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Reliability Improvement of Merchant Mill Drive Gearboxes through improved and suitable Gear oil

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In Steel Industry there is a growing demand of heavy-duty industrial lubricants to increase the machine efficiency. With the technological advancements, the new age gear oil is exposed to extreme operational challenges mainly due to increased power density surface hardened gear metallurgy & finer filtration. Hence, this gear oil is formulated with various combination of additives, base oil considering the balance formulation approach to achieve the best fit.

Lubrication requirements of steel industry is very challenging as the operating condition of machineries are very harsh with respect to very high load, temperature, dust, and water ingress. Further, due to prevailing hazardous condition an increased demand of reducing man machine interface is vital to achieve sustainable growth.

Problem Statement:

Merchant Mill stand gear boxes provide drive to stand rollers for reducing the size of billet as per the required finished product. In the process these gear boxes are exposed to heavy shock loads and temperature along with other external and internal contamination. Earlier, Normal ISO VG 320 gear oil was used for lubrication of mill drive Gearboxes.

Although traditional EP type gear oil additives provide good protection of gears, they have certain drawbacks for ex -at higher oil temperatures they tend to become aggressive which can lead to attack on non- ferrous parts and promote deposit formation. They also tend to have a negative impact on fatigue processes such as micro pitting or pitting which reduces both gear and bearing life.

MM is more than 60-year-old plant and mill drive gearboxes are exposed to high oil temperature of about 60 degree Celsius due to absence of heat exchanger and high-water ingression through vertical stand Gearboxes. Some of the issues faced in the plant:

- Pitting on gear tooth. Metal wear at addendum and dedendum of tooth.
- Mild Corrosion in old gears
- Increased wear/ failure of Babbitt bearing
- Water retained in oil and separated partially through centrifuge.

View of Gears

Solution:

Thorough investigation and study were conducted on all the aspects to capture all the causal factors and root cause of the problem and it was decided to replace the existing gearoil with new gear oil which has enhanced gear wear protection from micro pitting and excellent resistance to oil oxidation and thermal degradation.

Salient Features of New Oil:

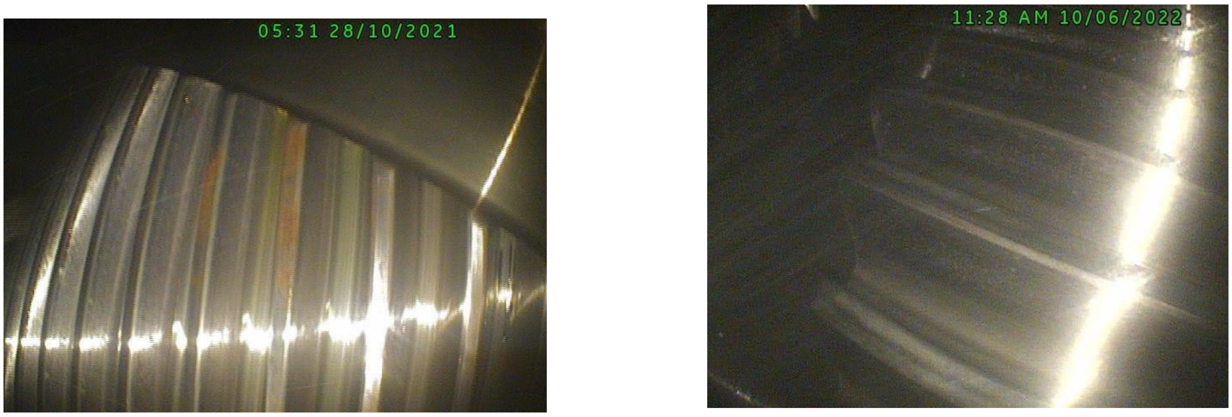
APPROVED BY-M/S FLENDER, GERMANY

Meets DIN 51517 Part 3 (CLP), AGMA 9005-F16, ISO 12925 Type CKD

- Superb protection from micropitting fatigue wear & scuffing –
  Pass –FZG Micropitting, Fail Stage, Rating, FVA 54 FZG Micropitting, GFT- Class, Rating, FVA 54
- FZG scuffing load stage- (A/16.6/90): >12
  (A/8.3/90) : >12
- FAG FE 8 wear test: Pass (DIN 51819/3)
- Outstanding compatibility with range of seal materials
- Resistance to foaming and emulsion formation

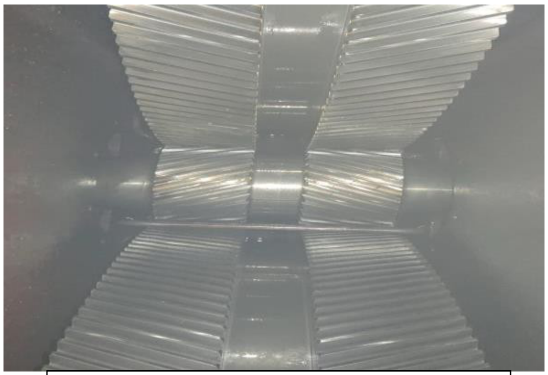
Continuous Monitoring

Onsite physical and baroscopic inspection which was conducted after more than 6 months of operationand all gear condition was found normal



Images of Gear teeth of Gear Box no -2

Finding: Minor rust at the gear teeth edges and few spots on tooth face was observed which have a reducing trend in comparison to the last inspection.

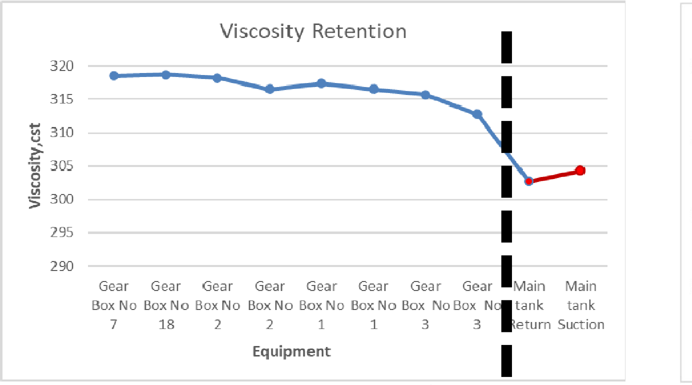


Last Inspection Image-Oct’21

Last Inspection Image-June’22

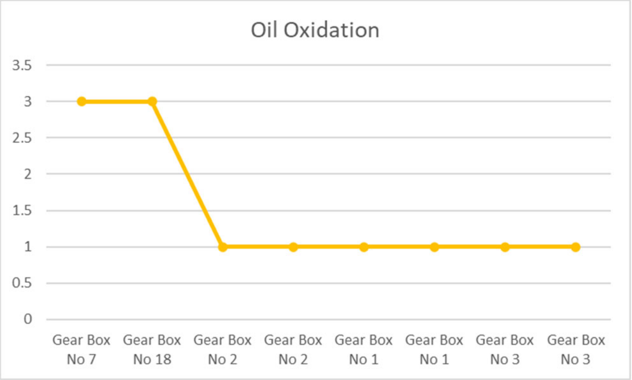
Finding: Minor rust at the gear teeth edges and few spots on tooth face was observed which have a reducing trend in comparison to the last inspection.

