample **'B'** , Sample **'E'** & Sample **' F'** indicating difference in composition. However , Sample **'C'** & Sample **'D'** have similar IR spectral features with Sample 'A' indicating similar type of composition .Intensity of peak around 3005 cm-
1 indicative of extent of unsaturation due to unsaturated fatty acid as well as higher oxidisable hydroxyl group presence in the ester fluid.

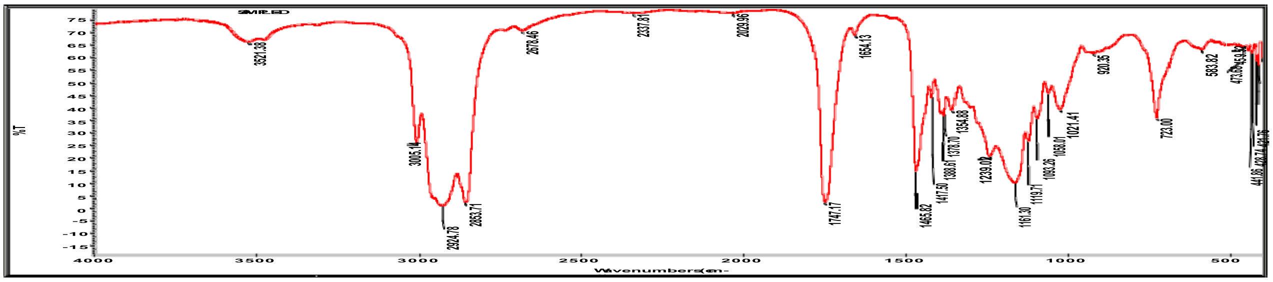
Table 1

S.No	**Sample Code**	**Type of Ester Under Study**	**IR Spectral Characteristic Peaks**
1	**A**	**Polyol Ester**	IR Spectrum indicates characteristic peaks ; bifurcates peaks at 3543cm-1 & 3468 cm-1(mainly from unreacted –hydroxyl OHgroup / from free OH from polyol ester, 3005 cm- 1from –CH from unsaturated carbon (mainly unsaturated fatty acid) ,1743 cm-1 carbonyl group absorption ester functionality, trifurcated peaks at 1240 cm-1,1152 cm-11119 cm- 1,due to COO-absorption , 1016 cm-1(due to C-O –absorption), 722 cm-1(-CH - 2 Repetitive methylene group from fatty acid chain).
2	**B**	**Polyol Mono Ester**	IR Spectrum indicates characteristic peaks ; broad strong peak at 3405 cm-1(mainly from unreacted –hydroxyl OHgroup / from free OH from polyol mono ester, 3008 cm- 1from – CH from unsaturated carbon (mainly unsaturated fatty acid) ,1741 cm-1 carbonyl group absorption ester functionality, , trifurcated peaks at 1242 cm-1,1173 cm-11119 cm-1,due to COO-absorption , 1016 cm-1(due to C-O –absorption), 872 cm-1, 722 cm-1(-CH - 2 repetitive methylene group from fatty acid chain).
3	**C**	**Mixed type Polyol Ester**	IR Spectrum indicates characteristic peaks ; bifurcates peaks at 3520cm-1 & 3436 cm-1(mainly from unreacted –hydroxyl OHgroup / from free OH from polyol ester, 3007 cm- 1from –CH from unsaturated carbon (mainly unsaturated fatty acid) , ,1743 cm-1 carbonyl group absorption ester functionalitytrifurcated peaks at 1239 cm-1,1162 cm-11112 cm- 1,due to COO-absorption , 1020 cm-1(due to C-O –absorption),913 cm-1, 722 cm-1(-CH - 2 Repetitive methylene group from fatty acid chain).
4	**D**	**Polyol Ester**	IR Spectrum indicates characteristic peaks ; bifurcates peaks at 3521cm-1 & 3432 cm-1(mainly from unreacted –hydroxyl OHgroup / from free OH from polyol ester, 3005 cm- 1from –CH from unsaturated carbon (mainly unsaturated fatty acid),1747 cm-1 carbonyl group absorption ester functionality, , trifurcated peaks at 1239 cm-1,1162 cm-11112 cm-1,due to COO-absorption , 1021 cm-1(due to C-O –absorption),920 cm-1, 723 cm-1(- CH2- repetitive methylene group from fatty acid chain).

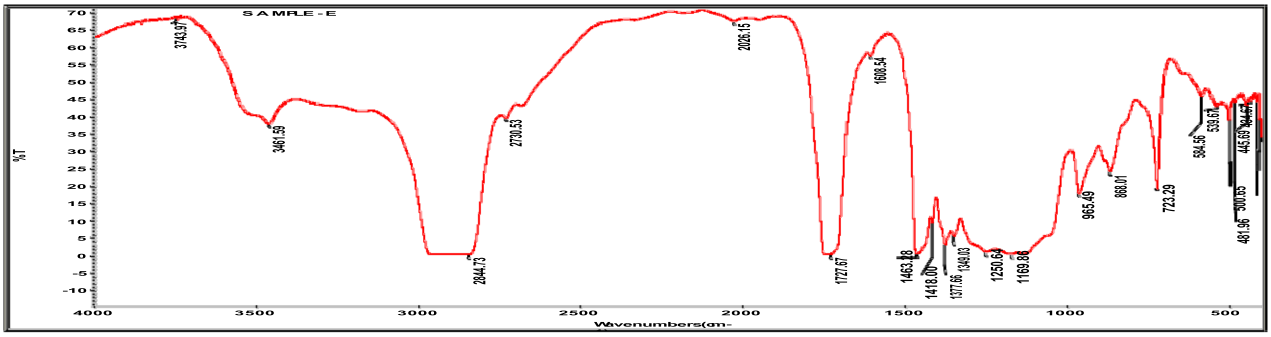
5	**E**	**Polymeric Ester (PAG Ester)**	IR Spectrum indicates characteristic peaks ; broad strong peak at 3465 cm-1(mainly from unreacted –hydroxyl OHgroup / from free OH from polyol mono ester, 3002 cm- 1from – CH from unsaturated carbon (mainly unsaturated fatty acid),1727 cm-1 carbonyl group absorption ester functionality ,trifurcated peaks at 1250 cm-1,1169 cm-11117 cm-1,due to COO-absorption , 1016 cm-1(due to C-O –absorption), 965 cm-1 ,868cm-1, 722 cm- 1spiky peak (-CH$_2$ - repetitive methylene group from fatty acid chain).
6	**F**	**Mono Ester**	IR Spectrum indicates characteristic peaks ; bifurcates peaks at 3554cm-1 & 3457 cm-1(mainly from unreacted –hydroxyl OHgroup / from free OH from polyol ester, 3004 cm- 1from –CH from unsaturated carbon (mainly unsaturated fatty acid) ,,1739 cm-1 carbonyl group absorption ester functionality, trifurcated peaks at 1243 cm-1,1174 cm-11119 cm- 1,due to COO-absorption , 1029 cm-1(due to C-O –absorption),966 cm-1 ,769cm-1724cm-1(-CH - Repetitive methylene group from fatty acid chain).



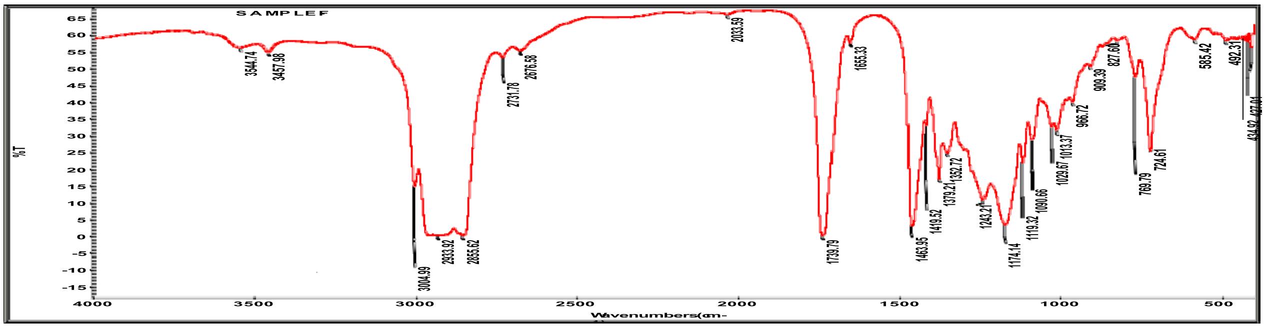
FTIR Spectrum of Sample'B'



FTIR Spectrum of Sample 'D'



FTIR Spectrum of Sample 'E'



FTIR Spectrum of Sample' F'

Figure A typical IR spectra of Four different Ester Fluids used in Synthetic Lubricants

2. Gas Liquid Chromatographic (GLC) Analysis of the Ester samples under study :

Table 2 shows the fatty acid composition of Ester samples under study obtained from Gas Liquid Chromatographic (GLC) Analysis . The fatty acid composition indicates the unsaturation & saturated fatty acid distribution which in turn contribute to oxidation to thermal stability to ester derived from the reaction of alcohol with fatty acid composition. The selection of ester fluid depends on type of alcohol as well as fatty acid composition for a given end application.

Table 2

S,No	Fatty Acid asMethyl Ester	Area % ‘A’ Polyol Ester	Area %‘B’ Polyol Mono Ester	Area %‘C’ Polyol Mixed Ester	Area % ‘D’ Polyol Ester	Area %‘E’ PAG Ester	Area %‘F’ Mono Ester
1	Lauric acid	<0.1	< 0.10	<0.10	1.29	---	<0.10
2	Myristic acid	0.23	0.13	0.69	0.61	---	<0.10
3	Palmitic acid	16.14	5.82	30.48	3.50	---	6.54
4	Palmito-oleic acid	--	--	--	0.10	---	--
5	Stearic acid	1.31	1.43	1.42	1.40	---	0.20
6	Oleic acid	41.90	22.45	38.94	72.89	---	70.50
7	Linoleic acid	38.29	32.85	26.69	20.31	---	22.46
8	Linolenic acid	1.01	33,81	1.54	<0.10	---	0.10
9	Arachidic acid	1.02	2.65	0.24	---	---	0.10
10	Behenic acid	---	0.70	---	---	---	---
11	Erucic acid	---	---	---	---	---	---
12	Ricineoleic acid	---	---	---	---	---	---

From the above table ,it was observed that there is a distinct variation in the fatty acid composition of the ester samples under study . Among the samples of Ester under study , Sample ‘E’ is not fatty acid based but dimerate based.

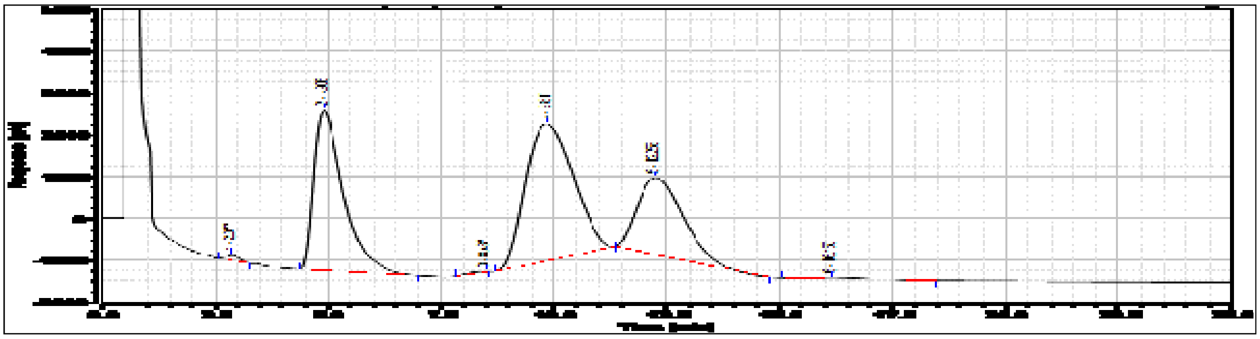


Figure 4 shows a typical Gas Liquid Chromatogram showing peaks due to fatty acids distribution.

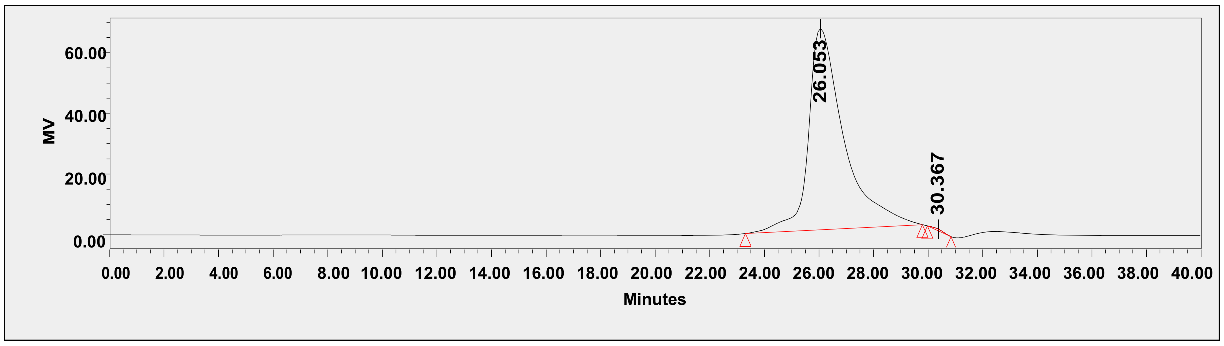
3. Gel Permeation Chromatographic (GPC) analysis of Sample under study :

Table 3 shows Molecular weight and its distribution of all the Ester samples under study. It was observed from the table that peak molecular weight obtained from GPC analysis is inline with respect to expected range .

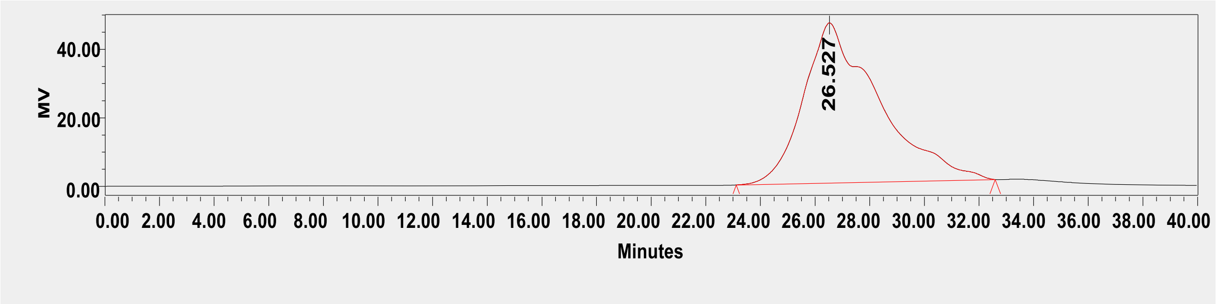
Table 3

S.No	Sample Description	Type of Ester	Peak Molecular weight	Molecular Weight Range	Expected Range
1	**Sample 'A'**	**Polyol Ester**	**921.7**	**Sharp Narrow distribution 1400-600**	**928.5**
2	**Sample 'B'**	**Polyol Monoester**	**494.2**	**Releatively broader distribution 600-200**	**446.6**
3	**Sample 'C'**	**Polyol Mixed Ester**	**1138.3**	**Sharp Narrow distribution 1200-600**	**1153.4**
4	**Sample 'D'**	**Polyol Ester**	**1167.6**	**Sharp Narrow distribution 1400-600**	**1193.0**
5	**Sample 'E'**	**PolymericEster**	**2190.6**	**Very Broad Distributioncovering Molecular weight 3500-400**	**1050**
6	**Sample 'F'**	**Mono alcohol Ester**	**406.9**	**Sharp Narrow distribution 400-420**	**412.68**

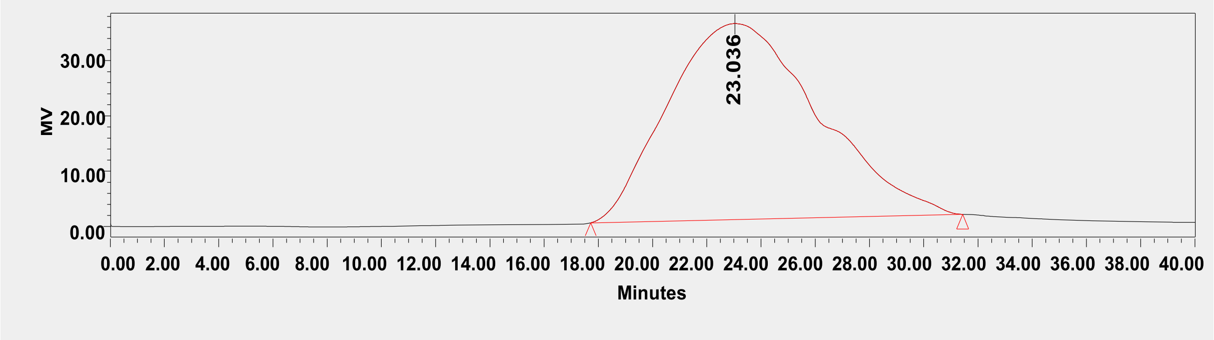
It was observed from the table that sample 'E' has shown peak molecular weight much higher than expected range . The possible reason may be due to polymerisation of dicarboxylate ester may have occurred while manufacturing these type of Esters.Molecular weight of remaining esters are in close aggrement with expected range . It was also observed that shape of curve of Sample 'E' is also broad indicating the broader /wider molecular weight distribution .The remaining samples samples' A', 'C', 'D' & 'F' have shown much sharper distribution . Sample 'B' has shown a hump at lower molecular weight region which indicates it may be crosslinked / internalcyclisation because of many adjescent hydroxyl group .



