

Separation and quantitative estimation of complexing agents used in complex soap thickener based lubricating greases

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Abstract :

In recent years, there is a growing demand on complex soap thickener based lubricating greases in both industrial and automotive applications . The main advantage of complex soap thickener over simple conventional soap thickener based greases are their capability of maintaining an excellent stability at high temperature besides other enhanced performance properties such as load bearing , shear stability, water resistance ,rust protection etc.. Complex soap thickener formed by the combined reaction of an active metal with a fatty acid and a non-fatty acid. The non fatty acid component usually a complexing agent being used, are based on boron compounds such as boric acid and borated esters as well as mono and di carboxylic organic acids such as Benzoic acid, Azealic acid, Sebacic acid, etc. In the present work ,an attempt has been made to separate, identify and estimate quantitatively these complexing agent in a few market samples of multipurpose complex lubricating greases. These samples were subjected to analysis using various analytical techniques based on infrared spectrometry, gas liquid chromatography in addition to wet chemical method and physico chemical tests. The information obtained from the above study will be useful in understanding the attributes of the component - complexing agent in the products available in the market in terms of composition and performance for a given application. The method is sensitive, reliable, accurate with good repeatability and can be easily adopted to cover wide range of complex soap thickener based lubricating greases.

Introduction :

In recent years, there is a growing demand for lubricants including lubricating greases with advent of newer type of highly efficient equipments and machineries operating in wide range of extreme application conditions such as temperature, load, etc. In order to meet the such demands, initially, simple multipurpose lubricating greases and Non soap lubricating greases were used which had limitations at extreme conditions. This was overcome by use of complex soap thickener based lubricating greases. In general, complex soap thickener are the salts (soap) formed of high molecular weight fatty acids and salts of short organic or inorganic acids. The combination of these two units exhibit

strong interactions which increases the dropping point of such greases. The main advantage of complex soap thickener over simple conventional soap thickener based greases are their capability of maintaining an excellent stability at high temperature besides other enhanced performance properties such as load bearing, shear stability, water resistance, rust protection etc.. Not many methods are known and reported to separate these ingredient complexing agent from these complex soap thickener based lubricating greases. The methods reported are very few in literature to identify and quantitatively estimate the complexing agents used in the lubricating greases.

In the present study, an attempt has been made through an analytical approach to identify, separate & quantitatively estimate the complexing agent from the few market samples of lubricating greases used for both industrial and automotive applications. In the proposed approach, initially the type of complex lubricating greases were characterised by Dropping Point and Fourier Transform Infrared Spectrometric (FTIR) technique. Subsequently, this is followed by separation & quantitative estimation of the complexing agent by suitable wet chemical analytical procedure and Gas Liquid Chromatographic (GLC) technique. The information obtained from the study will be very useful in understanding of the products with different types of complexing agent used in lubricating greases for a given application.

EXPERIMENTAL :

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

Labware : Standard glasswares of Borosil make were used for analysis. Standard Soxhlet Extraction Apparatus, Whatman 40 (12.5 cm) Filter paper, Heating mantle, Oven, Vacuum desiccator, Separating flask 1000ml, Beaker 250ml & 500ml capacity, Gooch crucible G3, Heating Mantle.

Instruments : Nicolet Fourier Transform Infrared Spectrometer model Magna 560 ESP (FTIR), Thermo fisher make Gas Chromatograph Ceres 800 Plus and Koehler Instruments Inc. make Semi Automatic Point Apparatus.

PROCEDURE :

500 gms of six market samples of complex lubricating greases constituting aluminium, and lithium based soap thickener for both industrial & automotive applications marked as A to F were collected and were subjected to above study by adopting the following procedures.

A Dropping Point determination of Lubricating greases :

The standard procedure adopted for lubricating grease samples (A to F) as per ASTM D 566 was used. Dropping Point was determined by Semi automatic dropping point apparatus. The dropping point of grease is a very important parameter of the grease which defines the temperature up to which grease is able to retain the semisolid structure beyond which the soap melts leading to fluid state. A lubricating greases is simple or complex soap thickener based is known from the dropping point of the greases.

B FTIR Spectral analysis :

Infrared spectrum of each of above samples of lubricating greases were recorded in Potassium Bromide cell windows without spacer in a IR demountable cell. The Infrared spectral range used was 4000cm^{-1} - 400cm^{-1} . Nicolet Fourier Transform Infrared Spectrometer model Magna 560 ESP (FTIR). Infrared Spectral analysis provides information on the nature of complex soap thickener being used in the lubricating greases.

