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# STUDY OF THERMAL AND OXIDATION STABILITY OF VARIOUS LUBRICATING GREASES.

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## ABSTRACT

In recent years, there is a ever growing demand on lubricating greases in both Industrial and Automotive applications with numerous products available to end users .The thermal and oxidation stability of lubricating greases are important parameters for their performance towards end applications . Among the various lubricating greases, lithium based lubricating greases are most popular and widely used. This is mainly attributed to better thermal & oxidation behavior with variety of lubricating greases from simple , mixed and complex type available to customers . The performance of the lubricating greases is mainly due to nature of base oil , soap thickener and performance additives used . In the present work , an attempt has been made to study thermal and oxidation stability of few selected lubricating greases. Samples of simple lithium greases , mixed lithium & calcium greases and complex greases were taken along with aluminium complex & sulphonate complex greases for the study. The samples of above greases in mineral oil & synthetic basestock were compared for thermal and oxidation stability study . Samples of lubricating greases were subjected to oxidation stability using Rotary Bomb Oxidation Stability ( RBOT) Tester and thermal behavior study using Thermogravimetric Analyser ( TGA) for their performance.. Effect of oxidation was also observed before and after the test using FTIR spectral analysis . The information obtained from the above study will be useful in understanding the thermal and oxidation behavior pattern of different greases for suitability for use in given applications .

## Introduction

With the advent of newer technology ,various changes in machinery & equipments are observed in both industrial and automotive applications. This has made significant requirements on various lubricants including lubricating greases. In recent years ,wide range of lubricating greases with varying performances are available to the end users on given applications. Among the various lubricating greases, lithium greases, aluminium complex & sulphonate complex greases are most popular and widely used today. Base oil is one of the most important component used in lubricating greases are available in various grades with the current trend of shifting from mineral oil to synthetic base oils. Lubricating greases are designed to meet multipurpose requirements of end applications rather than specific one .The parameters such as thermal & oxidation stability, load bearing and water resistance properties are important parameters preferred by users for long life performance.

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

In the present work , an attempt has been made to study thermal and oxidation stability of few selected lubricating greases. Samples of simple lithium greases , lithium complex greases were taken along with aluminium complex & sulphonate complex greases for the study. The samples of above greases in mineral oil & synthetic basestocks were compared for thermal and oxidation stability study . Samples of lubricating greases were subjected to oxidation stability test using Rotary Bomb Oxidation Stability ( RBOT) Tester and thermal behavior/stability study using Thermogravimetric Analyser ( TGA) for their performance.. Effect of oxidation was also observed before and after the test using FTIR spectral analysis . The information obtained from the above study will be useful in understanding the thermal and oxidation behavior pattern of different greases for suitability for use in given applications .

**EXPERIMENTAL :**

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

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

**Instruments** :ThermoNicolet Fourier Transform Infrared Spectrometer model iS10 (FTIR), Thermal Analyser - Perkin Elmer Thermogravimetric Analyser TGA with DTA model STA 6000, Semi Automatic Dropping Point Apparatus, Rotary Bomb Oxidation Stability Tester ( RBOT) / Rotating Pressure Vessel Oxidation Tester ( RPVOT) with fabricated stainless steel pressure chamber and a vertical rack for the five grease samples in a glass cups which can be fitted inside the pressure chamber. Tannas make model Quantum with two units were used for the test.

**PROCEDURE :**

500 gms of Seven samples of multipurpose lubricating greases for industrial application marked as 'A to G ' were collected .These samples were subjected to above study by adopting the following procedures:

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

**Thermal Analysis (TGA) of Lubricating Greases** – 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 grease sample in the ceramic sample cup and placing it in a sample chamber in a furnace .The sample was heated at a heating rate of 10 $^0$C / minute from 50 $^0$C to 900 $^0$C and the mass loss was recorded against temperature in the form of thermogram (TGA graph) of the sample. Any variation due to type of base oil (major constituent) used in the grease as well as soap structure is reflected in the inflexions / plateau in the thermogram. All the samples were subjected to analysis by adopting above procedure. Recorded simultaneously Differential Thermal Analysis **( DTA)** study of Lubricating Greases temperature was obtained in the form of DTA graph for each sample of lubricating grease under similar conditions.