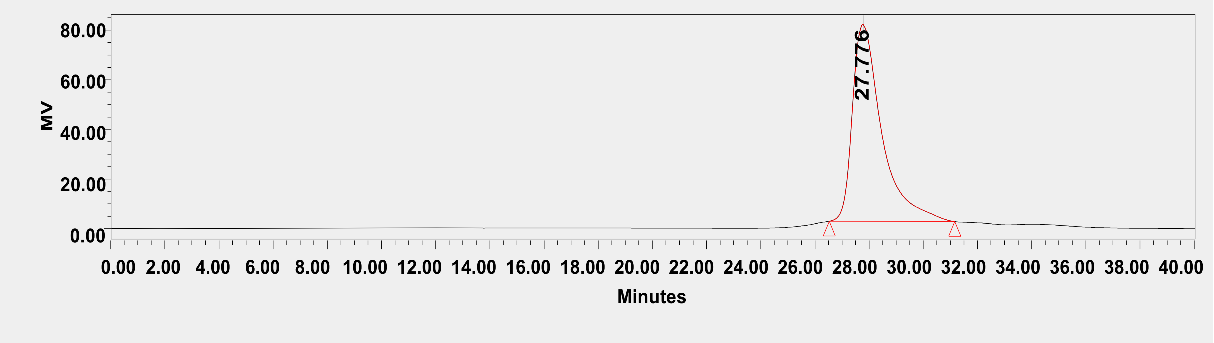
GPC Chromatogram of Sample ‘A’



GPC Chromatogram of Sample ‘B ’



GPC Chromatogram of Sample ‘E’

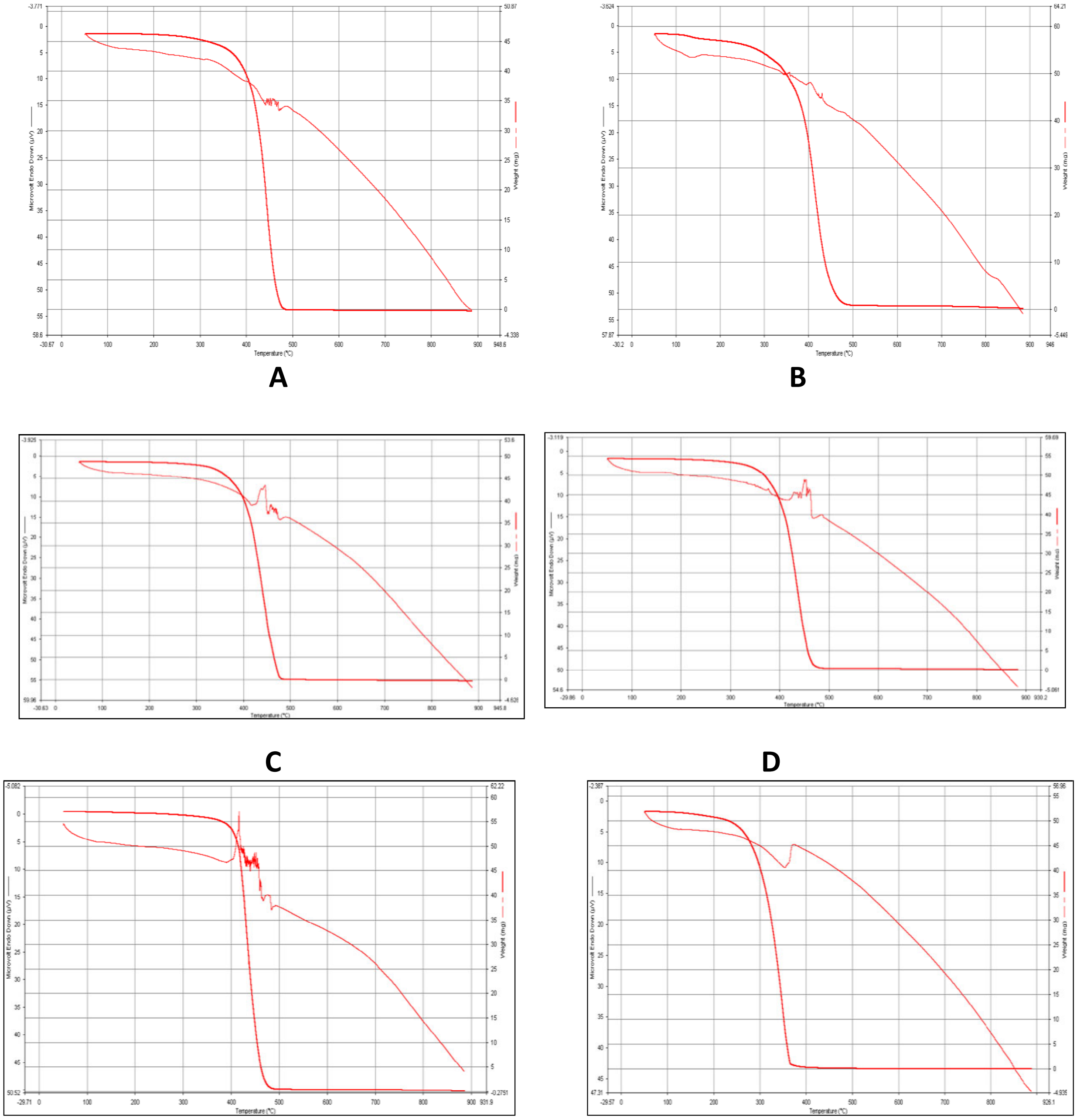


GPC Chromatogram of Sample ‘F’

Figure 5 : A typical Gel Permeation Chromatogram of each of Ester samples .

4.Thermogravimetric Analysis (TGA) with DTA Analysis : Thermogravimetric analysis of all the ester samples under study were carried out between 40 0C to 900 0C at a heating rate of 10 0C / minute under Nitrogen atmosphere.

Thermogram (TGA) and its differential thermogram (DTA) of each of the ester samples are recorded and analysed for their thermal behavior pattern as shown in Figure 5.



A B

C D

E F

Figure 6. A typical TGA Curve with DTA of Ester samples under study (A to F).

It was observed that all the samples under TGA study have shown different types of thermal decomposition pattern (also as seen as in differential thermograms) when the sample is heated between 50deg.C to 900 deg.C . Out of the samples of ester analysed, Sample **'E '**has shown better thermal stability over a wide temperature with flatter curve , followed by Sample **'D'** , Sample **'A'** and Sample 'C'. Sample 'B' and Sample 'F ' have shown relatively less flatter curve with less thermal stability. Sample 'B' has shown lowest thermal stability as observed in thermogram. and It was also observed that at high temperatures (at around 430 ^{0}C and around 470 ^{0}C) all the samples under study (Thermograms- '**A' to 'E'**) have shown thermo-oxidative degradation pattern. The remaining ester sample **'F '**have shown different type of decomposition pattern with single peak at 440 deg.C. Table 4 shows Decomposition temperature of each of the samples of Ester under study

Table 4

S.No	Sample Description	Type of Ester	Decomposition TemperatureDeg.C	Thermo oxidation temperature rangeDeg.C
1	Sample 'A'	Polyol Ester	292.1	400-489(457)
2	Sample 'B'	Polyol Mono ester	200.2	320-460(404)
3	Sample 'C'	Polyol Mixed Ester	310	400-485(452)
4	Sample 'D'	Polyol Ester	313	400-492(445)
5	Sample 'E'	Polymeric(PAG) Ester	390	394-494(451)
6	Sample 'F'	Mono alcohol Ester	220	290-373(355)

5. Rotary Bomb Oxidation Stability Test (RBOT) of Ester Samples under Study :

Table 5 shows oxidation of Ester samples under study being tested by RBOT Test as per modified method of ASTM D 2272 with temperature reduced from 150 deg.C to 100 deg.C . Initial pressure of oxidation chamber of all the ester samples under study. Time taken for pressure of oxidation chamber to drop from 90 psi to 65 psi.

Figure 7 : The physical changes after the test on Ester fluid and Copper Ring surface after Performing RBOT Test .

Table 5

S.No.	Sample Description	Type of Ester	Time interval taken pressure of oxidation chamber to drop from 90 psi to 65 psi in Minutes	Any other physical changes after the test on Ester fluid & Copper Ring surface
1	Sample A	Polyol Ester	87	Color of Sample become darkens with surface of copper ring partially black and partially shiny bronze shade
2	Sample B	Polyol Monoester	63	Color of Sample become darkens with surface of copper ring becomes black coated
3	Sample C	Polyol Mixed Ester	54	Color of Sample become darkens with surface of copper ring partially black and partially shiny bronze shade
4	Sample D	Polyol Ester	121	Color of Sample become darkens with surface of copper ring partially black and partially shiny bronze shade
5	Sample E	Polymeric (PAG) Ester	322	Color of Sample become very less darken more bright with surface of copper ring less black and Highly shiny bronze shade
6	Sample F	Mono alcohol Ester	1211	Color of Sample become very less dark with surface of copper ring very less black with highly shiny bronze shade

It was observed from the Table 5 that ester samples under study shows different oxidation pattern as seen from time interval taken pressure of oxidation chamber to drop from 90 psi to 65 psi in minutes. It was observed that sample **'B '** has shown lowest time interval and **'F '** being highest among the ester samples under study which indicates that oxidation stability of Ester **'B '**-Polyol Monoester is lowest and highest for sample 'F' Monoalcohol based Ester . Among the esters samples **'A', 'C', 'D'& 'E'** ,Sample **'E '**-Polymeric (PAG) based Ester has better oxidation stability than remaining samples **'A', 'C', & 'D'**. Among the remaining samples of polyol ester - ester **'A', 'C', 'D',** oxidation stability pattern is Sample '**D**' Polyol Ester >Sample '**A**' polyol ester > Sample '**C**' a mixed ester.

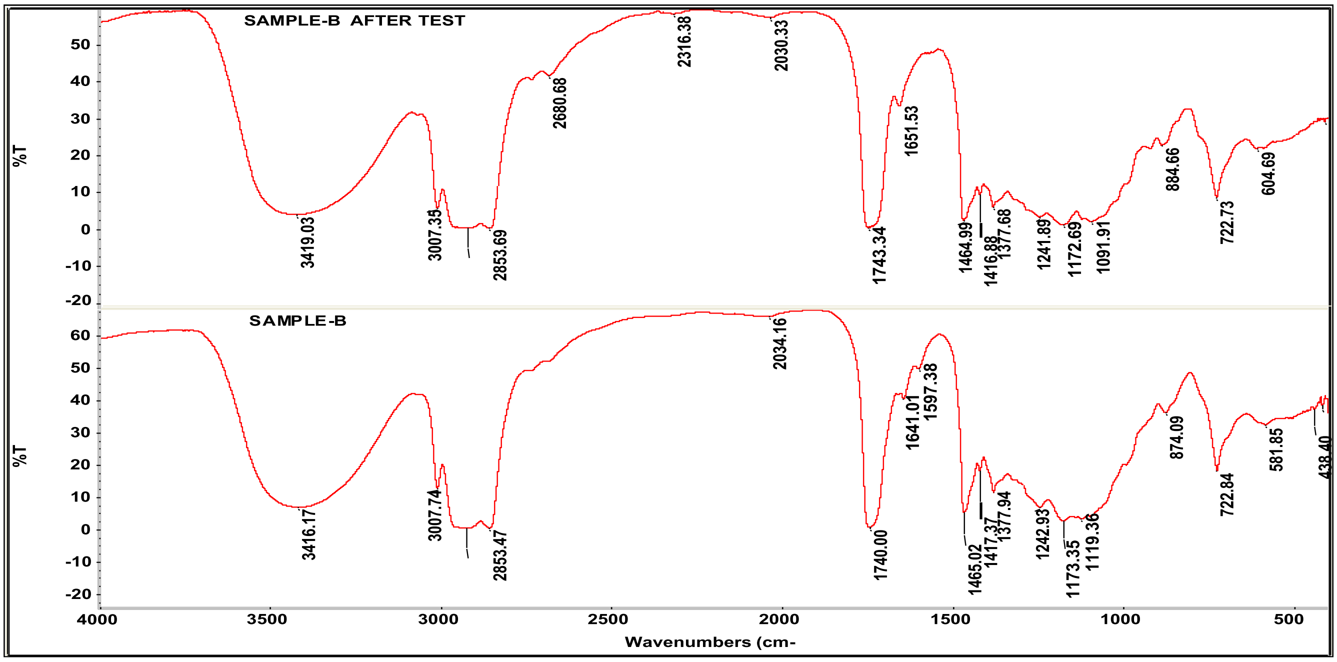
Fourier Transform Infrared (FTIR) Spectral Analysis of Esters under study after RBOT Test :

A) 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 .