C Soap Thickener Content by Soxhlet Extraction Procedure :

The soap thickener content in the samples were estimated by soxhlet extraction method. About 10 grams of each sample was taken in previously weighed thimble made of filter paper and placed in Soxhlet Extraction apparatus in which 250 ml hexane was taken to extract the oil. The apparatus was kept on heating mantle and heated until hexane started boiling. Hexane under reflux condition re-circulated through the sample and extracted out the base oil with additive if any. This reflux condition was maintained for 8 hours under which entire base oil was extracted out completely. After 8 hours, Soxhlet extraction was stopped and the material was allowed to cool down. Transferred the hexane soluble portion into previously weighed 400 ml beaker with hexane washings and kept the beaker with content over a boiling water bath to evaporate off the hexane. The separated oil obtained was kept in a vacuum desiccator to remove completely a entrapped solvent hexane. Weighed the beaker with the separated oil until constant weight was obtained was obtained. Similarly, hexane insoluble portion-the filter paper thimble containing soap was removed and kept in a clean petridish in a desiccator for drying. After

complete drying to constant weight, weighed the thimble with residue. From the difference in weight of the thimble with residue and empty thimble, the percentage soap content was obtained. The separated oil from the sample obtained through Soxhlet extraction method were subjected to FTIR spectral analysis to know the clear separation of soap from greases .

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

Weighed about 5-10 grams of lubricating greases in a previously weighed 250 ml beaker , added 200 ml of hexane to disperse the soap thickener of the grease with stirring and warming over a boiling water bath. Once the grease was completely dispersed into the solvent hexane, transferred carefully the content into separating flask (500ml) with one to two washings with hexane. Added 2 x 200 ml proportion of (1:3) dilute hydrochloric acid solution made in distilled water into the separating flask containing hexane dispersed grease, stoppered the flask , shaken the solution with occasional release of pressure by opening the stopper. The soap thickener of grease was split using the hydrochloric acid. In the case of lithium based complex greases with use of different complexing agent – boric acid , borated esters. The aqueous solution with washings is very important and need to be carefully separate out and collected. The solution was filtered through Whatman 40 filter paper. Concentrated the solution through boiling over hotplate and suitable volume (100ml) used as a stock solution for further estimation of boric acid content by Boric acid (DL) Mannitol method given below (I).

Lubricating complex greases with commonly used organic based complexing agent - mono , di carboxylic acid such as benzoic acid in case of Aluminium complex grease and Sebacic acid / Azelaic acid as in the case of Lithium complex grease. The fatty acid with complexing agent dispersed in the organic layer is separated out by filtering through Gooch crucible G3 and thoroughly washed the collected solid with hexane to remove any adhering base oil. The solid obtained was dried and subjected to GLC analysis(II) . Generally solid contains mixture of fatty acid either Stearic acid / 12 - Hydroxystearic acid with organic acid - mono/di carboxylic acid.

- (a) Estimation of Boric acid content by(DL) Mannitol titrimetric method (from I) :
25 to 50 ml of stock solution was taken in 250 ml conical flask , added few drops of phenolphthalein indicator solution and titrated against 10% sodium hydroxide solution taken in burette until light pink color appears. Added few drops of 1N

Sulphuric acid solution until pink color disappears. Added few drops of methyl orange indicator and boiled the solution for 1-3 minutes to expel carbon dioxide over a hot plate and continued the titration carefully with 0.2 N standardised sodium hydroxide solution taken in burette to yellow color solution. 2 grams of (DL) mannitol with a few drops of phenolphthalein added to the solution and noted burette reading. Continued the titration with 0.2 N standardised sodium hydroxide solution further until pink color appears with no further disappearance. Noted burette reading, from the volume of 0.2 N sodium hydroxide consumed, boric acid content was estimated using 1 ml of 0.2 N Sodium Hydroxide = 0.0124 g boric acid. From the dilution factor and weight of the grease sample taken, boric acid content was estimated.

(b) GLC analysis of separated solid (from II) :

1-2 grams of solid was taken (from above II) 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 stoppered.

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 microliter of sample solution in chloroform was injected into the column for chromatographic separation. From the GC chromatogram, the percentage organic acid content was obtained. Calculation from the soap content of the grease, percentage organic acid present in grease was determined.