Performance Comparison- Old VS New Gear Oil :



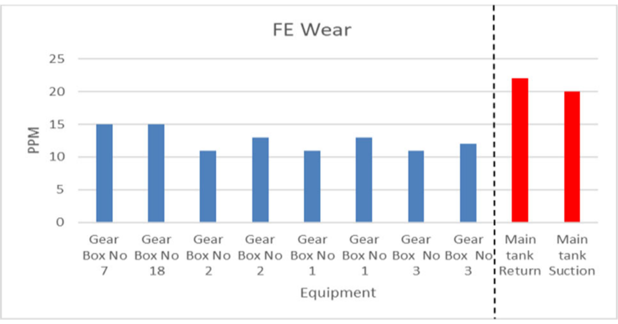
Viscosity Intact when running with New oil

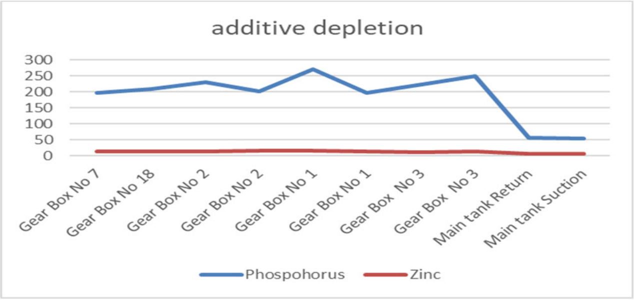
Severe Viscosity drop when running with old oil



Oxidation Stability demonstration

Oil oxidation- was in normal range for all the New gear oil samples even when water contamination was very high for gear no 7 & 18 ensuring its superior oxidation and thermal stability. However, oxidation values were not available for old oil,but considering the drop in viscosity reported earlier it can be concluded that old oil have poor oxidation and thermal stability compared to the new Oil.





Wear- Specially FE wear has been tabulated in above diagram to draw a comparison, thoughiron wear noted is well below the equipment or oil alert rating but for new oil, it is still well below from the old oil which demonstrates its capability to reduce wear and enhance equipment life.

Additives- Another very important aspect towards evaluating a lubricants performance is its capability to avoid additive depletion. As gear oil works mostly in extreme work condition with heavy loads and high contamination ingress which can cause aggressive abrasive wear loss in additive will lead to higher wear which can cause sudden breakdown and productivity loss. However, considering above graph it quite conclusive that New oil has inherent quality to retain additives and ensures overall protection in comparison to old oil which indicates significant depletion in additives.

Conclusion:

New gear oil is formulated to protect gear teeth from wear at its earliest stages and exceeds the industry requirement for bearing wear protection. Implementation of new suitable gear oil has shown good results with respect the problems faced earlier.

Use of Microwave Digestion Technique as a Sample Preparation Tool for Characterization of Lubricating Greases

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Abstract :
In the lubricant grease industry ,numerous high performance lubricating grease products are available to end users using different composition with varying types of base oil, soap thickener and different performance additives to meet application requirements. Lubricating greases are characterised for elemental and molecular composition. Elemental composition of Lubricating Greases provides information on the type of elements which are part of components of greases either from thickener (both soap & non soap type of thickener) , type of organic / organometallic additives and type of fillers-silicates , metal oxide ,over based carbonates , including solid lubricants such as graphite , molybdenum disulphide , tungstun disulphide etc. Analytical tool such as Spectroscopic techniques based on UV Visible (UV-VIS) ,Atomic Absorption(AAS) ,Inductively Coupled Plasma Optical Emission (ICPOES), X-Ray Fluorescence (XRF) is widely used techniques for characterising lubricating greases for Elemental Composition. Some of the spectroscopic techniques requires careful & precise sample preparation procedures. During earlier years , wet chemical acid digestion procedure using perchloric acid & sulphuric acid was used . Later, ashing procedure through oxide & sulphated ash was widely being adopted as sample preparation procedures for spectroscopic technique . It has limitation of only analysing elements

– metallic portion components of lubricating greases and does not provide information on non metallic portion such as sulphur, boron ,halides , nitrogen etc. In recent years , microwave digestion based sample preparation technique is being used which can be utilized for bringing both metals and non metals into solution without any loss of element. It has a advantage of being very rapid , require very small sample for digestion and require less acid for digestion than conventional ashing procedure / wet chemical digestion procedure .

In the present work , an attempt has been made to subject different types of lubricating greases to microwave digestion sample preparation procedure followed by determination of elemental composition by Inductively Coupled Plasma Optical Emission Spectrometric (ICPOES) technique using microwave digested samples. Samples of simple lithium greases , mixed lithium & calcium greases ,lithium , aluminium & sulphonate complex greases and Greases with solid lubricants were taken for the study. The study involves standardization work with digestion procedure using acid / acid mixture and digestion time may required for different samples under study . The information obtained from the above study will be useful in effective use of microwave digestion technique for reducing sample preparation time which in turn reduces substantial analysis time & manual error for determination of elemental composition lubricating greases. Analytical data obtained for elemental composition of lubricating greases using both the sample preparation procedures - conventional ashing procedure and microwave digestion system will be compared.

Introduction

With advent of newer technology ,various changes in machinery & equipment were observed in both industrial and automotive applications. This has made significant changes in composition requirements on various lubricants including lubricating greases to cater end application conditions . In recent years ,wide range of lubricating greases with varying performances are available to the endusers to meet the end applications which are mild to extreme stringent conditions . Requirements of lubricating greases must meet important parameters such as thermal , oxidation and good mechanical stability for their performance towards end applications . Lubricating greases of different types from simple thickener (sodium, lithium , lithiu -calcium , calcium) to complex thickener (lithium complex

, calcium complex aluminium complex), to non soap thickener (organo clay , polyurea to overbased calcium sulphonate complex) greases are most popular and widely used. In recent years lubricating greases are designed & developed with different composition to meet multipurpose requirements of end applications rather than specific one.