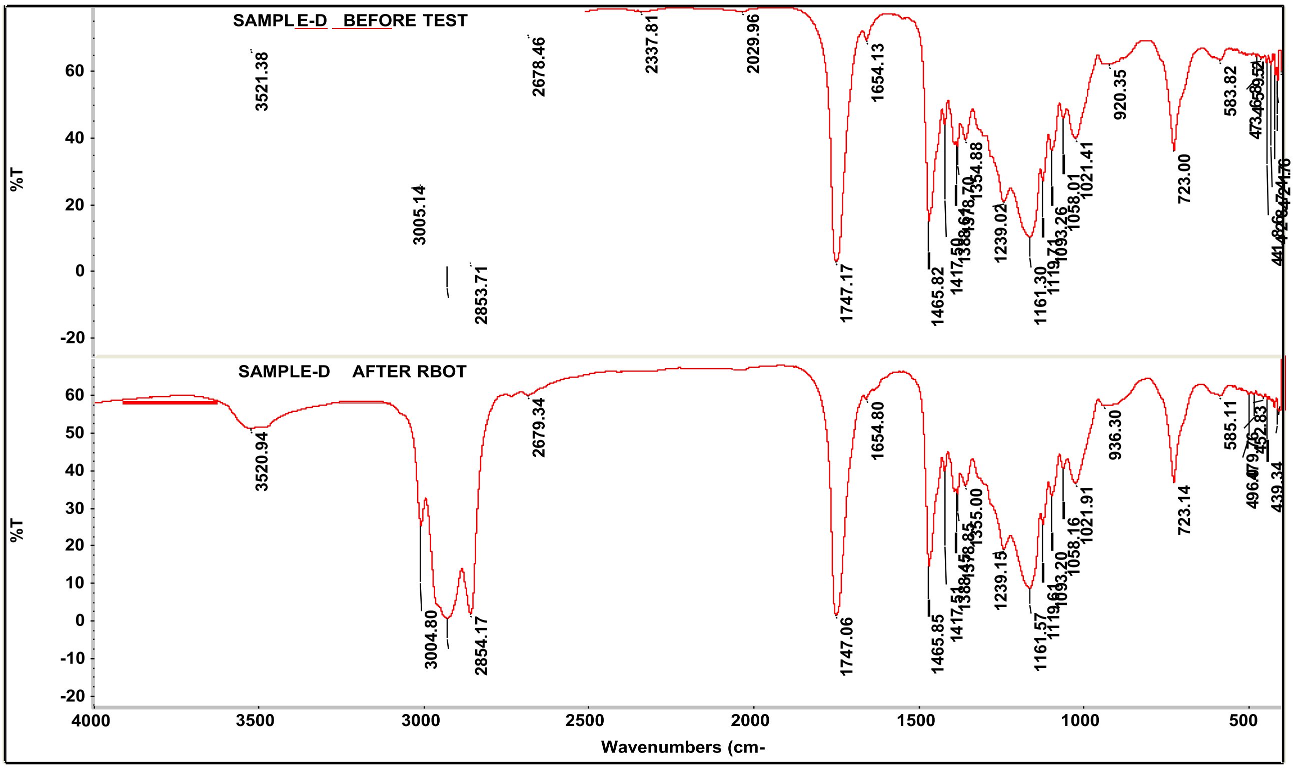
Table 6

S.No	Sample Code	Type of Ester Under Study	IR Spectral Characteristic Peaks changes observed after RBOT test
1	A	Polyol Ester	IR spectral changes observed -Intensity of Peak 3005 $cm^{-1}$from –CH from unsaturated carbon (mainly unsaturated fatty acid) reduces with rest of IR Spectral peaks remains unaffected
2	B	Polyol Mono Ester	IR spectral changes observed -Intensity of Peak 3008 $cm^{-1}$from –CH from unsaturated carbon (mainly unsaturated fatty acid) reduces with rest of IR Spectral peaks remains unaffected
3	C	Mixed type Polyol Ester	IR spectral changes observed -Intensity of Peak 3006 $cm^{-1}$from –CH from unsaturated carbon (mainly unsaturated fatty acid) reduces with rest of IR Spectral peaks remains unaffected
4	D	Polyol Ester	IR spectral changes observed -Intensity of Peak 3008 $cm^{-1}$from –CH from unsaturated carbon (mainly unsaturated fatty acid) reduces with rest of IR Spectral peaks remains unaffected
5	E	Polymeric (PAG) Ester	IR spectral changes observed -Intensity of Peak 3461 $cm^{-1}$from –OH become more and peak has become broad indicating polymeric ester breaking up to polymeric alcohol.
6	F	Mono Alcoholbased Mono Ester	IR spectral changes observed -Intensity of Peak 3004 $cm^{-1}$from –CH from unsaturated carbon (mainly unsaturated fatty acid) reduces with rest of IR Spectral peaks remains unaffected

The changes if any in the IR Spectra will indicate oxidation resistivity/ stability of the Ester fluid .The Ester fluid in the Synthetic Lubricants is prone for oxidation of unsaturated fatty acid with formation of carboxylic acid indicated by the presence peak at 1700 cm^{-1}. In all these samples under study did not show distinct 1700cm^{-1} The fall in the intensity of the characteristic peak around 3005cm^{-1} indicative of oxidation stability of the Ester fluid, Higher the intensity fall less is the oxidation stability of Ester fluid used . Sample ‘A’, ‘B’, ‘C’, ‘D’& ‘F’ have shown similar behavior pattern . However , Polymeric Ester Sample ‘E’ has shown different pattern with Intensity of Peak 3461 $cm^{-1}$from –OH become more and peak has become broad indicating polymeric ester breaking up to partially to polymeric alcohol & partial ester.

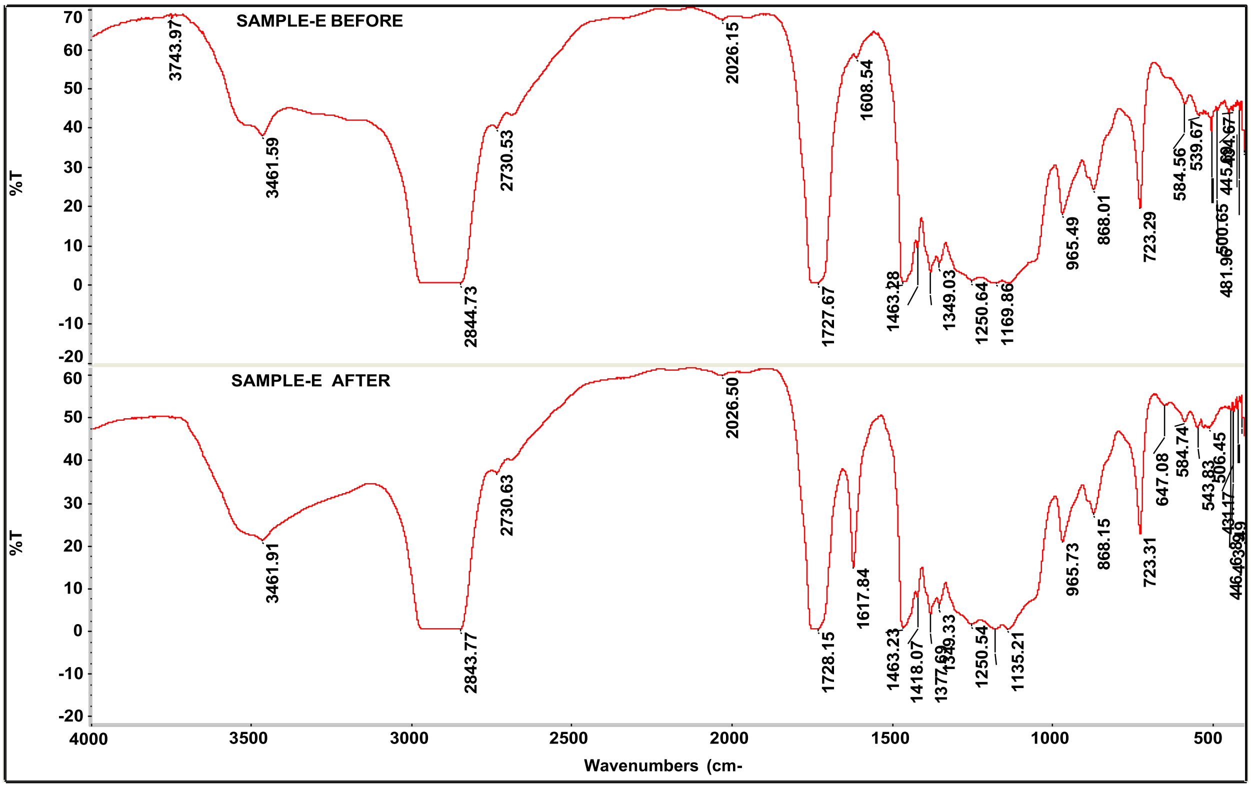


Sample **B** before and after RBOT test

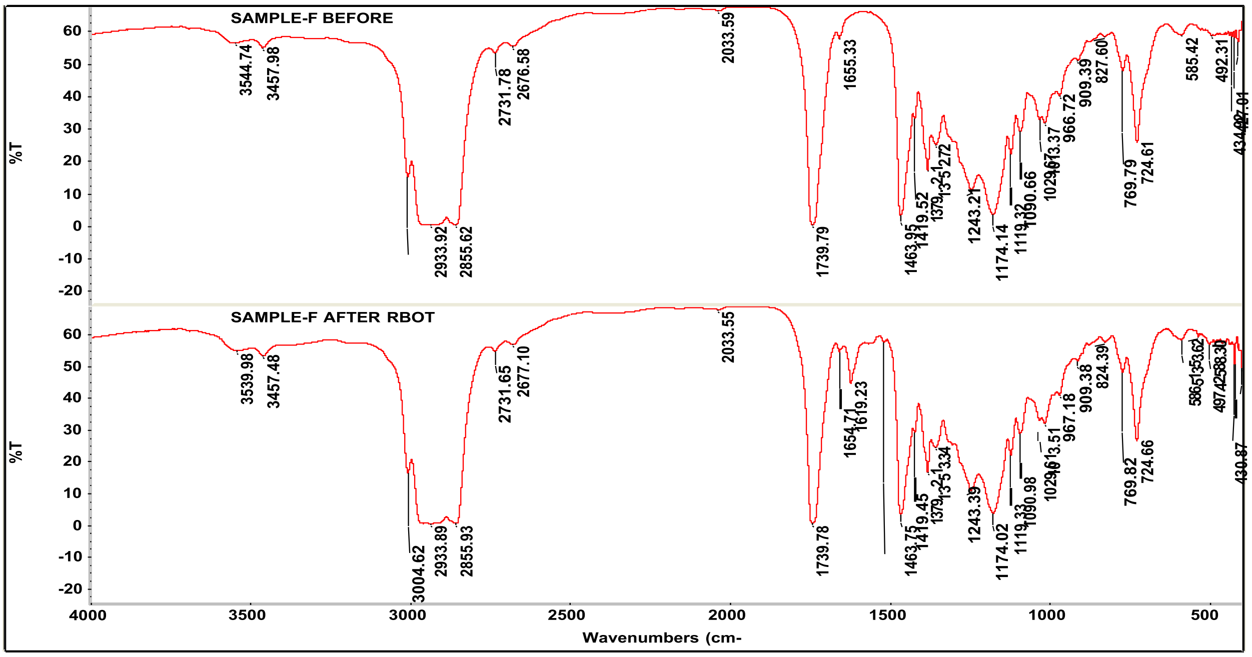


Sample **D** before and after RBOT test

Figure 8 : IR Spectral changes of Ester samples before and after RBOT Test



Sample **E** before and after RBOT test



Sample **F** before and after RBOT test

Figure 8 : IR Spectral changes of Ester samples before and after RBOT Test

B) **Effect of Antioxidant on the Ester fluid samples under study**:

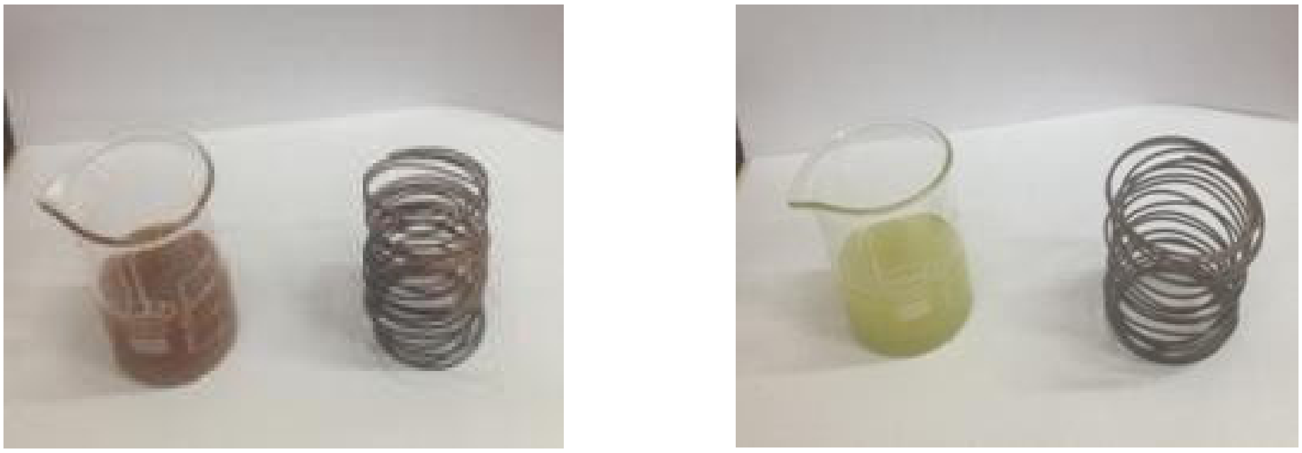
Table 7 shows comparative study of the effect of Aminic Antioxidant and Phenolic Antioxidant in similar dosage level on the selected ester under similar instrumental conditions.
It was observed that performance of these esters with treatment with both the type of antioxidant has enhanced time interval manifold when compared with virgin Ester sample under study. Phenolic antioxidant in Ester samples in 1% dosage level in IR spectrum is identified by the peak at 3650cm^{-1} and Aminic antioxidant by peak at 3420cm^{-1} & 1611cm^{-1} .

Table 7

Sl. No	Sample Description	Time interval taken forpressure of oxidation chamber to drop from90 psi to 65 psi **Without Antioxidant in Minutes**	Time interval taken for pressure of oxidation chamber todrop from 90 psi to 65 psi with **1% Aminic Antioxidantin Minutes**	Time interval taken for pressure of oxidation chamber to drop from 90 psi to 65 psi with **1% Phenolic Antioxidant in Minutes**	Any other physical changes after the test on Ester fluid &Copper Ring surface
1	Sample A	87	107	247	**Color of Solution becomes green to dark green with phenolic Antioxidant and brown to black.in case of Aminic Antioxidant. Copper ring surface become mixed black to shiny bronze color**
2	Sample B	63	199	316	**Color of Solution becomes green to dark green with phenolic Antioxidant and brown to black in case of Aminic Antioxidant.. Copper ring surface become mixed black to shiny bronze color**
3	Sample C	54	61	128	**Color of Solution becomes green to dark green with phenolic Antioxidant and brown to black in case of Aminic Antioxidant. . Copper ring surface become mixed black to shiny bronze**

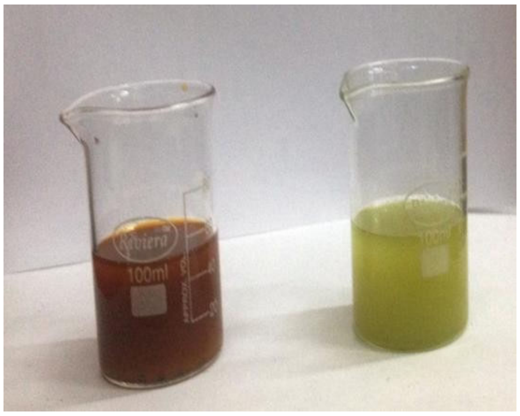
					color
4	Sample D	121	520	616	**Color of Solution becomes green to dark green with phenolic Antioxidant and brown to black. Copper ring surface become mixed black to shiny bronze color**
5	Sample E	322	486	592	**Color of solution becomes light green with phenolic Antioxidant and brown color with aminic antioxidant. Copper ring surface become mixed black to shiny bronze color**
6	Sample F	1211	1341	1478	**Color of Solution becomes green to dark green with phenolic Antioxidant and brown to black in case of Aminic Antioxidant.. Copper ring surface become mixed black to shiny bronze color**