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

20gms each of the sample were taken for this study.5x 4 gms of each grease sample are taken in previously weighed small circular standard glass dishes and each of the 4 gms were filled in the five racket inside the stainless steel rack . Placed the rack carefully with sample of grease in a petradishes inside a pressure vessel as shown in Fig 1.the pressure vessel with 20gms of grease was kept in a sample chamber of RBOT unit as shown in Fig 2.

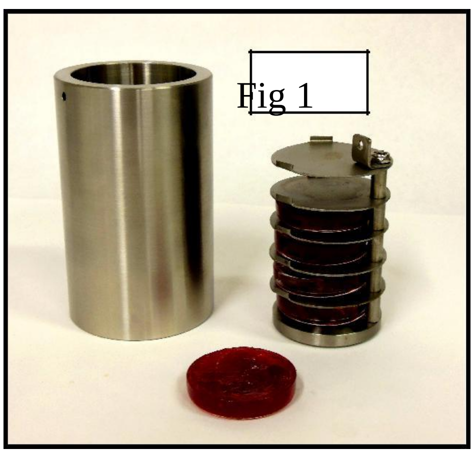


Fig 1

Fig.2

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

The combined stack of grease-filled dishes are then inserted into a cylindrical pressure chamber and then placed on a stainless steel rotating base and entire vessel with rotating base inserted into the unit with sealing gasket which is bolted with three nuts

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

**Fourier Transform Infrared Spectral Analysis of Lubricating Greases :**

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 instrumental conditions are spectral range 4000cm-1 to 400 cm-1, 32 number of scans and resolution of 4 cm-1. The changes if any in the IR Spectra fresh grease against grease after oxidation test will indicate oxidation resistivity/ stability of the lubricating greases .

**Results and Discussions :**

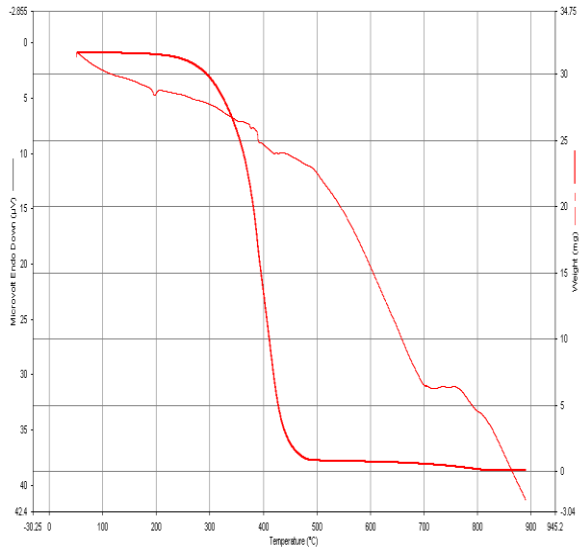
**Dropping Point determination of Lubricating greases** : Table 1 shows the results of dropping point of the greases under study as per standard test method ASTM D 566.