Lubricating Greases are characterized by elemental composition & molecular compositions. Not numerous method are reported in the standards & literature to characterize this products due to commercial interest of manufacturers. Till date , most commonly used method for analysis of lubricating greases are ASTM D 128 which gives an outline for characterizing different lubricatinggreases. Elemental composition of lubricating greases provides information on the type of elements which are part of components of greases either from thickener (both soap & non soap type of thickener) , type of organic / organometallic additives and type of fillers- silicates , metal oxide ,over based carbonates , including solid lubricants such as graphite , molybdenum disulphide , tungstun disulphide etc. Analytical tool such as Spectroscopic techniques based on UV Visible (UV-VIS) ,Atomic Absorption(AAS) ,Inductively Coupled Plasma Optical Emission (ICPOES), X-Ray Fluorescence (XRF) is widely used techniques for characterising lubricating greases for Elemental Composition. Some of the spectroscopic techniques requires careful & precise sample preparation procedures. During earlier years , time consuming hazardous wet chemical acid digestion procedure using perchloric acid & sulphuric acid was used . Later, relatively less time consuming & safe ashing procedure through oxide & sulphated ash was widely being adopted as sample preparation procedures. Ashing procedure has limitation of only analysing elements (metals) ,i.e. metallic portioncomponents of lubricating greases and does not provide information on non metallic elemental portion such as sulphur, boron ,halides , nitrogen etc. In recent years , microwave digestion based sample preparation technique is becoming popular and being used which can be utilized for bringingboth metals and non metals into solution without any loss of element. Microwave Digestion System has a advantage of being very rapid ,requires very small sample for digestion and require less acid for digestion and environmentally safe as digestion is done on closed vessels under microwave exposure as compared to conventional ashing procedure / wet chemical digestion procedure . The information obtained from the above study will be useful in understanding composition of different type of lubricating greases available in the market for both industrial & automotive end applications .

EXPERIMENTAL :

Chemicals & Labwares	: Nitric Acid and Hydrochloric Acid Analytical Reagent Grade were used . Silica Crucibles(50ml capacity) Standard glassware of Borosil make Beakers , Volumetric flask (250ml with stopper) Glass Rod 12.5cm ,were used for analysis.
Gases	: Argon Gas Purity (99.999 %) for Instrumental ICPOES .
Instruments	: Kohler Make Microprocessor controlled Muffle Furnace Operating Range (100^0C -1000^0C) , Anton Paar Microwave Digestion System model Multiwave 5000 , Laboratory Hot Plate and Thermo Fisher make Inductively Coupled Plasma Optical Emission Spectrometric (ICP OES) Model 6300 Duo .

PROCEDURE :

500 gms of collected ten samples of lubricating greases of consistency NLGI 00 to 3 marked as ‘A to K’ were taken for study .These samples were subjected to study by adopting the following procedures :

A Sample Preparation Procedure by Ashing Method of Lubricating Greases :

Each of the lubricating grease samples taken in previously weighed silica crucible and kept over a bunsen burner with flame to remove any volatile material and carbon soot which is followed by placing the silica crucible in a microprocessor controlled muffle furnace previously maintained at **750+/- 25** ^{0}C. kept for three hours. The ash with crucible from of each of the sample obtained was kept in a

250ml beaker , added 50ml mineral acid concentrated hydrochloric acid & 50 ml of distilled water and kept over hot plate in hot condition for till complete dissolution of ash and suitable dilute stock solution was made with distilled water (250ml) which was subjected to elemental composition for major elements (calcium , lithium ,sodium, aluminium, zinc, molybdenum and other elements such as potassium , magnesium , boron , & silicon). A blank solution was prepared for the analysis .
Elemental composition (metals) will provide information of nature of thickener, filler , common complexing agent if any present in the greases. Boron presence will indicate the type of complex thickener present and their level indicate whether it is boric acid based or borated ester based. Presence and level of zinc will indicate from additive or from filler like zinc oxide. Presence of molybdenum indicates presence molybdenum from either additives or from solid lubricant molybdenum disulphide (MoS2). Incase it is absent , solid lubricant present may be graphite based .

B. Sample Preparation Procedure for Microwave Digestion System of Lubricating GreasesInductively Coupled Plasma Optical Emission Spectrometric (ICP OES) analysis of Lubricating Greases :

Weighed about 0.2gm to 1gm of each of the lubricating grease samples in a standard PTFE sample vessel of Microwave Digestion System and added 10-20ml of concentrated nitric acid to each of samples and covered with inner lid followed by outer lid and tightened with recommended procedure . Kept all the PTFE sample vessel with samples in a Sample tray which can accommodate 24 samples .Carefully kept the tray in to the instrument magnetron(Microwave) compartment of microwave digestion system and performed the operation with set program of instrumental conditions at 250 deg.C for one and half hours till complete digestion occurs . Microwave Digestion System wascooled for half an hour and removed one by one all the sample vessels from the tray. Both the lids of PTFE sample vessel after digestion was opened and observed clear yellow to orange color solution which indicates complete digestion as occurred. Incase, digestion is incomplete , add more nitric acidor repeat re-digestion with addition of nitric acid digestion which will improve the digestion.
Sample with solid lubricant based MoS2 and graphite lubricating greases required more oxidizing acid for digestion. Microwave digestion system needs careful increase of oxidizing reagent volume as recommended by manual keeping in safety in mind pressure buildup in the digestion vessel. Transferred the content in PTFE vessel carefully into 250 ml beaker with washing using distilled water . A stock solution 100ml of each of the digested samples of different lubricating greases were prepared and subjected to elemental composition by ICPOES instrument. A blank solution was prepared for the analysis .Some of the samples may show some insoluble mainly from Silica which is filtered off quantitatively while preparing the stock solutions .