Results and Discussions :

Table 1 shows the results of dropping point of samples of complex lubricating greases. It was observed that different samples shows different dropping point.

It is also observed from the table that dropping point is also dependent on sample consistency and varies accordingly. Complex lubricating greases with lower consistency shows lower dropping point though it may contain complex soap thickener based lubricating greases.

Table 1

S.No	Sample code	Sample Details	Dropping Point °C
1.	A	Industrial Grease NLGI 2	261
2.	B	Industrial Grease NLGI 0	193
3	C	Industrial Grease NLGI 2	238
4	D	Industrial Grease NLGI 0	197
5	E	Industrial Grease NLGI 2	247
6	F	Automotive Grease NLGI 2	273

Fourier Transform Infrared Spectral Analysis of Lubricating Greases :

The lubricating grease samples (A to F) were smeared between potassium bromide cell and IR spectrum was recorded. IR spectrum recorded between 4000cm^{-1} - 400cm^{-1} with number of scan 32 and resolution of 4 cm^{-1} in both the cases.

Table 2 indicates that nature of the complex soap thickener present in different greases in different samples of lubricating greases. The characteristics peaks of complex soap thickener indicates the type of Grease that for a given application.

Table 2

S.No	Sample Code	Sample Details	Characteristic peaks of Complex Soap thickener by FTIR Analysis
1.	A Industrial	Aluminium Complex Soap based Grease NLGI 2	3672cm⁻¹,3079 cm⁻¹ Trifurcated peaks 1604,1586& 1569 cm⁻¹, 998 cm⁻¹, 721 cm⁻¹
2.	B Industrial	Aluminium Complex Soap based Grease NLGI 0	3672 cm⁻¹, 3079 cm⁻¹ Trifurcated peaks 1604,1586 & 1569 cm⁻¹, 998 cm⁻¹, 721 cm⁻¹
3	C Industrial	Lithium Complex Soap based Grease NLGI 2	3335cm⁻¹(-OH), Bifurcated Peaks -1579 & 1560 cm⁻¹,relatively broad peak 1460 cm⁻¹(-B-O -C-), 721 cm⁻¹.* The region boric acid /borated ester complexing agent peaks appears overlap with peak methylene group absorption of hydrocarbon base fluid in the grease .
4	D Industrial	Lithium Complex Soap based Grease NLGI 0	3335cm⁻¹(-OH), Bifurcated Peaks -1579 & 1560 cm⁻¹,relatively broad peak 1460 cm⁻¹(- B-O -C-), 721 cm⁻¹.* The region boric acid /borated ester complexing agent peaks appears overlap with peak methylene group absorption of hydrocarbon base fluid.
5	E Industrial	Lithium Complex Soap based Grease NLGI 2	3330cm⁻¹(-OH), Bifurcated Peaks -1579 & 1558 cm⁻¹,relatively broad peak 1460 cm⁻¹(- B-O -C-), 721 cm⁻¹.
6	F Automotive	Lithium Complex Soap based Grease NLGI 2	3335cm⁻¹(-OH), Bifurcated Peaks -1579 & 1560 cm⁻¹,relatively broad peak 1460 cm⁻¹(- B-O -C-), 721 cm⁻¹.* The region boric acid /borated ester complexing agent peaks appears overlap with peak methylene group absorption of hydrocarbon base fluid.

From the Table 2 ,It was observed that FTIR spectral analysis was able to differentiate the Aluminium complex grease from Lithium complex greases(as observed in A & C) .However , it is unable to differentiate within Lithium complex greases as observed C ,E, & F having different complexing agent with no additional separate infrared peaks .

Figure 1 to 4 shows typical IR Spectrum of Four different lubricating complex greases.