From the **Table 7**, It was also observed that all the ester samples under study have shown much better oxidation stability interms of time interval taken with Phenolic antioxidant then with aminic antioxidant for similar dosage level. Similar trend is observed with both the antioxidants as observed for Samples without antioxidant mainly i.e. sample **‘B ’** has shown lowest time interval and **‘F ’** being highest among the ester samples under study which indicates that oxidation stability of Ester **‘B ’**-Polyol Monoester is lowest and highest for sample ‘F’ Monoalcohol based Ester . Among the esters samples **‘A’, ‘C’, ‘D’& ‘E’** ,Sample **‘E ’-**Polymeric (PAG) based Ester has better oxidation stability than remaining samples **‘A’, ‘C’, & ‘D’**. Among the remaining samples of polyol ester - ester **‘A’, ‘C’, ‘D’,** Oxidation Stability pattern is Sample ‘**D**’ Polyol Ester >Sample ‘**A**’ polyol ester > Sample ‘**C**’ a mixed ester.



a) Ester Sample E with Aminic Antioxidant

b) Ester Sample E with Phenoilic Antioxidant



c) Color of the Ester Sample E after RBOT test with both types of Antioxidant

Figure 9: The physical changes on Ester samples & Copper Ring surface after RBOT Test

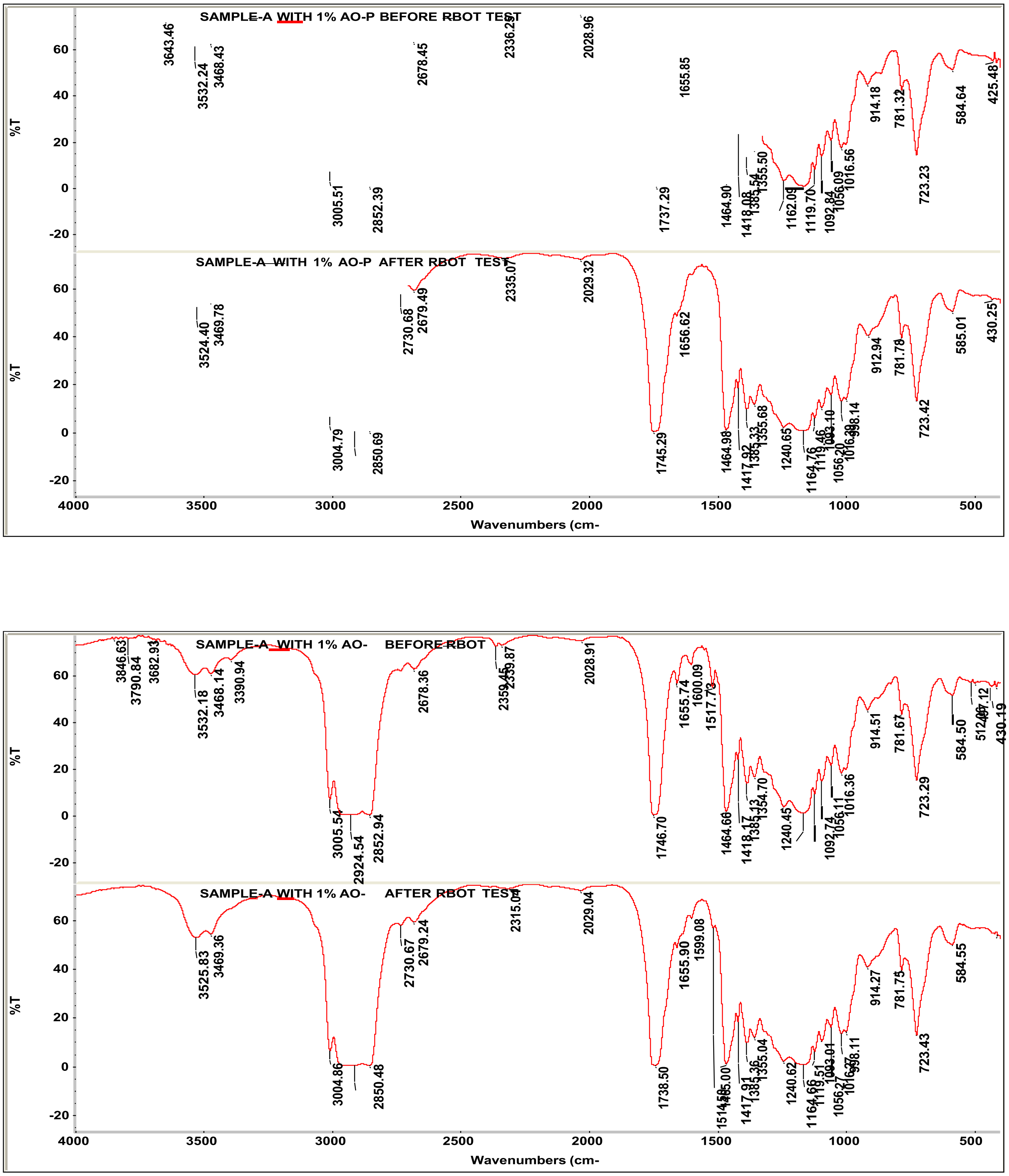


Figure 10: IR Spectral comparison of Ester Samples before and After RBOT Test after treatment with

Antioxidant Phenolic type (AOP) and Aminic Antioxidant (AO-A)

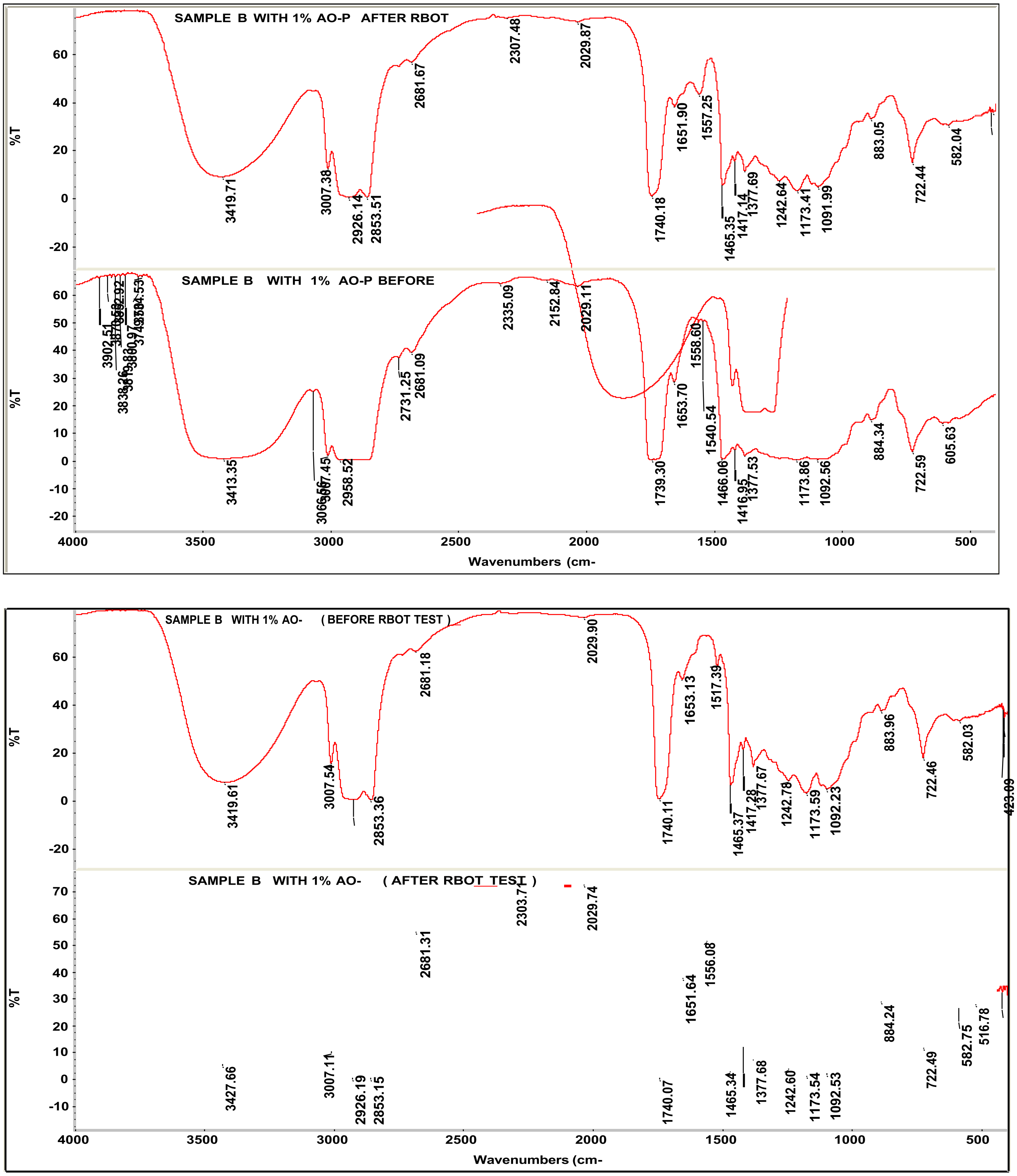


Figure 10: IR Spectral comparison of Ester Samples before and After RBOT Test after treatment with Antioxidant Phenolic type (AOP) and Aminic Antioxidant (AO-A)

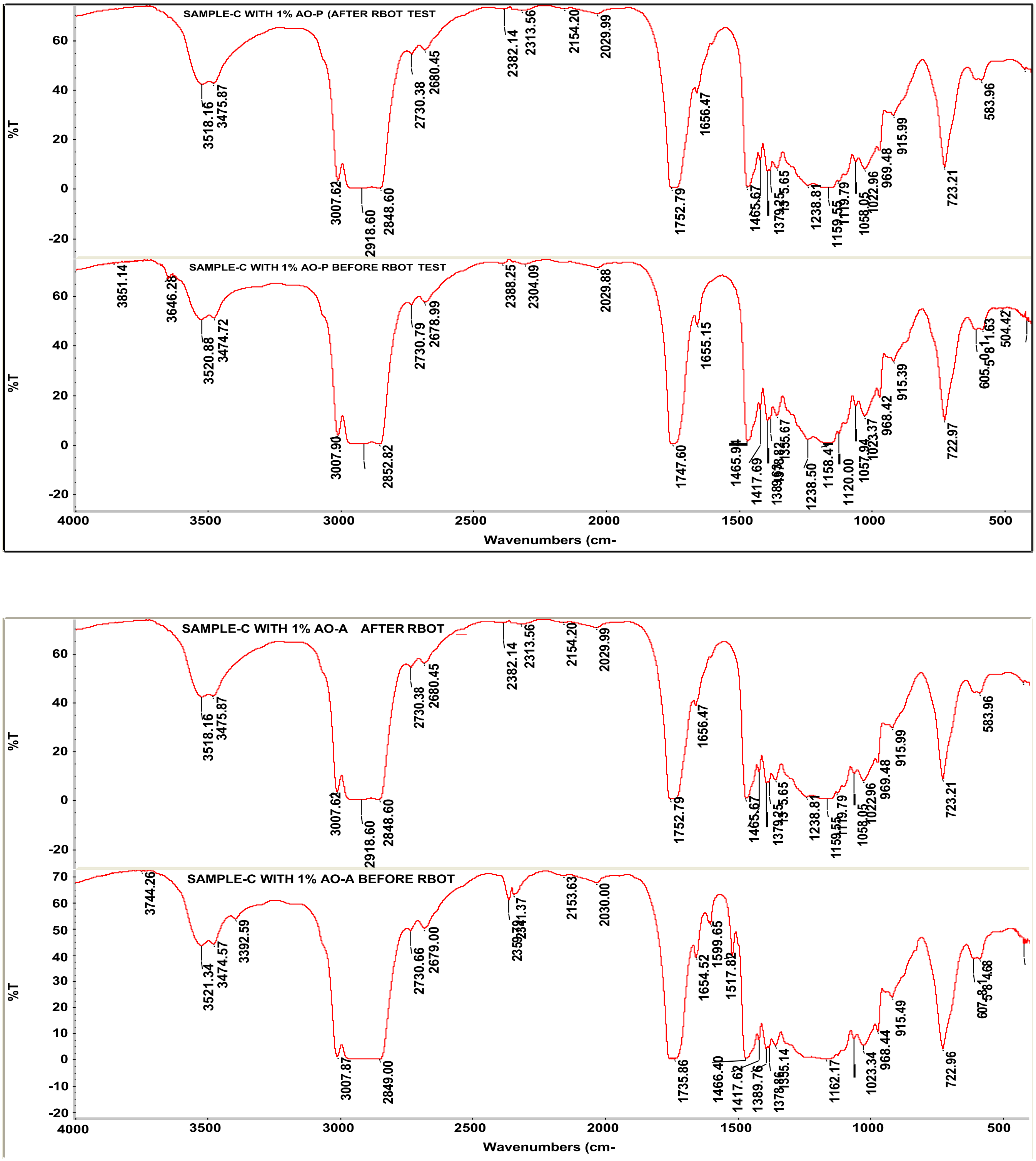


Figure 10: IR Spectral comparison of Ester Samples before and After RBOT Test after treatment with Antioxidant Phenolic type (AOP) and Aminic Antioxidant (AO-A)

Conclusions :

In the present study, attempt has made to use instrumental techniques such as FTIR, GLC , GPC & TGA with DTA for characterizing of different type of Ester based Fluid used for Synthetic Lubricants. RBOT / RPVOT tester is used for the oxidation stability behavior of these ester samples under study and have shown distinct differences in pattern. This can be used as a tool to distinquish Ester fluids and help to select for suitability for given end applications. This also helps to study the effect of antioxidant on the oxidation stability of various esters as well as helping in selecting suitable antioxidant for given applications.

Fourier Transform Infrared (FTIR) Spectral Analysis . indicates that there is a distinct difference in IR spectral features of Sample **'A'**, Sample **'B'** , Sample **'E'** & Sample **' F'** indicating difference in composition. However , Sample **'C'** & Sample **'D'** have similar IR spectral features with Sample **'A'** indicating similar type of composition .Intensity of peak around 3005 cm^{-1} indicative of extent of unsaturation due to unsaturated fatty acid as well as higher oxidisable hydroxyl group presence in the Ester fluid Gas Liquid Chromatographic (GLC) Analysis of the Ester samples shows the fatty acid composition of Ester samples under study.The fatty acid composition indicates the unsaturation & saturated fatty acid distribution which in turn contribute to oxidation to thermal stability to ester derived from the reaction of alcohol with fatty acid composition. The selection of ester fluid depends on type of alcohol as well as fatty acid composition for a given end application. It was observed that there is a distinct differences in the fatty acid composition of the esters samples under study .

Gel Permeation Chromatographic (GPC) analysis of Sample under study indicates molecular weight and its distribution of all the ester samples under study. It was observed that peak molecular weight obtained from GPC analysis is inline with respect to expected molecular weight range and can be used as a quality check for selecting the suitable esters for given applications .

Thermogram (TGA) and its differential thermogram (DTA) of each of the Ester samples were recorded and analyzed for their thermal degradation behavior pattern. Out of the samples of ester analysed, Sample **'E '**has shown better thermal stability over a wide temperature with flatter curve , followed by Sample **'D'** , Sample **'A'** and Sample **'C'** . Sample **'B'** and Sample **'F '** have shown relatively less flatter curve with less thermal stability **. Sample 'B' has shown lowest thermal stability as observed in thermogram.** and It was also observed that at high temperatures (at around 430 ^{0}C and around 470 ^{0}C) all the samples under study (Thermograms- **'A' to 'E'**)have shown thermo-oxidative degradation pattern . The remaining ester sample **'F '** have shown different type of decomposition pattern with single peak at 440 deg.C.