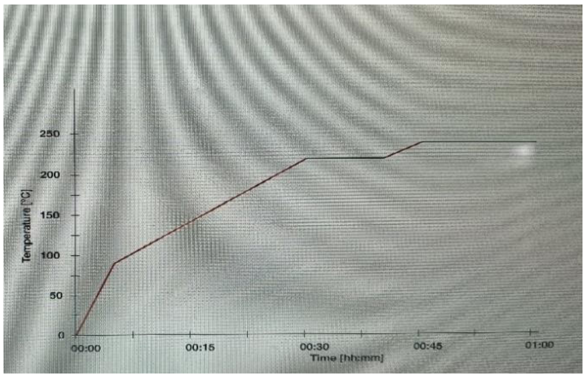
Microwave Digestion Condition Used :

Figure 1 shows Microwave Digestion Sample Vessel with Tray and instrument .

S.No.	Sample Weight ofLubricating Greasestaken for study	Reagent used	Volume ofReagent Used	Programming Mode	Time Duration
1.	0.2 gms – 1.0gms	Nitric acid / Aqua Regia	10ml-20ml	yes	2 Hours

Instrumental Condition Used :

Temperature Programming Recommended :



S.No.	Profile Step	Temperature ^{0}C	Duration (minutes)
1	Step 1	90	5.0
2	Step 2	220	25.0
3	Step 3	220	10.0
4	Step 4	240	5.0
5	Step 5	240	15.0
6	Cooling Step	70	Allow to cool down to ambient level before opening

During the process of digestion, pressure of the digestion vessel is also monitored to take care of safety along with Temperature profile.

C. **Inductively Coupled Plasma Optical Emission Spectrometric (ICP OES) analysis ofLubricating Greases** :

A suitable stock solutions of each of the lubricating grease samples were subjected to both the sample preparation procedures - Ashing & Microwave digestion system methods followed by subjecting elemental composition by Inductively Coupled Plasma Optical Emission Spectrometric (ICP OES). Elements of interest were checked for Fresh Greases – calcium ,lithium ,sodium, barium, aluminum, magnesium, potassium, zinc, molybdenum and Silica . Table 1 shows elements with emission atomic lines used for quantitative analysis by ICPOES for analyzing both Fresh & Used Lubricating Greases and information obtained related to components used in lubricating greases and wear metal debris and contaminants on usage of lubricating greases .

Table 1

Sl.No .	Element	Emission Wavelength for Study by ICPOES (nm)	Fresh/Used Samples of Lubricating Greases	Information Obtained based onpresence & its level
1	Aluminium	309.2	Fresh	Soap thickener , Filler – Clay
2.	Calcium	393.3	Fresh	Soap Thickener -Simple to Complex Type
3.	Lithium	670.7	Fresh	Soap Thickener -Simple to Complex type
4.	Sodium	588.9	Fresh	Soap thickener type
5.	Magnesium	279.5	Fresh	Filler based
6.	Potassium	766.4	Fresh	Filler based
7.	Zinc	213.8	Fresh	Additives, Filler
8.	Boron	249.7	Fresh	Complexing agent , Fillers
9.	Sulphur	182.0	Fresh	Base oil & additives
10	Phosphorus	213.6	Fresh	Additives
9.	Molybdenum	379.8	Fresh	Solid Lubricant , Additive

10.	Silicon	251.6	Fresh /Used	Silicates (clay) ,fumed Silica , sand and dust (Contaminant) and Wear Metal Debris
11.	Iron	259.9	Used	Wear Metal Debris
12.	Copper	324.7	Used	Wear Metal Debris
13.	Chromium	267.7	Used	Wear Metal Debris
14.	Nickel	221.6	Used	Wear Metal Debris
15.	Lead	220.3	Used	Wear Metal Debris

NIST Multielement Standard (21elements 1000ppm) Stock Solution along with individual NIST standards of 1000ppm of Sulphur, Phosphorus & Molybdenum were used for the calibration purpose of analysis. Suitable dilute calibration standards for elemental composition were prepared for each elements by ICPOES Analysis .

Standard Instrumental Condition used in ICPOES determination of Elemental Composition are given below . Present study is confined to fresh lubricating greases .

Instrumental Condition for ICPOES Instrument :

Plasma View : Radial mode , Peristaltic Flush pump rate : 50rpm, Analysis pump rate : 5rpm , Pump Nebulizer gas flow 0.6L/min Average of three measurement for each element were taken for quantitative analysis by ICPOES .

Results and Discussions :

A Inductively Coupled Plasma Optical Emission Spectrometric (ICPOES) analysis of LubricatingGreases by Ashing method :

Table 2

S.No.	Sample Description	% Li Lithium	% Ca Calcium	% Na Sodium	% Al Aluminium	% Mg Magnesium	% Zn Zinc	% Si Silicon	% Mo Molybdenum	%B Boron	Remarks Information
1	**A**	---	0.054	**1.39**	---	---	---	---	---	---	Sodium Soap Thickener
2	**B**	**0.245**	---	0.009	---	---	0.086	---	---		Simple Lithium Soap thickener , Additive
3	**C**	**0.222**	**0.289**	---	---	0.006	**0.011**	--	--		Mixed Lithium /Calcium Soap Thicken Additive
4	**D**	--	**1.25**	0.005	----	0.019	---	--	--	---	Simple Calcium Soap Thickener
5	**E**	--	**0.690**	--	---	0.008	0.005	---	---	**0.036**	Calcium Complex Soap
6	**F**	---	**3.48**	---	--	0.018	---	--	--	--	Calcium Non Soap Thickener
7	**G**	--	**0.080**	**0.103**	0.010	**0.084**	---	High (Insoluble)	**0.637**	---	Nonsoap thickener clay based With MoS2
8	**H**	0.054	**0.606**	0.011	---	0.010	**0.079**	--	---	0.034	Calcium soap thickener with lithium soap with Graphite (S.L)
9	**I**	0.005	**3.42**	---	0.006	0.14	**0.066**	--	**0.97**	---	Drak color, Calcium soap thickenerwith MoS2
10	**J**	**0.034**	0.009	----	**0.087**	**0.440**	---	**High (Insoluble)**	--	---	Lithium soap thickener with Silicates - Talc
11	**K**	**0.003**	0.014	0.012	**0.169**	**0.005**	**0.312**	---	---	---	Aluminium Complex Soap Thickener with Graphite & filler ZnO

Table 2 shows elemental composition of different samples of lubricating greases under study bysample preparation by Ashing Method .
Ashing method adopted provides information regarding elements mainly metals besides indicative of presence of non metal boron in the complex greases.Non metals Sulphur and Phosphorus are not determined by this method . % level of element gives information regarding presence of metals and non metals with their level indicating presence of thickener type , filler , complexing agent used in the lubricating grease. From the table 2, Element (metal) present in major amount indicated the element associated with thickener whether it is soap type or non soap type thickener present.