**Table 1**

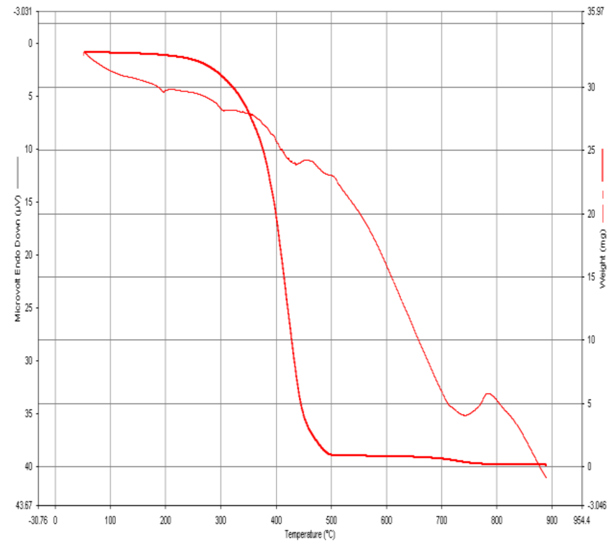
| S.No. | Sample Description | Thickener type | Base Fluid | Drop point $^0C$ |
|---|---|---|---|---|
| 1 | A | Lithium | Mineral Oil | 203 |
| 2 | B | Lithium | Synthetic Base fluid | 194 |
| 3 | C | Lithium complex | Mineral Oil | 245 |
| 4 | D | Lithium complex | Synthetic Base fluid | 265 |
| 5 | E | Aluminium Complex | Mineral Oil | 240 |
| 6 | F | Aluminium Complex | Synthetic Base fluid | 260 |
| 7 | G | Sulphonate complex | Mineral Oil | >300 deg.C |

From Table 1, it was observed that different samples have different dropping points . As seen sample-A is the lowest and sample-G with no dropping point till 300 deg.C . This is important parameter to remember that lubricating greases considered for the study have different dropping point due to different thickener & base fluid.

**Thermogravimetric Analysis (TGA**) : Thermogravimetric analysis of all the grease samples under study were carried out between 40 $^0$C to 900 $^0$C at a heating rate of 10 $^0$C / minute.
Thermogram (TGA) and its differential thermogram ( DTA ) of each of the lubricating greases were recorded and analysed for their thermal behavior pattern as shown in Figure 3.




**A**

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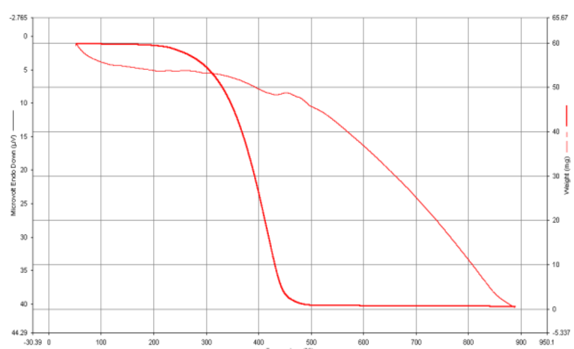


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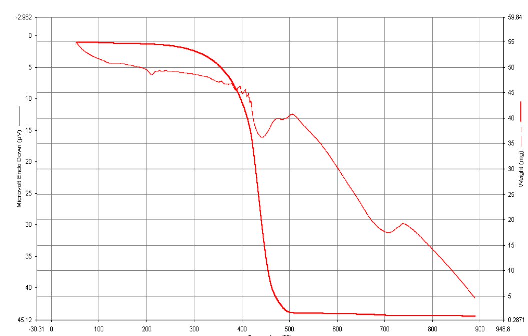
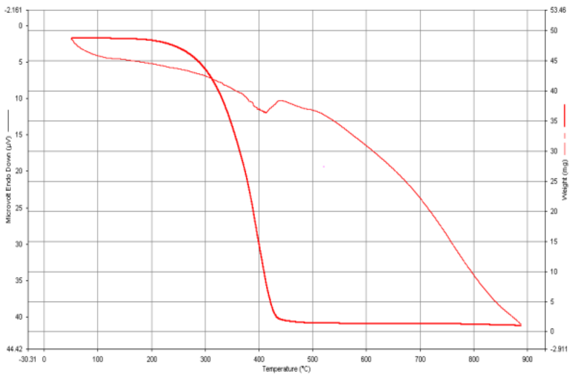
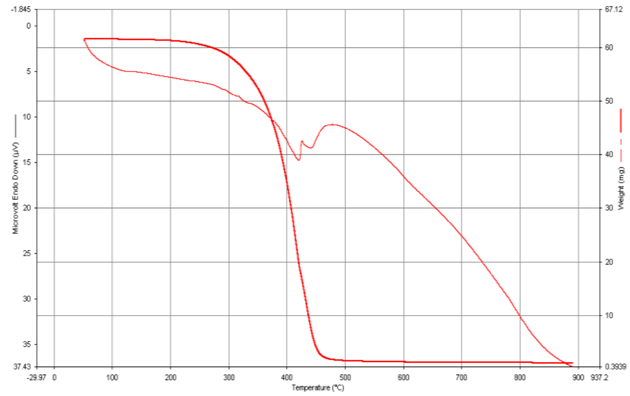