Oxidation Stability Test of Ester samples under study shows different oxidation pattern as seen from time interval taken pressure of oxidation chamber to drop from 90 psi to 65 psi in minutes. It was observed that there is a distinct variation in oxidation stability of the Ester samples under study. sample 'B ' has shown lowest time interval and 'F ' being highest among the ester samples under study . Among the esters samples 'A', 'C', 'D'& 'E' ,Sample 'E '- has better oxidation stability than remaining samples 'A', 'C', & 'D'. Among the remaining samples of polyol ester - ester 'A', 'C', 'D', oxidation stability pattern is Sample 'D' >Sample 'A' > Sample 'C' . Similar pattern is observed on the effect of Antioxidants (Phenolic & Aminic Type) on these ester samples on same dosage level . It was also observed that these esters samples showed similar trend of relatively much better performance with Phenolic Antioxidant over aminic antioxidant although latter ispreferred.

Infrared spectra of each of the samples before and after the oxidation test were recorded and compared for any IR spectral changes in the respective samples were Studied . The partial splitting of Ester to acid & alcohol with appearance of peak at 3400cm^{-1} (- OH) and appearance of carboxylic acid indicated by the presence peak at 1710 cm^{-1} and reduction of Intensity of peak at 3005 cm^{-1} indication the oxidation of Ester functionality. The intensity of these characteristic peaks indicative of oxidation stability of the Ester samples . Similar observation was observed with effect of antioxidant study on the ester samples with peaks associated with antioxidants getting depleted such as 3650cm^{-1}or 3400cm^{-1} .

The information obtained from the above study will be useful in understanding the characterizing the ester based fluids for selection of Ester based fluids for suitability for use in given applications .Correlation with field experience of performance of the Synthetic Ester based lubricant based on these ester base fluids with above study can provide useful information.

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Acknowledgements

The authors are sincerely grateful to the Management of M/s Balmer Lawrie & Co. Ltd. and NLGI IC for giving an opportunity to present the above work.

Synthesis and Characterization of Hybrid Thickener Containing Greases for Bearing Applications

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1. Abstract

Greases are widely applied in bearings. The main purpose of greases in bearings is to separate the contacting surfaces and thus to improve the bearing life. Greases also provide inherent sealing, corrosion protection and lesser friction. Limitations of lubrication with greases in bearings includes, deterioration of lubrication conditions over a time due to grease hardening, aging and oil depletions from grease fractions stored close to rolling contact. In many instances, bearings also suffer from a relatively unfavorable grease distribution. Present study manufactured laboratory scale grease with lesser process complexity and energy requirements. The synthesized grease is characterized for bearing lubrication and experimental results showed better film formation, with lesser friction and self-induced temperature. Bearing corrosion studies showed improved corrosion resistance to the water with lesser amount of additives. The synthesized hybrid thickener containing grease with lesser friction, better film formation and longer relubrication interval provides the improved bearing life.

2. Introduction:

Lubricating greases are semisolid product containing a thickening agent and base oil. Grease also contains various performance enhancing compounds in tis formulations called as additives. The type and concentration of additives in the formulations is depends upon its course and field of application. Greases are the most common lubricants in bearings. Bearings are important mechanical components involved in the rotating parts of all the materials utilized in different fields like automobiles, railway industries, machine tools, aviation industries, marine industries, off highway equipment's, paper mill industries, cement industries and many more(1). Behavior of oil lubrication is most understood type of lubrication for rolling bearings than behavior of grease lubrication in the similar types of Tribological systems, although greases are the most preferred lubricants for rolling bearings

(2). Greases are important to rolling bearings for the purpose of proper operation, low friction and longer life (3). Primary reason of using lubricating grease over lubricating oil for lubrication of rolling bearings is which prevents the lubricant flowing out of the bearing systems and provides good sealing effect. Along with performing lubricant functions, lubricating grease avoids the external contamination within the rolling bearings system (4). Unless lubricating greases, the rolling elements of the bearings are not separated from the rings, severe stress will occurs and cause the failure of bearings (5). Primary functions of lubricating grease in rolling bearings include providing a film of lubricant between the contacting surfaces with lesser friction. Avoiding wear surfaces and providing corrosion protection is the second to the primary functions. The most widely used mechanism to describe the grease lubrication rolling bearings is from Booser and Wilcock (6). They postulated that, the grease acts as an oil reservoir, where the oil is slowly released into the contacting surface of the rolling bearings. Over a time period of application the lubrication conditions in rolling bearings deteriorates due to grease hardening, aging (7, 8) and oil depletions from grease fractions (9) stored closer to the rolling contact. Due to the presence of churning inside the rolling bearings, the grease is pushed out of the contacting surfaces into the edges of the bearings. In many instances bearings suffers from a relatively unfavorable grease distribution over a time period. Greases are sensitive to physical and chemical aging and that is an irreversible process. Due to the aging or hardening, replenishing greases by relubrication can be difficult. Along with few inherent limitations of greases in the rolling bearings, grease manufacturing process itself is a complex and energy intensive process (10). Performance reliability and product quality requires extensive experience and in depth knowledge of grease processing technology. Large portion of grease produced by manufacturers are lithium based greases and it is the most commonly used grease in the rolling bearings. The cost of Lithium hydroxide, one of the raw materials in the lithium greases are increased by three fold in the recent months and expected to increase further in near coming future (11). There is a huge scarcity of Lithium Hydroxide in the global market due to the huge requirement of lithium metal in the recent developed technology like Hybrid battery manufacturing (12). Many of the grease manufacturers and its end users are looking forward for alternative products with cost competitiveness to the Lithium greases along with retaining the equal or superior performance quality of the lithium greases. In general greases are considered as Gel or sol based colloidal solutions. Gels are made up of a dispersing medium dispersed in the dispersing phase. The principles of grease as a product is similar to the sols, where a thickening agent or thickeners acts as the dispersing phase and the base oil acts as the dispersing medium. There are many products available in the market, which are made up of thickening agents as dispersing phase and base oil or thinner as dispersing medium, for example candles, paints, paste, resin based adhesives etc. Present study utilized combination of two different polymers as the thickening agents and traditional base oil of the greases as the base oil for the product. The synthesized finished products were tested for its grease properties like oil bleeding rate, corrosion resistance, film forming capability in the bearings, dropping point, load carrying ability and anti-wear properties. Synthesized products were added with performance enhancing additives to have better anti-corrosion and anti-oxidation properties.

3. Materials and Methods:

Following methods and materials were utilized in the work.

Raw materials like polymers for thickening the greases were obtained commercially with purity level of more than 95 percentile. Synthesizing materials required for synthesis process like glass reaction vessel, temperature controller and quenching plate were obtained commercially.

3.1. Synthesis of Hybrid Thickener containing grease:

Total concentration of thickener was fixed to 19.2 percentile, in that 12.48 percentile of polymer-I, which is ester terminated polymer and Polymer-II has two components, one is a Homo polymer with concentration of 6.384 percentile and second component is a copolymer with concentration of 0.336 percentile. Three different types of base oils (65cSt of viscosity at 40°C) like mineral oil, ester oil and Synestic oil were utilized. To enhance the grease performance 4 percentiles of additives like antioxidants, anticorrosion and anti-wear were added. Synthesis of the grease was performed in a glass reaction kettle of 1 kilogram capacity. Polymer-I was charged in to the glass reaction vessel, which is connected with temperature controller, thermocouple, dry nitrogen gas and a motorized mechanical stirrer. Reaction vessel was heated to a temperature above the melting point of Polymer-I. Base oil was slowly added to the reaction vessel with constant stirring and keeping the temperature above than melting point of Polymer-I. Temperature of reaction vessel was raised to 180±2°C and Polymer-II containing mixture of homo and copolymer was added. Once the Polymer-II was completely melted in the reaction vessel, temperature of the vessel was raised to 200±2°C and kept under constant stirring and dry nitrogen gas for about 30 minutes. After the completion of 30 minutes, entire reaction mixture was poured into a quenching plate. After recovering from quenching plate grease was stored in room temperature. A batch grease capacity of 3kilogram was synthesized in the grease reaction kettle by utilizing same above methodology. Synthesized product was characterized for its grease like properties. Following are the details about different characterization tests utilized in the present work.

3.2. Dropping point of the grease:

Method followed for dropping point was DIN ISO 2176 and experiment was done in the automated Metler machine. The dropping point of grease is the temperature at which the grease starts to flow, usually due to melting of the thickener. The sample is placed in a cup and heated at a uniform rate. When the first drop of oil falls from the lower end of the cup, the temperature is observed and reported as dropping point.

3.3. Mechanical Stability:

3.3. (i) Work Penetration after 60 Strokes

ASTM D217 method was followed to perform work penetration test after 60 strokes. The sample is brought to 25±0.5°C (77 6 1°F) and placed in the worker cup. The sample is subjected to 60 double strokes in the grease worker. The penetration is determined immediately by releasing the cone assembly from the penetrometer and allowing the cone to drop freely into the grease for 5 seconds. Three determinations are made and average was taken as final penetration.

3.3. (ii). Roll stability test:

Modified ASTM D1831 method was followed to perform the shell roll stability test. 50gram of test grease sample was placed into the grease cup and measured the work penetration. The measured sample was applied to rolling cylinder and roller with uniformity. Closed cylinder was run in the standard roll stability tester for 50hours at 80°C. After sample was cooling to 25°C work penetration was measured as per ASTM D217 method.

3.4. Four ball weld load:

Standard SKF method was utilized to find the maximum load carrying capability of the greases. The tester is operated with one steel ball under load rotating against three steel balls held stationary in the ball pot. The test grease was filled completely in the ball pot. The rotating speed is 1450± 50 rpm. Lubricating greases are brought to room temperature and then subjected to a series of tests of 60 seconds duration at increasing loads of 200N, until welding occurs.

3.5. Four ball wear scar:

Standard SKF test method was followed to find the anti-wear properties of different greases. Three 12.7-mm [1⁄2-in.] diameter steel balls are clamped together and covered with the grease to be evaluated. A fourth 12.7-mm diameter steel ball, referred to as the top ball, is pressed with a force of 1000 N into the cavity formed by the three clamped balls for three- point contact. The temperature of the test lubricant was not maintained and then the top ball is rotated at 1400 rpm for 60 seconds. Lubricants are compared by using the average size of the scar diameters worn on the three lower clamped balls.

3.6. EMCOR- Anti corrosion Test:

Standard DIN 51802 method was followed to perform EMCOR test. Test is to find the capability of grease to protect against corrosion when steel bearings in contact with distilled water. Bearing type used was 1306K/236725 (special bearing with stamped steel cage). Conditions used were, 80rpm of speed for 8 hours of first three days, then bearing with greases were standstill for about 108 hours with the presence of water. 10gram of grease sample was utilized for testing. Two bearings were utilized per grease; each was filled with 20ml of distilled water after 30 minutes of running in. After dismounting, outer ring was visually inspected for the presence of rust spots and rated according to the standards.

3.7. Oil Separation/ Bleeding rate:

DIN 51817 standard method was utilized to find the tendency of grease to separate the oil under stationary conditions. 30±5 gram of sample was placed into grease filter and 100 gram dead weight was placed upon the grease. The complete set up was placed in a cup and kept under oven at 40°C for 168 hours. Amount of separated oil, which is collected in the cup, was weighed and measured for percentage of oil separated.

3.8. Bearing Characterization:

Bearing characterization was performed with a specialized test rig called as SKF vertical rig. Both base grease and grease with 4 percent of additives were tested with standard SKF Thrust Ball Bearing (TBB-51104) and SKF tapered Roller bearings (TRB-30204J2/Q). Equipment can measure the self-induced temperature, Friction torque and film thickness between the contacting surfaces (Lubcheck) of the bearings. Experiments are performed at the spindle speed of 1500 rpm, approximately 1 GPa of contact pressure. Total amount grease applied before starting of experiment to the bearing was 1.25g. Test was run for 3 hours for TBB and for TRB test was run for 4 hours with 1gram grease relubrication at the end of the third hour.

4. Results:

Three different composition of grease with three different base oils like mineral oil, ester oil and Synestic oil were synthesized in the laboratory scale. Thickener used consists of two different polymers. The process was simple and less energy consuming when compared to the traditional grease synthesis process. The synthesized grease does not require any processing or shearing technology to soften the grease before applied in the application. Synthesized greases were very sensitive to mechanical stress and thermal stress, grease was very easy to work out once put under pressure. During application under shear, grease became softer and comparable to the NLGI 0 or 1 grade but once the conditions were reverse grease came back almost into its original consistency level. Synthesis processes of traditional greases like lithium are laborious and require intensive energy input into the process. After the grease synthesis, post processes also require energy to soften the greases to the required NLGI grade by the application. Due to higher shear resistance of traditional greases, it requires an intense milling process to get proper mixing of additives and to obtain the smoother texture of the greases. Alternative to the traditional greases, the newly synthesized greases does not require high energy consuming milling process.
Synthesized greases were characterized for its grease properties and for its bearing application. Commercially available standard Lithium soap based grease with mineral oil as base oil was considered as a reference sample for all the properties. Following is the test results for the characterization of newly synthesized greases.

4.1 Dropping point:

Dropping was tested as per DIN ISO 2176 standard. Dropping point of different greases are shown in the table-1

Sample Name	Dropping Point in °C
Hybrid Thickener Grease with mineral oil	146
Hybrid Thickener Grease with Ester oil	179
Hybrid Thickener Grease with Synestic oil	157
Standard Lithium grease with Mineral oil	185

Table-1: Dropping point of different greases

Hybrid thickener grease with Ester oil showed better dropping point than any other two combinations. Reference sample had the best dropping point. Experimental results showed that dropping point is not only related to any one of the raw material of the composition, instead it is the synergistic combination of the raw materials. Although thickener and additives of all three synthesized greases were similar, but difference in the base oil formed the difference in the dropping point. It was assumed that synergistic interaction between the ester oil and thickener provided the higher dropping point. It was observed that, after finishing the dropping point test for reference grease, outer layer of the grease in the sample cup turned to brown and in many instances into the dark brown, which indicates the oxidation of the grease.

4.2. Mechanical stability

Mechanical stability of the grease was measured by using grease penetrometer. There were two different methods were employed to test the mechanical stability of the synthesized grease and reference standard grease.

(i) Work penetration after 60strokes.

Test grease samples were worked for 60 strokes with the standard manual grease worker (Table-2). After the 60 strokes test grease samples were measured for work penetration test as per standard ASTM D217 method.

Sample Name	Work Penetration after 60Strokes in mm/10	NLGI Grade
Hybrid Grease with mineral oil	215	3-4
Hybrid Grease with Ester oil	207	3-4
Hybrid Grease with Synestic oil	178	4
Standard Lithium grease with Mineral oil	240	3

Table-2: NLGI grade of different greases

(ii) Roll stability test:

50 gram of the different grease samples were applied to the cylinder and roller of the roll stability tester. Test was carried out as per the modified ASTM D1831 method. Cylinder was rolled with the speed of around 165 rpm at 80°C for 50 hours. Samples were tested for its penetration value with standard grease penetrometer (Table-3). Newly synthesized greases had very high NLGI grades, in normal instance the higher NLGI grade greases are not recommended to use in the bearings. New greases showcased less resistance to shear stress or thermal stress. It was observed in the roll stability tester, when the test was completed the greases were almost transformed into NLGI 0 or 1 grade but once the conditions reverse back greases were hardened enough to become NLGI 2 or 3 grade. The thixotropic behavior has a great impact during the application, where in under stressed conditions grease will become softer and thinner and enter into narrow contact region to perform the lubricant function.

Sample Name	Work Penetration after Roll stability tester in mm/10	Change in mm/10
Hybrid Grease with mineral oil	267	52
Hybrid Grease with Ester oil	254	47
Hybrid Grease with Synestic oil	250	72

Standard Lithium grease with Mineral oil	325	85

Table-3: Work penetration of different greases after roll stability

4.3. Four Ball weld load:

Standard SKF method was utilized to perform the four ball weld load test. Spindle speed was set at 1450± 50 rpm and series of tests were continued for 60 seconds with increasing of 200N load for every step until weld occurs. The results were mentioned in the table-4. Four ball weld load indicates the film forming capability during extreme pressure/ load situation. Although all the greases had same type and concentration of thickener and additives but difference in base oil type and its interaction with the thickener and additives provided the ester oil containing hybrid thickener grease better load carrying capability.