Generally , zinc presence checked with phosphorus and Sulphur presence indicative of Additive or as zinc oxide as a filler. Dropping point provides additional information regarding simple, complex to non soap thickener type FTIR Spectral analysis provides molecular composition regarding type of thickener , Additive used, base line drift indicates type of solid lubricant present .Visual appearance of lubricating greases indicates solid lubricant present or absent . Presence of Boron indicates type of complexing agent used and their level in lubricating grease indicated boric acid or borated ester presence .
From the above study ,it was observed that variation in elemental composition of different lubricating greases. Some of the greases provides information regarding components with type of thickener , filler / solid lubricant present together .

B Inductively Coupled Plasma Optical Emission Spectrometric (ICPOES) analysis ofLubricating Greases by Microwave Digestion Method :

Table 3

S.No.	Sample Description	% Li Lithium	% Ca Calcium	% Na Sodium	% Al Aluminium	% Mg Magnesium	% Zn Zinc	% Si Silicon	% Mo Molybdenum	% B Boron	Remarks Information obtained
1	**A**	---	0.054	**1.44**	---	---	---	---	---	---	Brown Color Sodium Soap Thickener
2	**B**	**0.242**	---	0.008	---	---	0.076	---	---		Simple Lithium Soap thickener, Additive
3	**C**	**0.232**	**0.281**	---	---	0.006	**0.009**	--	--		Mixed Lithium /Calcium Soap Thickener, Additive
4	**D**	--	**1.27**	0.005	----	0.017	---	--	--	---	Simple Calcium Soap Thickener
5	**E**	--	**0.710**	--	---	0.010	0.005	---	---	**0.040**	Calcium Complex Soap
6	**F**	---	**3.54**	---	--	0.018	---	--	--	--	Calcium Non Soap Thickener
7	**G**	--	**0.084**	**0.110**	0.010	**0.091**	---	**High** **(Insoluble)**	**0.642**	---	Nonsoap thickener claybased With (SL)MoS2
8	**H**	0.054	**0.610**	0.014	---	0.012	**0.083**	--	---	0.041	Calcium soap thickener with lithium soap with Graphite (SL)
9	**I**	0.005	**3.49**	---	0.006	0.161	**0.070**	--	**0.94**	---	Calcium soap thickener with MoS2
10	**J**	**0.036**	0.009	----	**0.087**	**0.451**	---	**High** **(Insoluble)**	--	---	Lithium soap thickener with Silicates -Talc
11	**K**	**0.009**	0.012	0.011	**0.172**	**0.007**	**0.340**	---	---	---	Aluminium Complex Soap Thickener with (SL) Graphite & filler ZnO

Sample Preparation of lubricating greases by Microwave Digestion method adopted provides information regarding elements mainly metals besides indicative of presence of non metal boron in the complex greases. Sample Preparation by Microwave digestion method followed by ICPOES determination of elements adopted provides information regarding elements metals besides indicative of presence of non metal boron in the complex greases. Non metals Sulphur and Phosphorus determination by ICPOES in lubricating grease processed by microwave digestion system are in progress . The percentage level of element gives information regarding presence of metals and non metals with their level indicating presence of thickener type , filler , complexing agent used in the lubricating grease.
From the above study , it was observed that the results obtained from use both the sample preparation procedures - Ashing procedure and Microwave Digestion System were in close agreement and comparable .

Conclusions :

In the present work , attempt has made to comparative study of use sample preparation procedure - Ashing and Microwave Digestion System for determination of Elemental Composition by ICPOES of different types of lubricating greases with varying composition .
Microwave digestion system is very sensitive digestion method (single step) , requires small sample and less digestion oxidizing reagent to bring very rapidly digestion of organic portion & elements into solution form relative to ashing procedure which requires larger quantity of sample, more time for ashing and bringing ash into solution form using reagent mineral acid (involves two steps) .
Suitable stock solutions from both the methods were followed by elemental composition by very sensitive ICPOES techniques .
From the above comparative study , it was observed that the results obtained from use both the sample preparation procedures - Ashing procedure and Microwave Digestion System were in close agreement and comparable .
Work is in progress to analyse phosphorus and sulphur by microwave digestion sample preparation procedure followed by quantitative determination by ICPOES.
Dropping point provides additional information regarding simple, complex to non soap thickener type.
FTIR Spectral analysis provides molecular composition regarding type of thickener and Additive used.
Visual appearance of black to grey color of lubricating greases indicates solid lubricant present or absent.
The information obtained from the above study using Microwave assisted digestion system will be useful rapidly determining the elemental composition of different lubricating greases in terms of , thickener type , additive present, type of solid lubricant used and type of complexing agent mainly boron based used. The study will be useful in analyzing unknown samples of lubricating Greases mainly from market for given end applications .

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9. EPA Method 6010B Method Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution

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Twin disc evaluation of top of rail friction modifiers and greases - A status report

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Abstract:
Top of rail (ToR) friction modifiers and flange lubricants are used to reduce wear, noise, and vibration at the rail-wheel interface without affecting the safety factors like braking distance and acceleration. Although there are no laboratory test standards for lubricant selection, the preference to any brand/supplier is based on the field performance metrics like grease pick-up, retentivity and carry down. An important drawback of field testing is that it is difficult to control parameters that can help lubricant formulation. In this regard there are several working groups in ELGI, NLGI and ASTM organizations working on development of lab test standards and protocols for railway lubricants. In this presentation, we will present a case study of two different ToR products (MoS2 and graphite based) and describe the test protocols that can evaluate three key performance metrics i.e., (a) traction vs. creepage characteristic for effectiveness in reducing friction/noise/vibration (b) traction vs. time characteristic for effectiveness in retentivity and carry down (c) wear rate vs. creepage characteristic for effectiveness in reducing rail-wheel profile deviation. Ongoing efforts on standardization of twin disc tribometer for evaluating TOR products would be discussed

Keywords: creepage, retentivity, wear rates, twin disc

1. Introduction

Railway transportation is highly efficient (6 times better) with low emissions (6 times lower CO2, NOx and PM) compared to road and air travel, yet contributes to only 10% of the global passenger and freight traffic (*source: IEA report*). This is rapidly changing with development of high speed rail networks and electrification in India and China. Moreover, urbanization and smart cities require metros for mass mobility with clockwork schedules and point to point connectivity. High speeds in long distance trains and heavier freight axle loads tend to accelerate other failure modes at the rail-wheel interface (*Figure 1*).