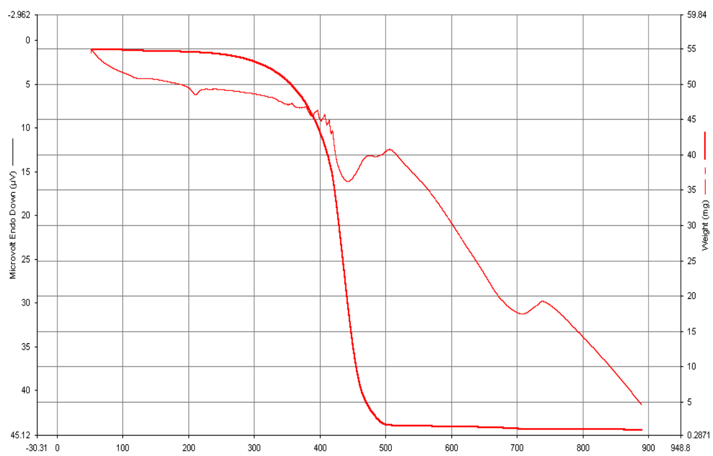

**D**




**E**




**F**




**G**

**Figure 3 typical TGA with DTA curves of lubricating greases (A to G )**

It was observed that the samples under study have shown two types of thermal decomposition pattern ( Differential thermograms) when the sample is heated. Out of the samples analysed, Sample **'B'** , Sample **'D'** and Sample **'F'** have indicated one particular type of thermal decomposition pattern with two inflexion points/humps at high temperatures (at around 430 $^0$C and around 470 $^0$C) (Figure 3 Thermogram **'B' , 'D' & 'F'** ). All the remaining lubricating grease samples **'A', 'C`, 'E'** have shown conventional type of decomposition pattern with single peak at 420 deg.C.

Sample 'G' having have shown different thermal degradation behavior although grease is b mineral oil based . This may be attributed to type of thickener used.

This difference is mainly attributed due to different thermal degradation of base oil being used .The synthetic base oil shows higher thermal stability behavior as

compared to conventional mineral oil based as Sample **'B' 'D', 'F'** uses superior synthetic base oils with better thermal stability .

It is also observed that the samples of complex based lubricating greases such as **‘B’, ‘D’ and ‘F’** observed no distinct characteristics peaks of soap melting but seen as humps in spread out pattern covering wide range of temperatures. This observation is quite different from simple soap thickener greases which indicates no distinct composition of complex soap with no clear complex soap melting .

Sample ‘G’ which is high temperature grease with different type complex thickener based has shown hump with no clear thickener peak.

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

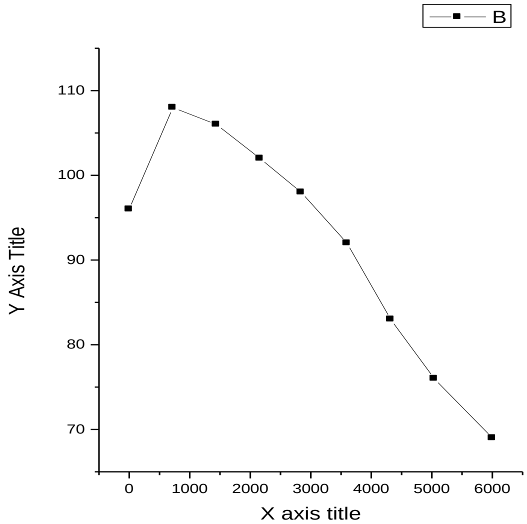
Table 2 shows the recorded pressure in PSI of oxidation chamber at mentioned regular time intervals of lubricating greases being tested by RBOT Test . Initial pressure of oxidation chamber of all the lubricating greases under study was around 96 PSI