Sample Name	Weld load in N
Hybrid Grease with mineral oil*	2200
Hybrid Grease with Ester oil*	≥2200
Hybrid Grease with Synestic oil*	2200
Standard Lithium grease with Mineral oil*	1400

Table-4: Four ball weld load test for different greases (*with additives)

4.4. Four ball wear scar:

Standard SKF method was utilized to test the four ball wear scar for different test greases. Spindle speed of 1400± 50 rpm, normal load of 1400N were utilized and test was run for 60 seconds. Wear scar diameter (table-5) was measured under optical microscope.

Sample Name	Average wear scar in mm
Hybrid Grease with mineral oil*	2.2
Hybrid Grease with Ester oil*	2.3
Hybrid Grease with Synestic oil*	2.5
Standard Lithium grease with Mineral oil*	Welded (2.2mm at 1000N)

Table-5: Four ball wear scar test results for different greases (* with additives)

4.5. EMCOR corrosion tester:

EMCOR was utilized to find the anti-corrosion properties of greases with distilled water. All the greases showed excellent anti-corrosion properties with distilled water (table-6). EMCOR test showed all the greases were able to provide good corrosion resistance in the presence of distilled water. However new greases showed absorbance of water, due to which color of the grease turned into white (Figure-1). It was observed that, little squeezing of grease expelled the absorbed water.

Figure-1: Grease color was changed during EMCOR test with distilled water

Sample Name	EMCOR Ratings
Hybrid Grease with mineral oil*	0-0
Hybrid Grease with Ester oil*	0-0
Hybrid Grease with Synestic oil*	0-0
Standard Lithium grease with Mineral oil*	0-0

Table-6: Evaluation of anti-corrosion properties of different greases with EMCOR (*with additives)

4.6. **Oil separation test:**

Oil separation/ oil bleeding test was performed as per DIN51817 method to evaluate the tendency of grease to separate during storage (Table-7). Experimental result showed that less amount of oil leaked by grease with Synestic oil. It may be due to the higher grade of NLGI.

Sample Name	Oil bleeding rate in %
Hybrid Grease with mineral oil*	1.1
Hybrid Grease with Ester oil*	1.6
Hybrid Grease with Synestic oil*	0.3
Standard Lithium grease with Mineral oil*	0.8

Table-7: Oil bleeding rate of different greases (* with additives)

4.7. **Bearing characterization**

Bearing performance of the greases was performed in vertical rig equipment. Tests were performed to evaluate the friction torque, film thickness and self-induced temperature of different greases. Conditions used for test was 1500rpm and approximately 1GPa of contact pressure. Two different bearings like Thrust Ball Bearing (TBB-designation of 51104) and Tapered Roller Bearing (TRB-designation of 30204J2/Q) were utilized for test. Initially bearings were filled with 1.5gram of grease. Test was run for 3 hours for TBB and for TRB test was run for 4 hours with 1gram grease relubrication at the end of the third hour.

4.7.1. Grease Characterization with TBB

Friction Torque of grease samples in TBB:

Hybrid thickener grease with the ester oil showed a smooth friction torque and commercial standard grease showed a very less but variable friction torque.

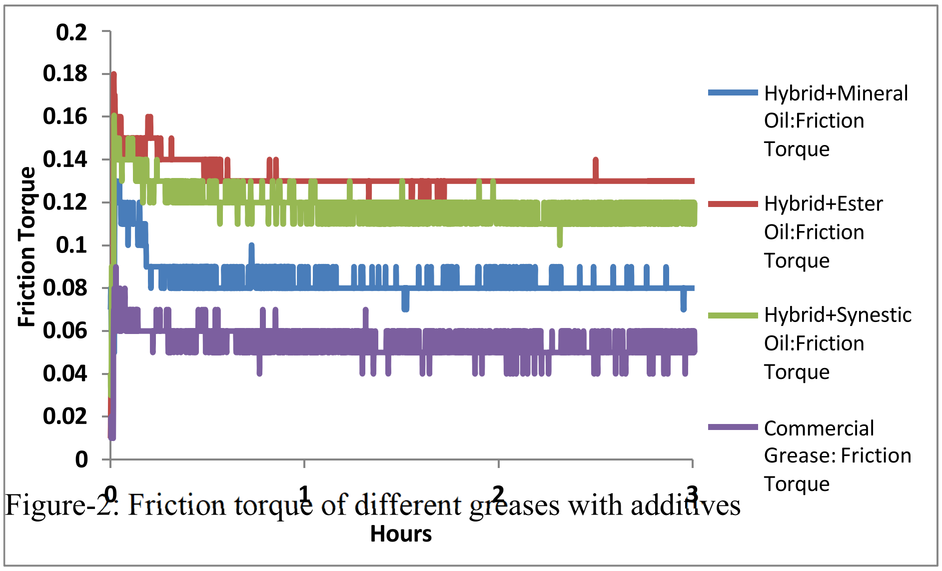

Figure-2: Friction torque of different greases with additives

Self-induced temperature of grease samples in TBB:

Hybrid thickener grease with ester oil showed the lowest self-induced temperature. Although friction torque of commercial grease was lower but it has the highest self-induced temperature. This signifies that commercial grease had the maximum variation in the friction torque during the test.

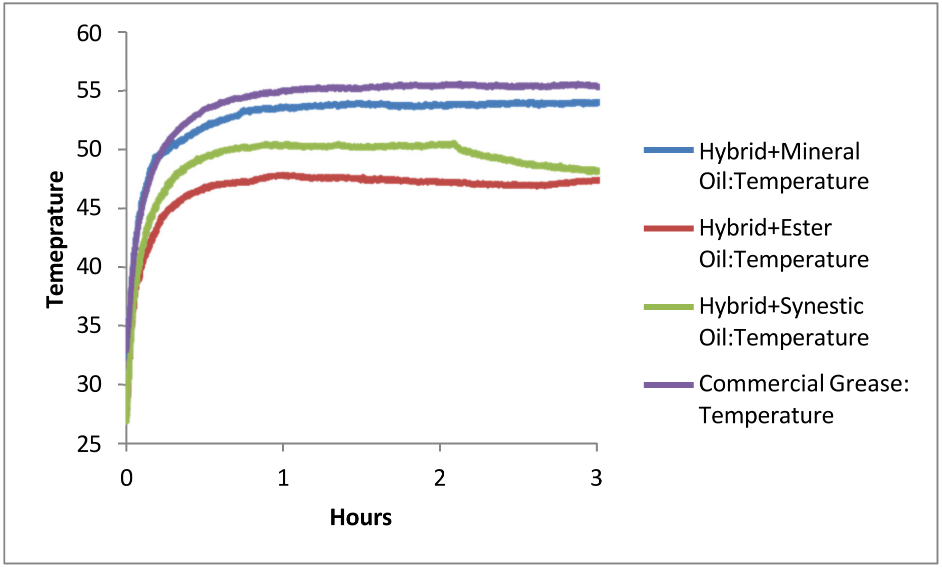

Figure-3: Self-induced temperature of different greases with additives

Lubricant film thickness of grease samples in TBB:

Hybrid thickener grease with ester oil had the uniform lubricant film thickness during the test period. Commercial grease showed peak and valleys and thus indicates that bearing was not running smoothly.

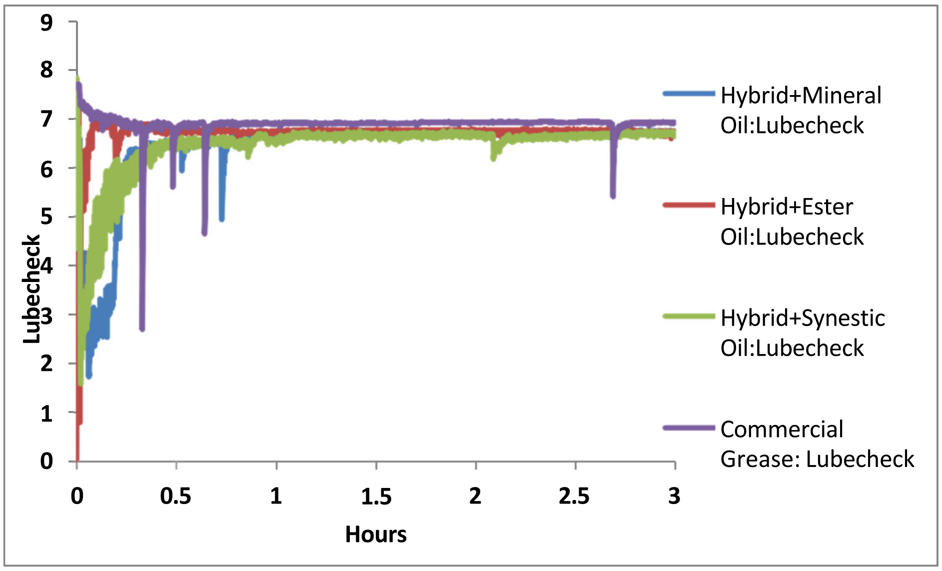

Figure-4: Lubricant film thickness of different greases with additives

4.7.2. Grease Characterization with TRB (Tapered Roller Bearings)

Friction Torque of grease samples in TRB:

Commercial grease had a consistently varying friction. Hybrid thickener grease with ester oil and mineral oil showed uniform friction torque throughout the test.

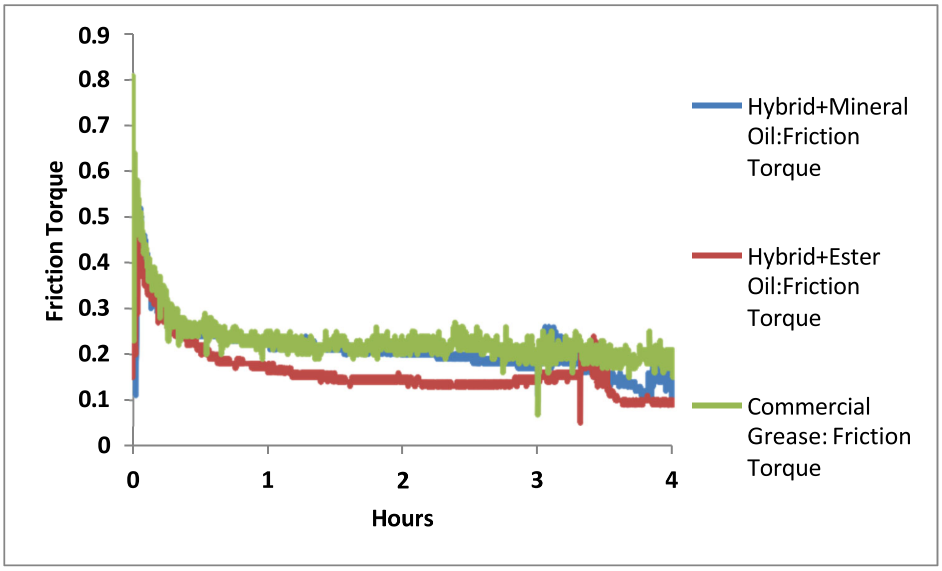

Figure-5: Friction torque of different greases with additives in TRB

Self-induced temperature of grease samples in TRB:

Hybrid thickener grease with ester oil showed lower self-induced temperature. After relubrication of 1 gram of grease at the end of 3 hour, commercial grease and Hybrid thickener grease with mineral oil showed rapid increase in the temperature, whereas hybrid thickener grease with ester oil showed lesser slope for increase in temperature

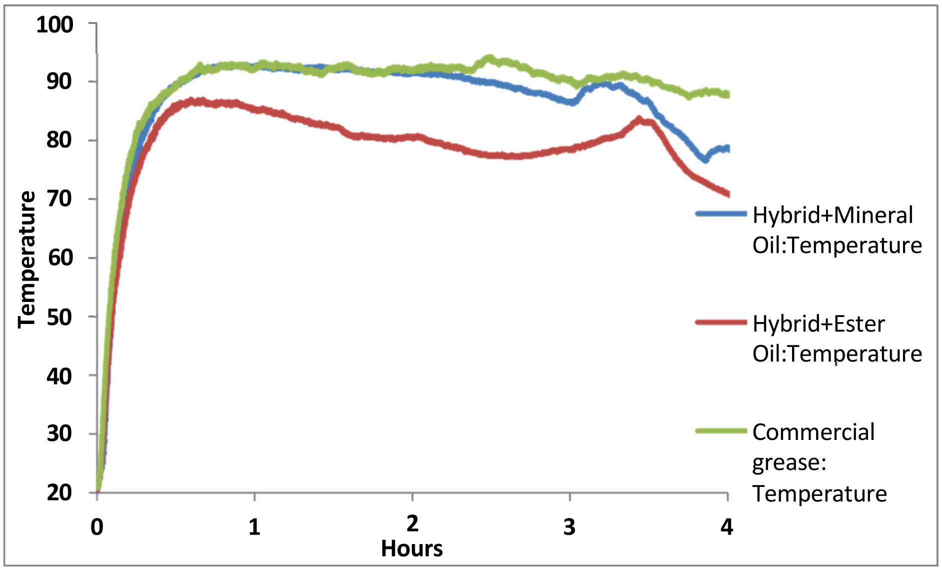

Figure-6: Self-induced temperature of different greases with additives in TRB

Lubricant film thickness of grease samples in TRB:

Grease with ester oil showed very good film forming capability and commercial grease was the least capable to form the film. After relubrication film was completely lost in commercial grease but other greases it was lost but not completely and grease with ester oil showed faster regain of the film.

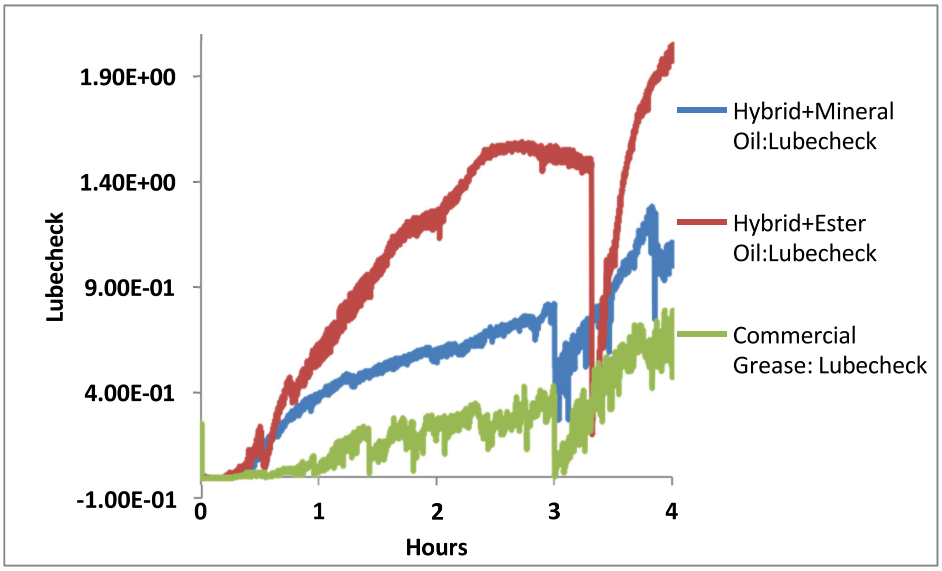

Figure-7: Lubricant film formation of different greases with additives in TRB

Bearing characterization was performed with Thrust Ball bearing and Tapered Ball Bearing. Both the bearing studies showed that, grease with ester oil performed better than other greases including the commercially available standard grease.