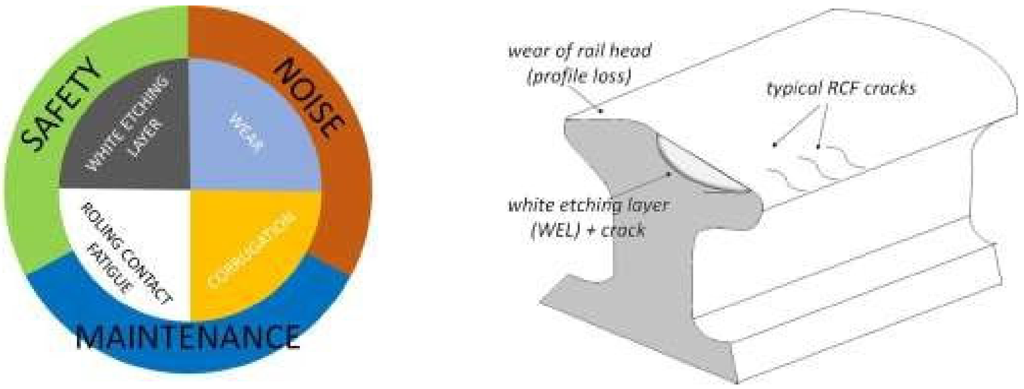

Fig 1. Different failure modes at rail-wheel contact that affect safety, maintenance and ride quality

Reports indicate millions of Euros in UK and Netherlands spent annually for track maintenance due to squats and other defects. Historically three important strategies have been deployed to address failures

(1) Advanced materials - high strength and tough pearlitic and bainitic steels, laser cladding for higher wear resistance and rolling contact fatigue life (RCF).

(B) Flange and top of rail (ToR) lubricants - to control friction at the rail wheel interface to reduce subsurface stresses, intensity of wear and RCF. A typical friction coefficient CoF < 0.15 is required for flange lubrication and CoF between 0.3 to 0.4 for rail head lubrication.

(C) Preventive maintenance - rail grinding to remove surface cracks (i.e., controlled wear) and restoring rail profile to reduce stress hotspots and extend RCF life.

Often the top of rail lubricants is a water-based polymer friction modifier and the wheel flange lubricants is a grease. Rail networks have preferences/approvals to certain lubricants/grease suppliers, however there is no preferences for ToR friction modifiers. For example, UK rail network standard NR/L3/TRK/3530/A01 recommends the use of RS Clare Supreme and Whitmore BioRail EP 1.5 grease for wheel flange lubrication in UK rail networks.

2. How Can Railway Lubricants Reduce Noise?

Noise comes from the wheel vibration due to stick-slip at the wheel-rail interface. The vibration is higher at the curves,that is widely known as wheel squealing. Friction modifiers in ToR lubes and wheel flange grease can reduce noise by suppressing these vibrations and maintain a positive or neutral traction coefficient. Recommended friction coefficient on top rail is between 0.25 to 0.40 for optimum braking and acceleration. Stick-slip is a result of difference in lateral and longitudinal motion of the wheels. Minimum difference between lateral and longitudinal motion enables energy efficiency and reduction in fuel consumption.

Greases and oils that are not consumed at the rail-wheel interface are bound to pollute the surrounding environment. Environmentally acceptable lubricants (EALs), for example the biodegradable ester base oils can be a suitable replacement to mineral oil-based lubricants used in wayside or onboard lubrication system Another widely adopted solution is solid lubricant stick, a matrix embedded with graphite or MoS_2 solid lubricants, used in onboard lubrication of wheel/wheel flange. Solid lubricant stick is known to reduce lubricant wastage and reduce fatigue cracks compared to grease.

3. Test Methods

Although there are no laboratory test standards for lubricant selection, the preference to any brand/supplier is based on the field performance metrics like friction, grease pick-up, retentivity and carry down. An important drawback of field testing is that it is difficult to control parameters that can help lubricant formulation. In this regard there are several working groups in ELGI, NLGI and ASTM like standards setting organizations working on development of lab test standards and protocols for railway lubricants. Twin disc or roller on roller tribometer has been widely used for railway lubricants characterization by rail network research labs, industrial and academic tribology labs. The rollers can be carved out of the rails and wheel, therefore the tests are closer to the field contact conditions. Therefore, it will not come as a surprise when we read that twin disc is the preferred screening test method in the BS EN 15427 and BS EN 16028 standards for rail friction management.

4. What type of tribometers are used for screening rail lubricants?

Tribometers must enable test methods to simulate the key rail/wheel contact conditions. Five essential control parameters can be used in selection of a tribometer as described below.

a) Generate contact pressure (0.5 to 2.5 GPa) over a larger contact area
b) Control creepage (0.1 to 20 %) at a surface speed of 1 m/s.
c) Holders compatible with top disc carved out of railway wheel and bottom disc carved out of rails
d) Sensors that enable traction coefficient vs. creepage curves for rail materials
e) Ability to evaluate all key lubricant metrics such as traction, wear rate, retentivity and rolling fatigue

Twin disc tribometer complies with all the five essential parameters required for railway lubrication research. In this report, we will briefly describe a case study on twin disc test method and relevant metrics used to characterize “railway solid lubricants”.

5. Case Study

Institute of Railway Technology in Monash University (Australia) (Reference - Fasahi, et al Tribology International (2021), 157, 106866) has designed a unique test method to characterize solid lubricants on Twin Disc or Roller on Roller Tribometer (Figure 2a). A specialized solid lubricant stick holder is designed for controlled application of lubricant in contact with the top roller (carved from railway wheel) (Figure 2b).