**Table 2**

| S.No. | Sample Description | 12 hours Pressure PSI | 24 hours Pressure PSI | 36 hours Pressure PSI | 48 hours Pressure PSI | 60 hours Pressure PSI | 72 hours Pressure PSI | 84 hours Pressure PSI | 100 hours Pressure PSI |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Sample A | 108 | 106 | 102 | 98 | 92 | 83 | 76 | 65 |
| 2 | Sample B | 109 | 107 | 102 | 100 | 94 | 88 | 80 | 72 |
| 3 | Sample C | 108 | 106 | 104 | 103 | 97 | 90 | 86 | 79 |
| 4 | Sample D | 109 | 107 | 106 | 104 | 100 | 96 | 90 | 85 |
| 5 | Sample E | 108 | 106 | 104 | 100 | 98 | 91 | 87 | 79 |
| 6 | Sample F | 108 | 107 | 105 | 101 | 99 | 96 | 91 | 81 |
| 7 | Sample G | 109 | 108 | 106 | 104 | 99 | 96 | 93 | 89 |

It was observed from the Table 2 that lubricating greases under study shows different oxidation pattern as seen from pressure in PSI of respective oxidation chamber during the test. It was observed that sample **‘A’** has shown lowest pressure PSI after 100 hours test and sample **‘G’** being highest among the lubricating greases under study which indicates that oxidation stability of Lubricating grease **‘A’** is lowest and highest for sample ‘G’ . Among the four lithium based lubricating greases **‘A’, ‘B’, ‘C’& ‘D’** ,Lithium complex greases **‘C’ and ‘D’** have better oxidation stability than simple lithium based lubricating greases . As expected, among the lubricating greases under study , greases based on synthetic base fluid **‘B’ ,’D’ and ‘F’** have better oxidation stability than the greases based on Mineral oil origin ‘**A’, ‘C’ and ‘E’ .**

Sample ‘G’ based on mineral oil origin has high oxidation stability due to thickener type , did not have synthetic base fluid type for comparison.