5. Conclusion:

The present increased cost scenario of Lithium hydroxide and requirement of better efficient grease processing technology, it is very essential to develop new products to have advantageous over traditional grease products in both cost and technology of grease making. Present study developed greases with novel polymers based hybrid thickener and three different base oils. All the three formulations showed grease properties and ester oil based formulation showed better lubrication performance in bearing than commercially available standard greases. Although dropping point of synthesized greases were less, but bearing studies showed better lubricating ability of new greases compared to commercially available standard lithium grease.

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Development of Advanced Calcium-Lithium Soap Grease with Minimum Uses of Lithium Hydroxide

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ABSTRACT

Presently the use of lithium hydroxide in lithium soap and lithium complex soap greases is increasing because of good to excellent properties viz. heat resistance, shear stability, pumpability and thermal stability of these greases as compared to other metallic soap greases. These greases are also cost effective as compared to new generation overbase calcium sulphonate and polyurea greases. The use of lithium hydroxide is also increasing gradually in lithium batteries which are the power storage source of most of the electronics devices in this 'SMART' world. On the other hand the natural sources of lithium hydroxide are also depleting. As a consequence the price of lithium hydroxide is becoming costlier day by day with increasing demand of lithium hydroxide for grease manufacturing as well as electronics industries. In this situation it is highly demanding for grease manufacturing industry to come forward with alternatives of lithium soap greases in order to reduce the dependency on lithium hydroxide in grease making and thereby help the world to becoming 'SMARTER'.

The present paper elaborates about the development of advanced calcium-lithium soap grease with the minimum use of lithium hydroxide. The developed grease offers the properties closer to lithium soap greases i.e. dropping point, shear stability and pumpability alongwith the corrosion inhibition. The developed grease has proven to be energy saving in respect of processing and also resource conserving by way of lesser uses of lithium hydroxide.

INTRODUCTION

Lubricating greases generally consist of a thickener which is homogeneously distributed in a base oil. Early lubricating greases were thickened by metal soap salts of fats and fatty acids. Metals commonly used were sodium, calcium, aluminum, and lithium. Other metals have also been used with less frequency. Fatty acids included various vegetable and animal origin as well as those acids derived from petroleum sources. In recent years, the preferred fatty acids have been hydroxy stearic acids, most preferably 12-hydroxystearic acid. Soaps for greases were commonly provided by reacting the metal hydroxide, oxide, carbonate, or other metallic basic compound with the fatty acids or fats to form the corresponding soap. The saponification reaction usually carried out directly in base oils which in turn thickens the oil. Such fatty acid soap thickeners have been used for many years and are often referred to as simple soap thickeners. Depending on the metallic basic compound used, greases thickened by such simple soaps have dropping points of 100 ºC to about 200 ºC.

Calcium soap greases are oldest metal soap greases. These can be prepared by two methods hydration method and anhydrous method. The dropping point of calcium soap grease prepared by hydration method is quite low (approx. 90 ºC) and upper temperature limit in any application is only 40-50 ºC. For calcium soap greases prepared by hydration method water is very much essential to stabilize the structure of this grease. At high temperature applications this water evaporates leading to breaking in grease soap structure. While the dropping point of the calcium soap greases prepared by anhydrous method is about 130 ºC and this can be used upto 50-60 ºC and such greases called anhydrous calcium soap greases. Because of low dropping point these calcium soap greases are only used in less demanding applications (temp. upto 50-60 ºC) and not applicable for high temperature applications.

As the severity of lubricating grease applications increased, the need for thickener systems with higher dropping points became increasingly demanding. This gave rise to the development of complex soap thickeners. The complex soap thickeners most commonly used are calcium complex, lithium complex, and aluminum complex. Greases based on Calcium complex thickener have the high dropping point but such greases have other problems. Even when stored at room temperature, calcium complex greases will slowly harden when exposed to air.

The hardening will begin at the grease/air interface and slowly extend further into the bulk of the grease with time. This phenomenon is well known and is often referred to as “Case Hardening”. Calcium complex thickened greases can also severely harden under sustained high temperatures. This hardening tendency of calcium complex soap thickened greases can cause a number of problems in actual applications and therefore did not become popular and acceptable for uses.

In the present scenario the uses of lithium soap and lithium complex soap greases is increasing because of their good to excellent properties viz. heat resistance, shear stability, pumpability and thermal stability as compared to other metallic soap greases. The manufacturing processes of these greases are also simpler and cost effective as compared to new generation overbase calcium sulphonate and polyurea greases. Because of increasing uses of lithium soap and lithium complex soap greases the demand/consumption of lithium hydroxide is increasing for manufacturing the greases.

Present Uses of Lithium Hydroxide in Different Sectors

As per the grease production survey report 2012 of NLGI the largest volume of grease thickener sold globally are lithium soaps with around 58 % based on simple soaps and lithium complex at around 19 % of the global market. In India simple lithium soap grease dominates the market close to 85% while lithium complex greases is only around 7%. The use of lithium hydroxide is also increasing gradually in lithium batteries which are the electric power storage source for most of the electronics devices i.e. smartphones, smart watches, laptops, tablets alongwith the electric vehicles. There is a increasing demand for lithium ion batteries for Electric Vehicles (EV) and Hybrid Electric Vehicles (HEV) which are being designed based on lithium hydroxide recently. As a consequence of increasing demand for lithium hydroxide from grease manufacturing and electronics/automotive vehicle industries along with depleting natural sources of lithium, the price of lithium hydroxide is ever increasing day by day. The EV and HEV power storage battery manufacturer are also looking for large volumes of lithium hydroxide and offer to pay higher price for the timely and continuous availability of lithium hydroxide. This trend also pushes the price and lesser availability of lithium hydroxide.

In this situation it is highly demanding for grease manufacturing industry to come forward with alternatives of lithium soap greases in order to reduce the dependency on lithium hydroxide in grease manufacturing. The present development work particularly pertains to provide the lubricating grease thickener system by using easily available and cheaper calcium hydroxide as a main alkaline material with minimal uses of lesser abundant and costlier lithium hydroxide. The developed advanced calcium-lithium lubricating grease thickener system exhibits the improved lubricating properties which are very nearer to simple lithium soap greases.

EXPERIMENTAL

The developed grease has been designed by considering all the properties of simple lithium soap greases and drawbacks of hardening tendency by using calcium hydroxide as main alkaline material instead of lithium hydroxide. Manufacturing process of the developed grease is similar to the process of simple lithium soap greases or lithium complex greases which includes saponification and complexation reaction steps during cooking stage along with cooling, additive mixing and finally homogenization after cooling. Additives like anti-oxidant, anti-rust, extreme pressure and anti-wear are also incorporated and their respective dosages have been optimized. Grease batches were tested as per standard test methods such as ASTM, IP, DIN etc. against a set of specifications framed to develop this grease. Batches meeting the physico- chemical properties were tested for performance properties also. After achieving the best possible properties of developed calcium-lithium soap grease a detailed comparison between developed grease and other greases i.e. calcium soap, calcium complex and simple lithium soap greases have been carried out.

RESULTS AND DISCUSSION

An advanced lubricating grease thickener system is developed with improved lubricating properties. This advanced grease thickener exhibits surprisingly good results over the grease having more calcium hydroxide in their compositions. Among the many improved properties of the developed lubricating grease thickener systems are: shear stability, dropping point, oil separation over a wide range of temperatures, friction & wear, thermal and oxidative stability. In contrast to calcium complex thickener greases, the improved calcium-complex thickener does not suffer from loss of lubricating power due to case hardening which is concomitant with requirement of the pumpability properties. Furthermore, greases thickened with the developed thickener system exhibit substantially insignificant high temperature hardening as associated with calcium complex thickened greases. Also, case hardening is almost eliminated in the improved grease thickener system. The improved thickener system can be used in lubricating greases for a wide range of applications such as automotive and industrial requiring both normal and extreme pressure/anti-wear greases. Additives commonly used in soap and non- soap thickened greases may be used with equal success in greases thickened by the improved thickener system, thereby providing the grease formulator with a high degree of flexibility by which improved products can be developed. To this end, the improved thickener system comprises a calcium/lithium soap thickener having a minimal amount of lithium hydroxide and still exhibit, unexpectedly good properties. The detailed comparison of properties of developed advanced calcium-lithium soap grease with calcium soap, calcium complex soap and simple lithium soap greases has been undertaken.

Dropping Point

Dropping point of the developed grease was checked as per ASTM D 566 test method and results were compared with other greases. The dropping point data are given in Table 1. As per the dropping point testing data the dropping point of the developed grease was found 192 °C which is very close to the 198 °C dropping point of simple lithium soap grease.

Table 1: Dropping Point Test Data of Different Greases with Developed Grease

S. No.	Type of Grease	Dropping Point, °C, as per ASTM D 566
1.	Calcium soap grease (Hydration method)	86
2.	Calcium soap grease (Anhydrous method)	123
3.	Calcium complex Grease (Conventional Method)	266
4.	**Advanced calcium-lithium soap grease**	**195**
5.	Simple lithium soap grease	199

Stability Against Mechanical Shearing

Evaluation of the grease soap structure stability was carried out by up and down (vertical) shearing strokes for 100000 times in a standard grease cup with the help of grease worker as per ASTM D 217 test method and by rotational shearing in roll stability tester under the load of 5.0 kg roller in rotational motion as per ASTM D 1831 test method. The consistency of the grease was checked before and after the shearing test applied in both the cases. The difference in grease consistency before and after the shearing test shows the indication about the mechanical shearing stability of the grease.

Table 2: Test Data of Mechanical Shearing Stability of Developed Grease and Other Greases

S. No.	Type of Grease	Penetration after 60 strokes @ 25 °C ASTM D 217	Penetration after 100000 strokes @ 25 °C ASTM D 217	Penetration change after roll stability test @ rt, 16 hrs. ASTM D 1831
1.	Calcium soap grease (Hydration method)	287	353 (+70)	+63 Units
2.	Calcium soap grease (Anhydrous method)	292	366 (+74)	+66 Units
3.	Calcium complex Grease (Conventional Method)	285	376 (+91)	+87 Units
4.	**Advanced calcium-lithium soap grease**	**283**	**316 (+33)**	**+36 Units**

5.	Simple lithium soap grease	288	315 (+27)	+32 Units

As per the normal trends higher the difference in consistency lesser the shear stability and vice versa. In our case the difference in consistency after 100000 strokes and roll stability test at room temperature for 16 hours was found of 33 units which is very good result in terms of shear stability and very close to the results of simple lithium soap grease. The test results of mechanical shearing stability done by 100000 strokes and rolling stability tester are shown in Table 2.

Hardening Tendency

Case hardening tendency of the developed grease has been checked by keeping the grease in open air at room temperature for a long time. Before keeping in air we have checked the consistency (unworked) of the grease and after a certain period (after every month) we have again checked the consistency of that grease in similar conditions. On comparing the grease consistency hardening test results of developed grease with the test results of calcium complex and simple lithium soap greases it is found that there is no significant hardening effect in consistency of the developed grease and found similar to the simple lithium soap grease. On the other hand a significant hardening effect of 103 units was found in calcium complex grease in the period of 90 days (Table 3).

Table 3: Tendency of Case Hardening in Different Greases on Storage at Room Temperature

S. No.	**Type of Grease**	**Unworked Penetration @ 25 ^{0}C ASTM D 217**	**Penetration @ 25 ^{0}C after 60 days storage at rt ASTM D 217**	**Penetration @ 25 ^{0}C after 90 days storage at rt ASTM D 217**
1.	Calcium complex Grease	274	187 (-87)	171
2.	**Advanced calcium-lithium soap grease**	**276**	**273 (-3)**	**272**
3.	Simple lithium soap grease	279	277 (-2)	277

The hardening tendency of the developed grease was also checked with temperature by performing elevated temperature roll stability test at 82 ^{0}C for 96 hrs as per modified ASTM D 1831 and wheel bearing leakage test at 105 ^{0}C as per ASTM D 1263 test methods. On comparing the results of developed grease with simple lithium soap grease it is clear that there is no significant hardening tendency of the developed grease. Even after elevated temperature roll stability test the change in consistency is found lesser in developed grease as compare to simple lithium soap grease which indicates good shearing stability with temperature also. The results of elevated temperature rolling stability test and wheel bearing test are given in Table 4.

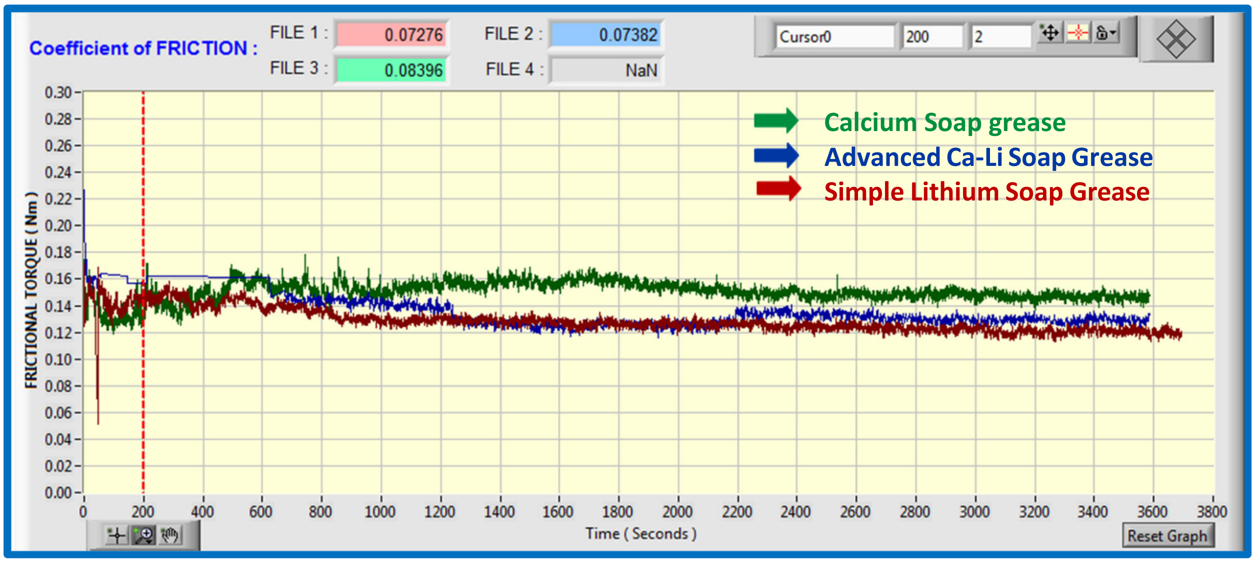
Table 4: Tendency of Case Hardening in Advanced Ca-Li Soap Grease and Simple Lithium Soap Grease with Temperature

S. No.	Test Performed	Test Results	
		Advanced Ca-Li soap Grease	**Simple lithium soap grease**
1.	Change in penetration after roll stability at 82 ºC for 96 hrs.	+43 units	+54 units
2.	Wheel bearing Leakage Test		
i	Oil leakage in grams	0.73	0.88
ii	Change in penetration of grease applied in bearing hub of the instrument	-9 units	-8 units
iii	Condition of the grease	Smooth	Smooth

Anti-wear Characteristics

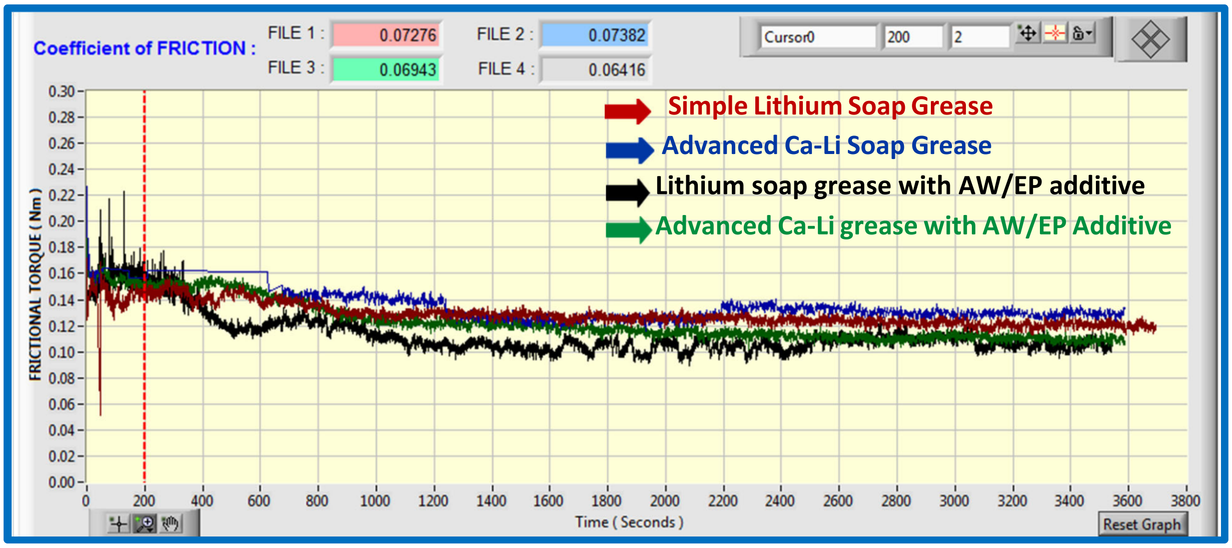
Anti-wear properties of the grease was testes by Four Ball wear scar diameter measurement as per ASTM D 2266 and by getting coefficient of friction from SRV instrument as per ASTM D 5707 test methods. Anti-wear properties of the greases have been checked with base grease and after mixing the similar type of anti-wear (AW) and extreme pressure (EP) additives in 1.0 % dosage in each type of grease. Figure 1 is showing the frictional torque values with time during the anti-wear tests of calcium soap grease, developed grease and simple lithium soap grease at Four Ball machine. Figure 2 is showing the effect of anti-wear additive on frictional torque during anti-wear test of developed grease and simple lithium soap grease with and without anti-wear/EP additives.