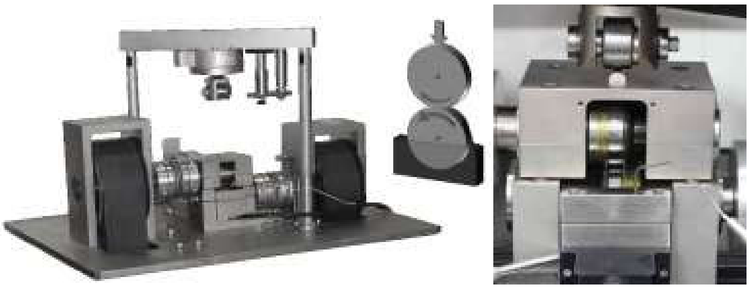

Fig 2a. Twin disc tribometer with two independent drives that offer 0 to 100%slip

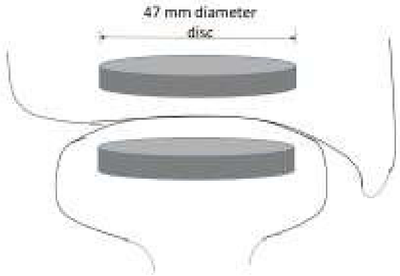

Fig 2b. Discs of diameter 47 mm machined from the actual rail head and wheel

Creepages in the range of 0.1 to 20 % is achieved using two direct drive servomotors for top and bottom rollers that are capable of speeds upto 3000 rpm. Pneumatic loading system is used to apply force in the range of 0.1 to 8 kN on the top roller that translates to a contact pressure range of 0.5 to 2.5 GPa. Retentivity, wear and traction curves were used in characterizing the solid lubricants. Retentivity is direct measure of longer product response time after single lubricant application. Wear is measured in terms of mass loss of roller after the test. Traction curves were derived from in-situ friction measurements at different creepages. The contact pressure (of 1 GPa) and % creepages comply with the BS EN 16028 standard. Two different solid lubricants, one based on graphite and another based on MoS2 both extreme pressure additives were tested. Results showed that the graphite based solid lubricant stick showed lower stable traction curve compared to dry condition or MoS based solid lubricant (*Figure 3a*). However, it showed a negative slope after saturation indicating tendency for stick-slip and potential higher noise compared to MoS2.

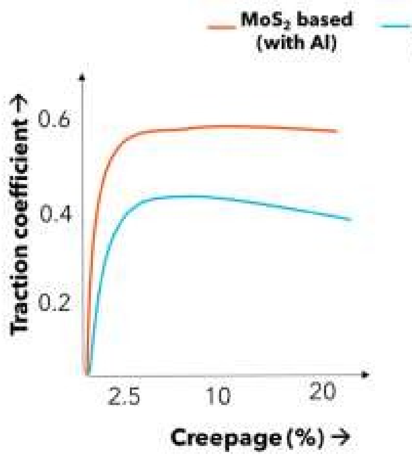

Figure 3a. Traction vs. creep characteristic for MoS2 and graphite based lubricants

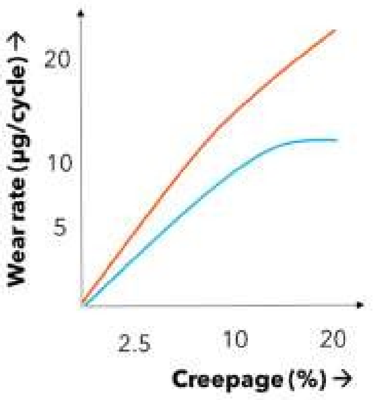

Figure 3b. Wear rate vs. creepage for MoS2 and graphite based lubricants

The rail wear was lower for graphite-based lubricant compared to MoS2 based solid lubricant (*Figure 3b*). Furthermore, retentivity of graphite-based lubricant was better than MoS2 (Figure 4) that translates to better carry down, protection of rails against wear as well as less material usage.

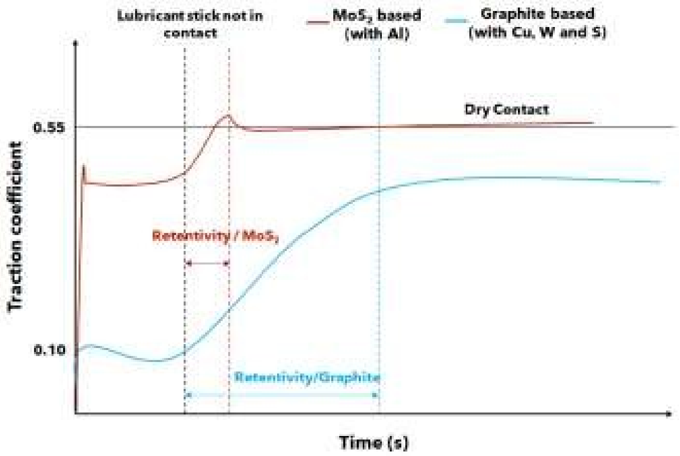

Figure 4. Evolution of traction coefficient over time for various lubricant contact conditions. Graphite based lubricants showed higher retentivity and lower traction coefficient compared to MoS2 based lubricant

6. Summary

Twin disc can enable development of railway lubricants for energy efficiency, safety and low maintenance cost. However, its general acceptance in the laboratory will depend on the precision in repeatability and reproducibility. Precision can be developed by collecting the traction coefficient and wear data from multiple twin disc tribometers following an established test protocol.

Identification and quantification of Lubricating Grease Components (Base oil and Thickener types) by IR / Raman / TGA / ICP

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Abstract: Greases mainly contains base oils, thickener and additives to meet the specific needs of machinery or industry. Most of the thickeners are long chain carboxylic acid salts (Ca, Na, Al, Li, Ba) and others are polyurea, clay, graphite, molybdenum sulfide, PTFE for special type of applications. Base oils used in greases are mineral type (Group I, Group II, Group III) and synthetic type (Group IV, Group V) to meet the target NLGI grades. Superior performance greases are always achieved by stringent product specifications with reference to base oil, thickener, and additive. Molecular level (component classes or functional groups) and Atomic level (elemental) is very important for understanding the structure property correlations. Most of the grease thickeners are different properties compared to base oils and additives. Poor solubility of thickeners (Organic, inorganic, stearate metal salts) in organic solvents makes it difficult to get the quantitative information (Base Oil & Thickener) from most of the analytical techniques (spectroscopy or chromatography) which needs the sample dissolution in polar or non-polar organic solvents.