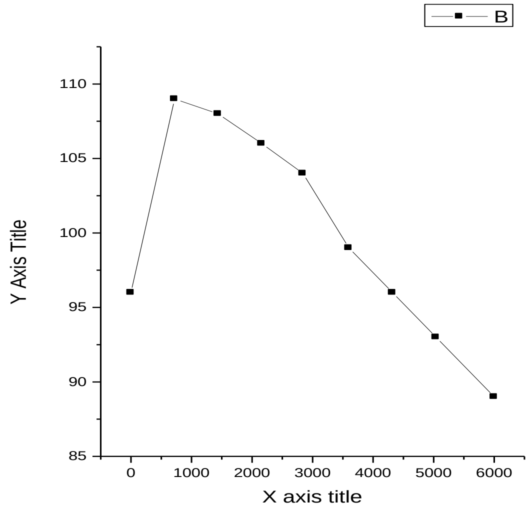




Figure 4 Sample A

Figure 5 Sample G

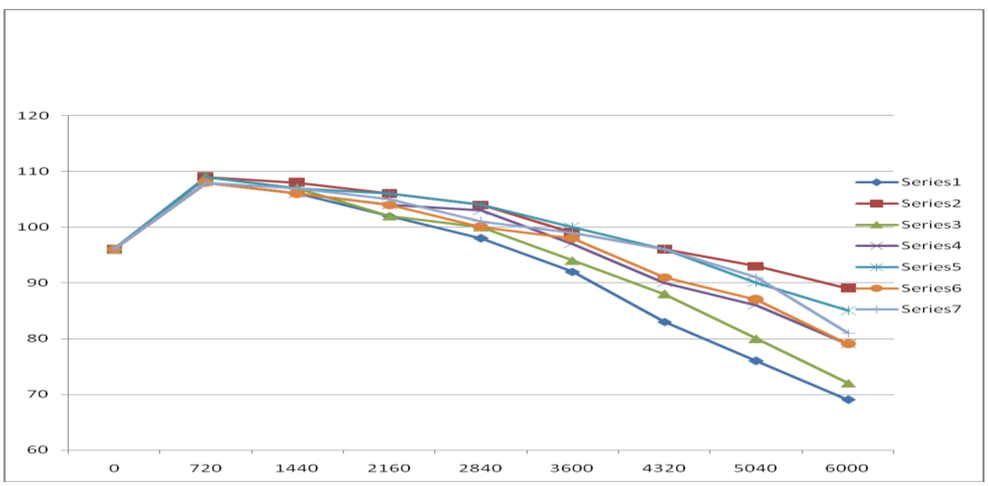



Figure 6 Oxidation Chamber Pressure PSI Vs Time Duration in minutes

**Fourier Transform Infrared Spectral Analysis of Lubricating Greases :**

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 3shows IR spectral changes after the Oxidation Test carried out for 100 Hours :

**Table 3**

| S.No. | Sample Description | Thickener type in base fluid | Appearance of Oxidation Peak At 1710 cm-1 | Any other physical changes after the test |
|---|---|---|---|---|
| 1 | A | Lithium soap in Mineral Oil | Observed with Strong intense peak | Grease become darken with softening |
| 2 | B | Lithium Synthetic Base fluid | Observed with less intense peak | Grease become less darken with no softening |
| 3 | C | Lithium complex Mineral Oil | Observed with less intense peak | Grease become darken with no softening |
| 4 | D | Lithium complex Synthetic Base fluid | Observed with less intense peak | Grease become less darken with no softening |
| 5 | E | Aluminium Complex Mineral Oil | Observed with Strong intense peak | Grease become darken with no softening |
| 6 | F | Aluminium Complex Synthetic Base fluid | Observed with less intense peak | Grease become darken with no softening |
| 7 | G | Sulphonate complex Mineral Oil | Observed with very less intense hump | Grease retains no color change with no softening |

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

It was observed that sample **'A'** has shown strong oxidation whereas sample 'G' has shown the least among the lubricating greases under study. Among the lubricating greases made in synthetic base fluids **'B'. 'D' and 'F'** have shown better oxidation stability than greases made in mineral oil. Sample **'G' .** although based on mineral oil origin as high temperature thickener based provides also high oxidation stability.