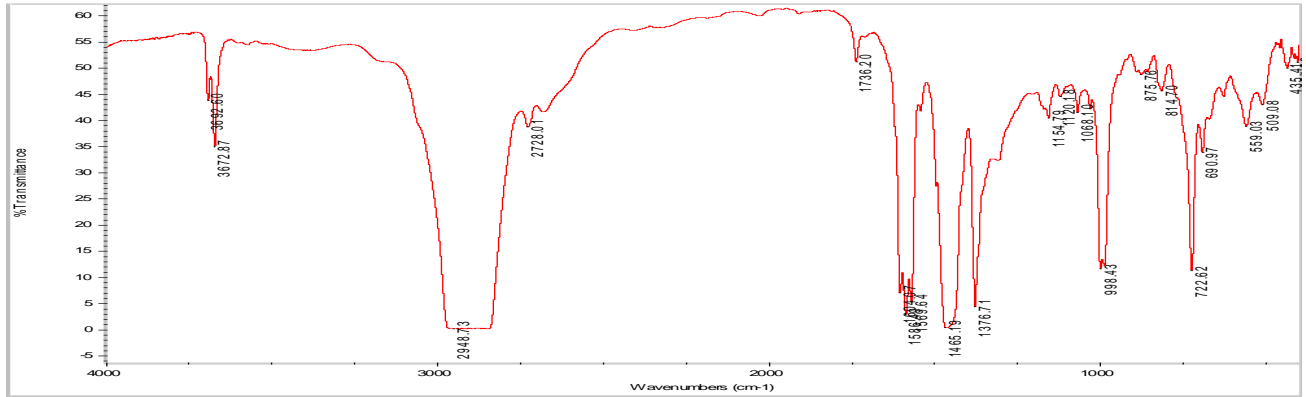


Fig 1 Sample A IR Spectrum of Aluminium Complex Grease

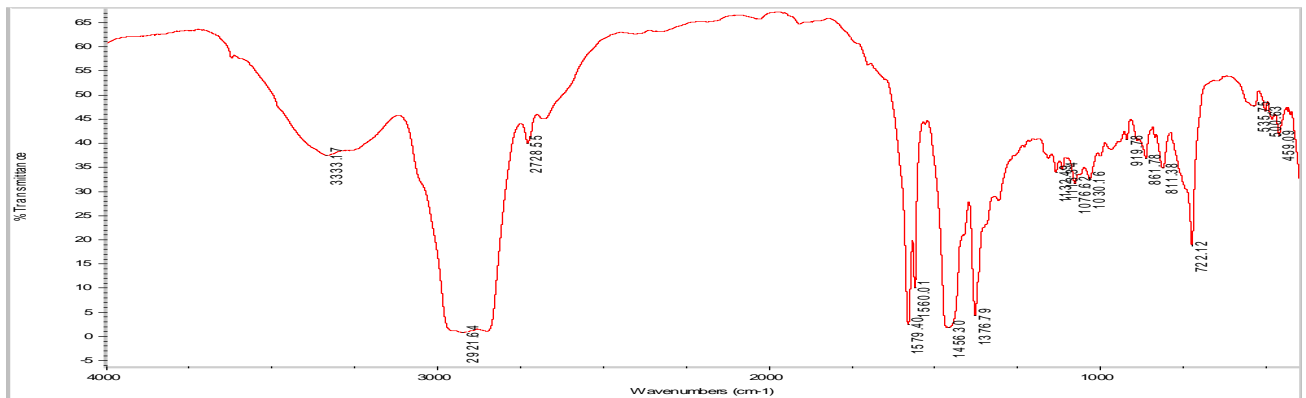


Fig 2 Sample C IR Spectrum of Lithium Complex Grease (Boric acid)

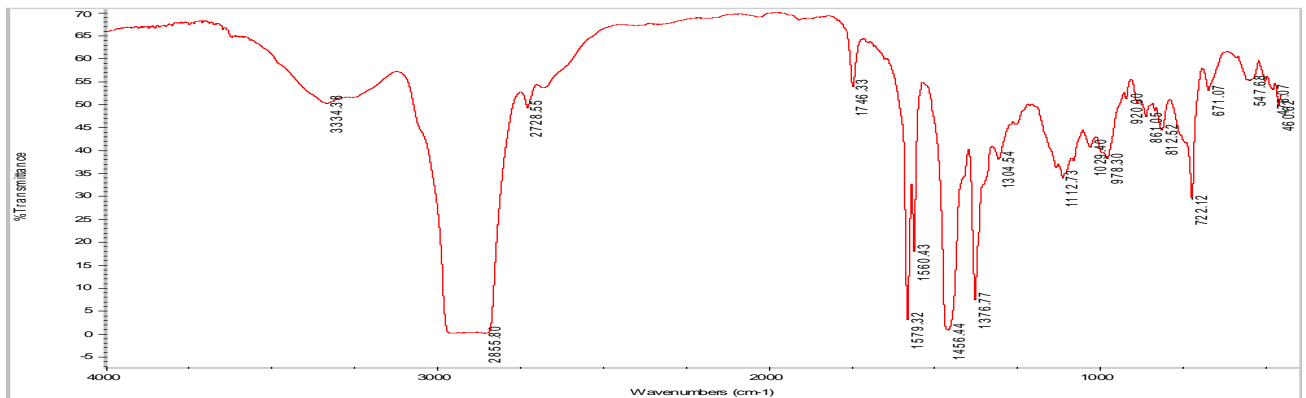


Fig 3 Sample F IR Spectrum of Lithium Complex Grease (Borated Ester)