From the Figures 1 & 2 and test results of wear scar diameter (in mm) of Four Ball method (Table 5) it is very clear that the developed advanced calcium-lithium soap grease give the exactly similar behavior against anti-wear properties even with or without using anti-wear additive. The coefficient of friction values obtained from SRV anti-wear profile are also showing the similar trend of anti-wear properties of both the greases. The coefficient of friction values are given in Table 5.



Coefficient of FRICTION :
FILE 1 : 0.07276
FILE 2 : 0.07382
FILE 3 : 0.08396
FILE 4 : NaN
Cursor0 200 2

Figure 1. Frictional Torque with Time During Four Ball Anti-Wear Test of Calcium Soap, Advanced Calcium-Lithium Soap and Simple Lithium Soap Greases.



Coefficient of FRICTION :
FILE 1 : 0.07276
FILE 2 : 0.07382
FILE 3 : 0.06943
FILE 4 : 0.06416
Cursor0 200 2

Figure 2. Frictional Torque with Time During Four Ball Anti-Wear Test of Advanced Calcium- Lithium Soap and Simple Lithium Soap Greases with and without Anti-Wear Additive.

Table 5: Anti-Wear Characteristics Data of the Greases Received from Four Ball and SRV Test Methods

S. No.	Type of Grease	Four Ball Wear Scar Dia, mm	Coefficient of Friction by Four Ball	Coefficient of Friction by SRV
1.	Calcium soap grease	0.71	0.84	0.119
2.	**Advanced calcium-lithium soap grease**	**0.57**	**0.74**	**0.113**
3.	**Advanced calcium-lithium soap grease with EP/AW additives**	**0.46**	**0.69**	**0.106**
4.	Simple lithium soap grease	0.55	0.73	0.111
5.	Simple lithium soap grease with EP/AW additives	0.45	0.64	0.104

Heat /Thermal Stability of the Grease Thickener

Application temperature limit for most of the metallic soap greases are generally decided by their dropping/melting points. The maximum application temperature of these greases are found about 70-100 ^{0}C lesser than their dropping points. In consequence of this the temperature limit for simple lithium greases is kept around 100-120 ^{0}C where this grease performs very well and most popular in the market. Therefore it is very essential to confirm the application temperature of the developed calcium-lithium soap grease. For this we have performed the anti-wear test at SRV instrument with ramping of temperature. Anti-wear test was done under the conditions of 50 Htz, 1.0 strokes, by varying the temperature after every 30 minutes starting from the temperature 50 ^{0}C to 80, 100, 120, 150 ^{0}C as different temperature stages. After performing the temperature ramping test very surprising information about maximum application temperature was obtained. When we performed the test with developed grease (grease prepared by using calcium hydroxide only) the anti-wear performance was very good upto 100 ^{0}C but after increasing the temperature to 120 ^{0} there was a big change in the coefficient of friction of anti-wear test and looks like a seizure (Figure 3). On the hand when same test was performed with advanced Ca-Li soap grease the anti-wear test was continued upto 120 ^{0} for approx 10 minutes and after that there was a sudden change in the coefficient of friction which may be because of breakdown in the soap structure of the grease. Similar result was obtained when the test performed with simple lithium soap grease. The only difference was in time duration at which the disturbance appears in coefficient of friction. In simple lithium soap grease this disturbance appear after 5 minutes more as compare to the advanced calcium-lithium soap grease. Therefore on the basis of this temperature ramping test results it is very clear that the maximum application temperature limit for advanced calcium-lithium soap grease is 100 - 120 ºC. The graphs of temperature ramping anti-wear test for advanced calcium-lithium soap and simple lithium soap greases are shown in Figures 4 and 5 respectively.

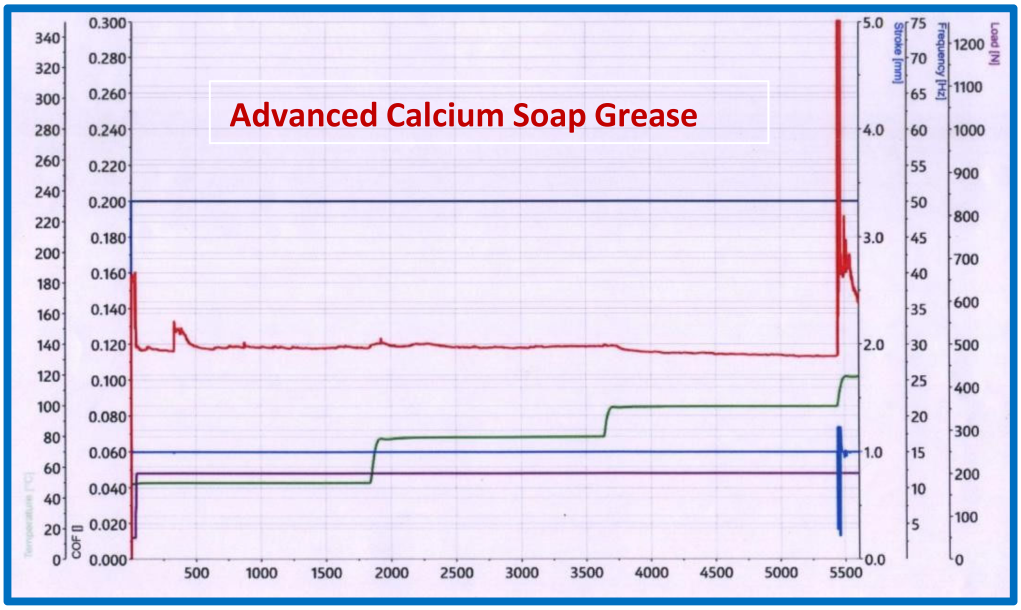


Figure 3: Anti-Wear Profile of Advanced Calcium Soap Grease with Temperature Ramping Test at SRV Machine

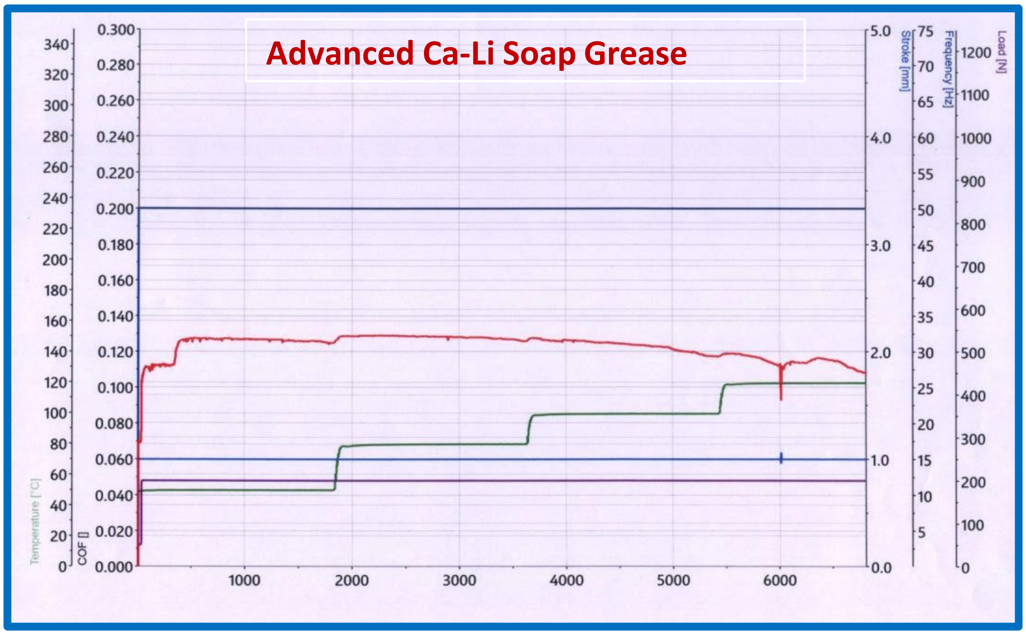


Figure 4: Anti-Wear Profile of Advanced Calcium-Lithium Soap Grease with Temperature Ramping Test at SRV Machine

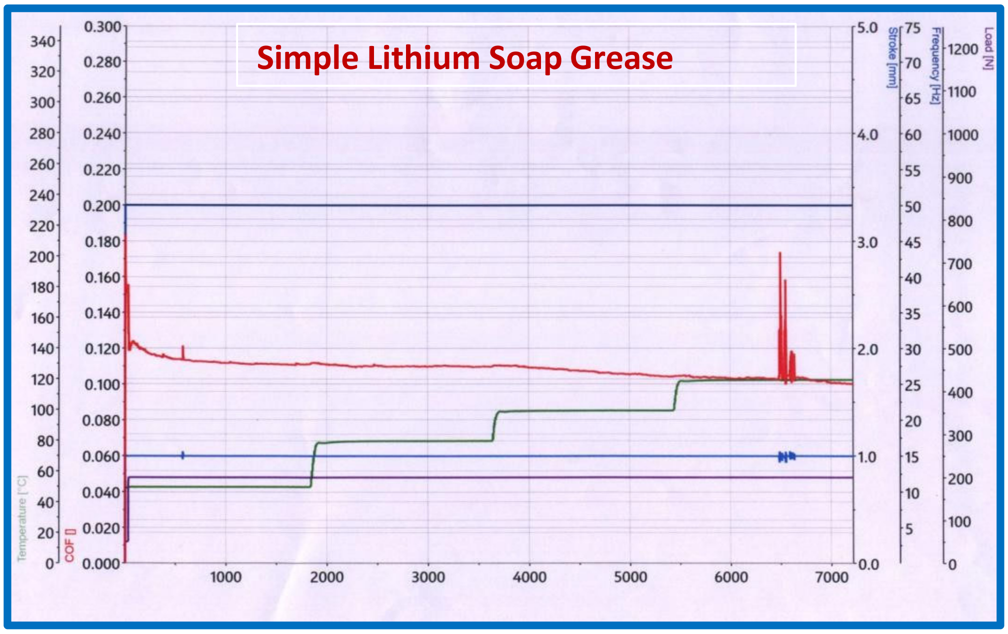


Figure 5: Anti-Wear Profile of Simple Lithium Soap Grease with Temperature Ramping Test at SRV Machine

Miscellaneous Characteristics

Apart from the above described properties the advanced calcium-lithium soap grease is substantially non-corrosive (with additive) under prolonged wet conditions towards ferrous metals and non reactive towards nonferrous metals at ambient and metal processing temperatures. The grease also retains its chemical composition for extended periods of time under operating conditions. Furthermore, the advanced grease offers substantial savings in terms of reduced power and fuel consumption due to lesser processing temperature required for manufacturing. The advanced calcium –lithium soap grease does not suffer from loss of lubricating power due to case hardening which is associated with an improvement in the pumpability properties. The detailed comparison of all the properties of advanced calcium-lithium soap grease with simple lithium soap grease is given in Table 6.

Table 6: Comparison of the Properties of Advanced Calcium-Lithium Soap Greases with Lithium Soap Greases.

S. No.	Characteristics	Advanced Ca-Li Non EP Grease	Advanced Ca-Li EP Grease	Simple Li Soap Grease	Simple Li Soap EP Grease	Test Method
1.	Appearance	Smooth & Homogenous	Smooth & Homogenous	Smooth & Homogenous	Smooth & Homogenous	Visual
2.	Worked Penetration, after 60 strokes (W60)	283	285	288	289	ASTM D 217
3.	Worked Penetration after 100000 strokes (change in Units)	316 (+33)	319 (+34)	315 (+27)	318 (+29)	ASTM D 217
4.	Dropping Point, °C	195	213	199	198	ASTM D 566
5.	Wear Scar Dia, mm	0.57	0.46	0.55	0.45	ASTM D 2266
6.	Four Ball Weld Load, Kgs.	160	250	160	250	IP 239
7.	Roll Stability test 16 Hrs @ room temp., Change in Penetration	+36 Unit	+38 Units	+35 Units	+37 Units	ASTM D 1831 (Modified)
8.	Roll Stability test 96 Hrs @ 82 °C, Change in Penetration	+43 Units	+47 Units	+54 Units	+57 Units	ASTM D 1831 (Modified)
9.	Wheal Bearing Leakage Test					ASTM D 1263
	(i) Oil Leakage in gms,	0.73	0.86	0.88	0.97	
	(ii) Evidence of abnormal change in consistency for structure of the material	No abnormal change	No abnormal change	No abnormal change	No abnormal change	
10.	Hardening on Storage after 3 months, change in penetration	No significant hardening	No significant hardening	No significant hardening	No significant hardening	ASTM D 1403

CONCLUSIONS

The advanced calcium-lithium soap grease has been developed by using easily available calcium hydroxide as a main alkaline material with minimal use of lesser abundant lithium hydroxide. The advanced calcium-lithium soap grease possesses excellent tribological properties and suitable for use in industrial applications. The developed grease exhibit very good mechanical shear stability in both vertical and rotational motion and offer the very good dropping point results which are comparable with the properties of simple lithium soap grease. Wear characteristics of the developed grease are also found closer to the simple lithium soap greases. The case hardening tendency associated with calcium soap greases and calcium complex greases has been overcome in the developed grease by observing the hardening after storage the developed grease upto three months and no significant hardening was also observed at elevated temperatures. The Developed calcium-lithium soap thickener provides equal flexibility to the grease formulators to develop high performance products by using same type of additives as used in lithium soap greases. Considering the present scenario of availability of lithium hydroxide the developed calcium-lithium soap grease may be very useful for the grease Industry to reduce the uses of lithium hydroxide in grease making to some extent.

ACKNOWLEDGEMENTS

The authors are sincerely thankful to the Management of Balmer Lawrie & Co. Ltd. for giving an opportunity to present the above developmental work.

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