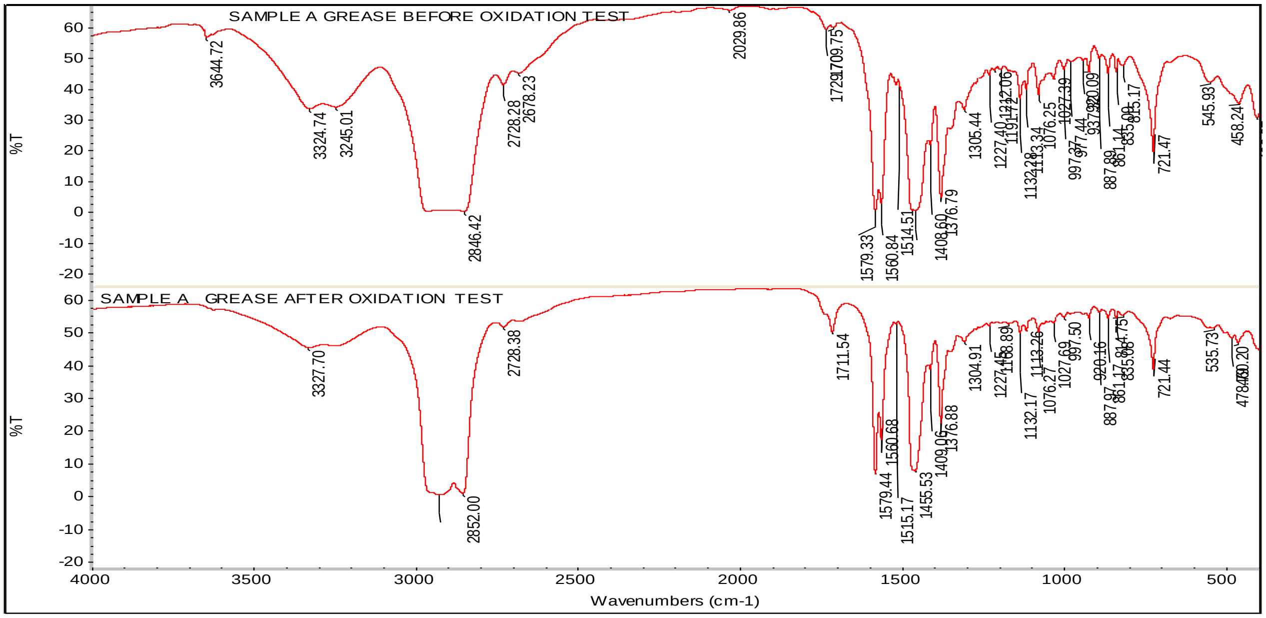



Figure 7 IR Spectral comparison of Sample A before and After Oxidation Test

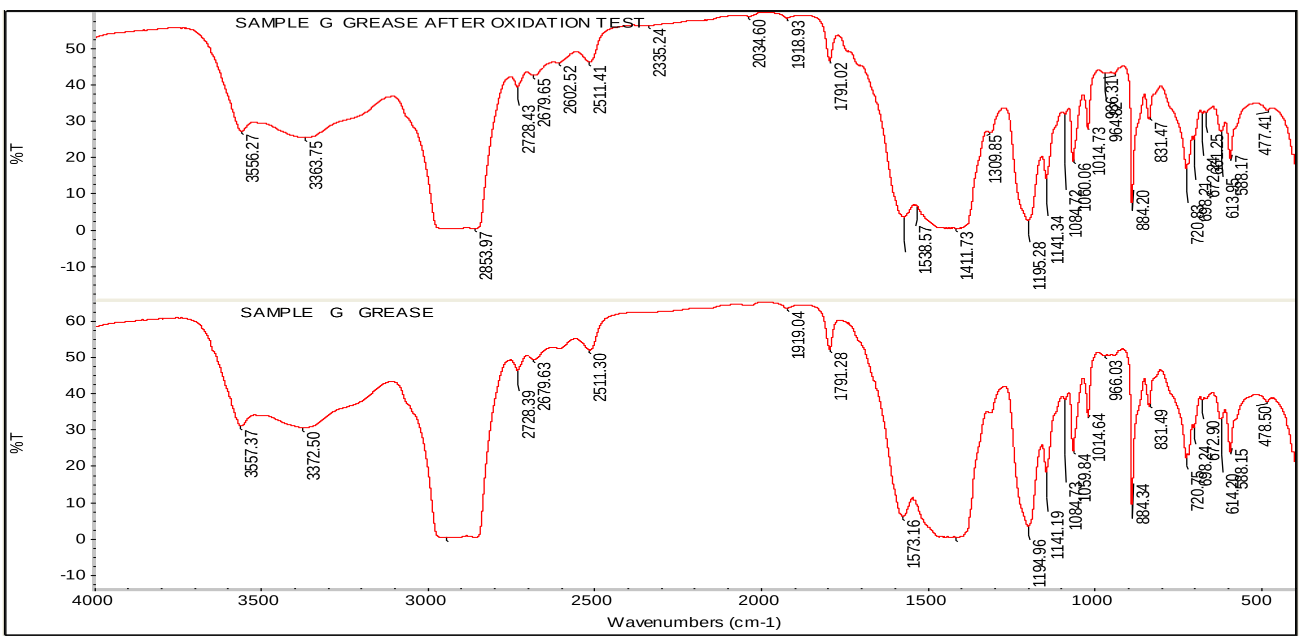



Figure 8 IR Spectral comparison of Sample G before and After Oxidation Test

**Conclusions :**

In the present study, attempt has made to use instrumental techniques such as Thermo gravimetric analyzer (TGA ) with Differential Thermal Analysis (DTA) for thermal stability characteristics of Lubricating greases . RBOT / RPVOT tester for oxidation stability property of the lubricating greases .This required fabrication of sample vessel suitable and amenable for testing the oxidation stability of lubricating greases study without use of oil bath . The advantage of the instrumental technique involves automated recording pressure of oxidation chamber with time unattended and secondly avoids oil fumes generated by the oil bath used in conventional method ASTM D 942 method.