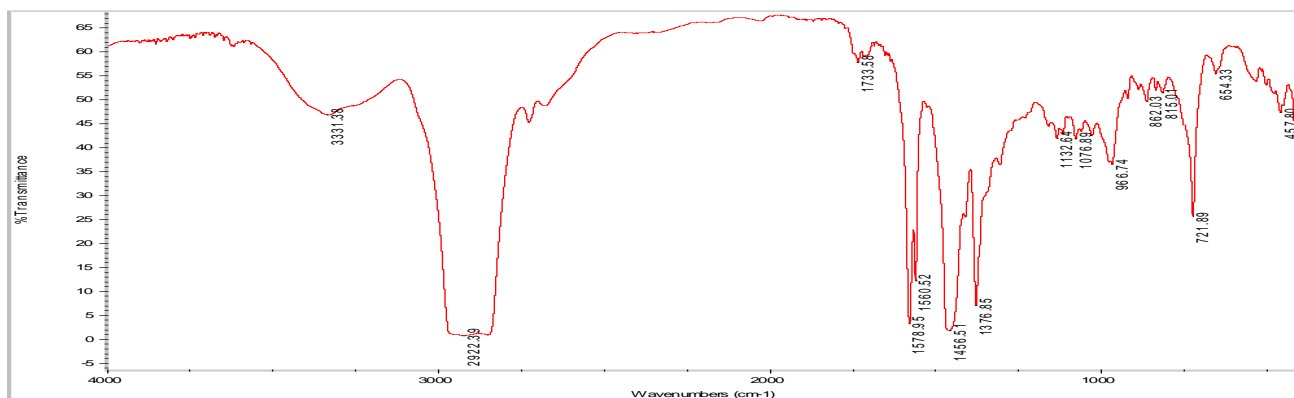


Fig 4 Sample E IR Spectrum of Lithium Complex Grease (Sebacic acid)

Soap Thickener Content by Soxhlet Extraction Procedure :

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

Table 3

S.No	Sample Description	Sample Details	Separated Soap content (Wt%)
1.	A	Aluminium Complex Soap based Grease NLGI 2	15.1
2.	B	Aluminium Complex Soap based Grease NLGI 0	4.2
3	C	Lithium Complex Soap based Grease NLGI 2	14.7
4	D	Lithium Complex Soap based Grease NLGI 0	4.6
5	E	Lithium Complex Soap based Grease NLGI 2	14.9
6	F	Lithium Complex Soap based Grease NLGI 2	13.8

From Table 3, it was observed that different samples have different soap contents. Samples with lower consistency have shown lower soap contents. Separated complex

soap can also be subjected to analysis for separating the complexing agent as given by procedure .

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

Table 4 shows the quantitative estimation of complexing agent by method mentioned above D (a & b).

Table 4

S.No	Sample Code	Sample Details	Type of complexing agent	Complexing agent (%)
1.	A	Aluminium Complex Soap based Grease NLGI 2	Benzoic acid	4.20
2.	B	Aluminium Complex Soap based Grease NLGI 0	Benzoic acid	1.08
3	C	Lithium Complex Soap based Grease NLGI 2	Boric acid	2.42
4	D	Lithium Complex Soap based Grease NLGI 0	Boric acid	0.72
5	E	Lithium Complex Soap based Grease NLGI 2	Sebacic acid	2.80
6	F	Lithium Complex Soap based Grease NLGI 2	Borated Ester	0.62 as Boric acid

From the above Table 4, it was observed that there is a distinct variation in quantity of complexing agent used in different complex greases. In the lithium complex greases , there is a different options available to manufacturers using different complexing agent to market their products for a given application.

Conclusions :

Based on the above analytical study , it was concluded that there is a distinct variation in complexing agent used in different greases available in the market for a given application. More prominent & widely used lithium complex greases , different type of complexing agents are available which are being used in varying amount by different Manufacturers. It was also observed that Dropping point of greases is also dependent on consistency of the grease . The method is easily adoptable in the laboratory, the results are reproducible and does not require very expensive chemicals and labwares.

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