Dropping point of lubricating grease is an important parameter for the end user to know whether the lubricating grease is simple soap / complex soap based thickener or non soap based thickener. As such it alone will not reflect on the quality and performance of grease. In other words, a higher dropping point grease need not give good performance properties.

Thermogram (TGA) and its differential thermogram ( DTA ) of each of the lubricating greases were recorded and analyzed for their thermal degradation behavior pattern. Sample **'B'** , Sample **'D'** and Sample **'F'** have indicated one particular type of thermal decomposition pattern with two inflexion points/humps at high temperatures (at around 430 $^0$C and around 470 $^0$C) (Figure 3 Thermogram **'B' , 'D' & 'F'** ). All the remaining lubricating grease samples **'A', 'C`, 'E'** have shown conventional type of decomposition pattern with single peak at 420 deg.C.
Sample 'G' having have shown different thermal degradation behavior although grease in mineral oil type . This may be attributed to type of thickener used.
This difference is mainly attributed due to different thermal degradation of base oil being used .The synthetic base oil shows higher thermal stability behavior as compared conventional mineral oil based as Sample **'B' 'D', 'F'** uses superior synthetic base oils with better thermal stability . Sample 'G' which is high temperature grease with different type complex thickener based has shown hump with no clear thickener peak.
Oxidation Stability Test of lubricating greases under study by ( RBOT ) indicated that sample **'A'** has shown lowest pressure PSI after 100 hours test and sample **'G'** being highest among the lubricating greases under study which indicates that oxidation stability of Lubricating grease **'A'** is lowest and highest for sample 'G' . Among the four lithium based lubricating greases **'A', 'B', 'C'& 'D'** ,Lithium complex greases **'C' and 'D'** have better oxidation stability than simple lithium based lubricating greases . As expected, among the lubricating greases under study , greases based on synthetic base fluid **'B' ,'D' and 'F'** have better oxidation stability than the greases based on Mineral oil origin '**A', 'C' and 'E'**

Infrared spectra of each of the samples before and after the oxidation test were recorded and compared for any IR spectral changes. The base oil in the lubricating greases is prone for oxidation of hydrocarbon with formation of carboxylic acid indicated by the presence peak at 1710 cm-1. The intensity of this characteristic peaks indicative of oxidation stability of the grease .Higher the intensity less the oxidation stability of lubricating grease and vice versa.
It was observed that sample **'A'** has shown strong oxidation whereas sample 'G' has shown the least among the lubricating greases under study.

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

## References

1.. Manufacture and Application of Lubricating Greases, National Lubricating Grease Institute (NLGI) C. I. Boner.
2. Lubricants and Related Products-Verlag Chemie, Dieter Klamann.
3. Analysis of Lubricating Grease D-128-94, Section *5.01,1998.* Petroleum products and Lubricants (1) : D 56-D2596, American Society for Testing and Materials (ASTM).
4. I.G.Krafft, 'Infrared Spectroscopy in the development and manufacture of Lubricating greases' NLGI SPOKESMAN August,1988 pp-165-236.
5 Dropping point of lubricating greases by ASTM D 566 / 97 Method, American Society for Testing and Materials (ASTM).
6. Oxidative Stability of Lubricating Greases by the Oxygen Pressure Vessel Method ASTM Method of Test D942-02.
7. Oxidative Stability of Lubricating Greases by the Oxygen Pressure Vessel Method ASTM Method of Test D972-02.
8. A Comparative Study of Grease Oxidation Using an Advanced Bench Test Technique :Theodore W. Selby, Jonathan C. Evans, Samina Azad & William VanBergen TAE 201 4 Grease paper .
9. R.J.Rosscup Lubrication Engineering , Jan 1958

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