Current study focused on development of methodology for grease components (Base Oil & Thickener) separation (Hexane solvent reflux, filtration, dialysis, open column) followed by identification using various analytical techniques viz FT-IR, Raman, ICP-OES, TGA. Hexane solvent reflux followed by filtration through 0.45micron size filter enables the separation of thickener from base oil and additives. Membrane dialysis of solvent reflux filtrate is subjected for the separation of components (Base Oil & Additives) based on the molecular weight. Dialysate or low molecular weight part further subjected to open column for separation of base oil from additives. After removal of solvent from all the fractions (solvent reflux, filtration, membrane dialysis, silica gel open column), weights are recorded and components are identified by IR or Raman. Developed methodology successfully demonstrated the component identification and quantification of Base oil & Thickener in different greases viz Polyurea, Clay, Lithium stearate, and Lithium stearate with Graphite, Molybdenum sulfide.

Key words: Grease, Lithium hydroxy stearate, polyurea, molybdenum sulfide, clay, graphite, base oil, viscosity improvers, open column, filtration, optical emission spectrometer, infrared spectroscopy, raman spectrometer, thermogravimetry analyzer

1. Introduction

Most greases produced today use mineral oil as their fluid components. These mineral oil-based greases typically provide satisfactory performance in most industrial applications. In temperature extremes (low or high), a grease that utilizes a synthetic base oil will provide better stability. The thickener is a material that, in combination with the selected lubricant, will produce the solid to semifluid structure. The primary type of thickener used in current grease is metallic soap. These soaps include lithium, aluminum, clay, polyurea, sodium and calcium. Lately, complex thickener-type greases are gaining popularity. They are being selected because of their high dropping points and excellent load-carrying abilities. Complex greases are made by combining the conventional metallic soap with a complexing agent. The most widely used complex grease is lithium based. These are made with a combination of conventional lithium soap and a low- molecular-weight organic acid as the complexing agent. Non-soap thickeners are also gaining popularity in special applications such as high-temperature environments.

Bentonite and silica aerogel are two examples of thickeners that do not melt at high temperatures. There is a misconception, however, that even though the thickener may be able to withstand the high temperatures, the base oil will oxidize quickly at elevated temperatures, thus requiring a frequent re-lube interval.

Additives can play several roles in a lubricating grease. These primarily include enhancing the existing desirable properties, suppressing the existing undesirable properties, and imparting new properties. The most common additives are oxidation and rust inhibitors, extreme pressure, anti-wear, and friction-reducing agents.

Grease and oil are not interchangeable. Grease is used when it is not practical or convenient to use oil. The lubricant choice for a specific application is determined by matching the machinery design and operating conditions with desired lubricant characteristics. Grease is generally used for:

- Machinery that runs intermittently or is in storage for an extended period of time. Because grease remains in place, a lubricating film can instantly form.
- Machinery that is not easily accessible for frequent lubrication. High-quality greases can lubricate isolated or relatively inaccessible components for extended periods of time without frequent replenishing. These greases are also used in sealed-for-life applications such as some electrical motors and gearboxes.
- Machinery operating under extreme conditions such as high temperatures and pressures, shock loads or slow speed under heavy load.
- Worn components. Grease maintains thicker films in clearances enlarged by wear and can extend the life of worn parts that were previously lubricated by oil.

Present paper experimented the conventional fractionation methods for grease components (Base Oil & Thickener) separation (Hexane solvent reflux, filtration, dialysis, open column) followed by characterization using FT-IR, Raman, ICP-OES, TGA. Being a quick separation method, solvent reflux followed filtration method is attempted for the quantification of thickeners from greases. Membrane dialysis of solvent reflux filtrate is subjected for the separation of components (Base Oil & Additives) based on the molecular weight. Dialysate or low molecular weight part further subjected to open column for separation of base oil from additives. FT-IR used for identification and quantification of base oils obtained through filtration, membrane dialysis, silica gel open column. Developed protocol (Fig 1) is used for clay, polyurea, Li stearate greases to understand its applicability for base oil and thickeners.

2. Materials - Methods - Equipment’s

2.1 Thermal Analysis

Thermogravimetry analyzer (M/s Leco, TGA701) used for measuring the weight loss changes at 100, 200, 300, 400, 500, 600, 700°C. Grease samples (2.0g) loaded to tared alumina crucibles and heated at 5°C / min under Nitrogen environment. Weight loss measuring program created to record the weight of the sample after 5min isothermal condition at desired temperatures. Heating rate 5°C or lower is preferred to control the boiling and slow evaporation of grease components. Macro TGA used (Fig 3) for the present study, is having the large furnace with 19 position motored carousel, simultaneously measures the weight losses in sample without any manual intervention. Data acquisition and processing were carried out using TGA equipment control software.

2.2 Elemental Analysis - Optical Emission Spectroscopy

A. Acid digestion of Greases:

Grease (0.1g) sample in platinum crucible are mixed with 1.0ml of Conc H2SO4 and kept on hot plate (300degC) till dryness. Transfer the crucible to muffle furnace (Pyro, Milestone, Italy) at 700°C for 3hours. Graphite based greases requires higher temperature (950°C) for its removal. Ash obtained is treated with 10ml of aqua regia (1:3 HNO_3 & HCl) on hot plate at 120°C till the clear solution appears. Transfer the contents to 50 / 100ml volumetric containing 0.2 ml of 1000 ug/g of Yttrium (Inorganic Ventures, USA) internal standard and make up to 100ml volume with MilliQ water (Metrohm, ELGA). Supra pure acids (Merck) are used for digestion of ash derived from greases and cleaning of labware to avoid contamination. Ash obtained from clay based thickeners is difficult to dissolved in aquaregia. Ash from clay based greases is further subjected to borate fusion (50mg of sample and 0.5g of Lithium borate powder) method at 1000° and solubilized in (20% HCl) for ICP elemental analysis.

B. ICP - OES Measurements

Single elemental standards (Inorganic ventures, USA) 1000 ug/g - Li, Al, Na, Mo, Fe, Mg and 1000 ug/g Yttrium internal standards are used for preparing the standards. 0.05, 0.5, 1.0 ml of 1000 ug/g single elemental standards are added to 100ml volumetric flasks (Class A, Poly Ethylene or Polymethylpentene) containing 0.2ml of Y 1000ppm and 5ml of Conc HCl. Mix the contents and made up to the mark with MilliQ water label the flaks 0.5, 5.0, 10.0 ug/g Elemental standards with 2 ug/g Yttrium Internal Standard. Calibration blank is prepared in the similar procedure with internal standard and 10ml of aqua regia.

Standards and samples are analyzed with 3 replicates using Optical Emission Spectrometer (Model: iCAP Pro & Make: Thermofisher, Fig 3) equipped with mineral acid compatible sample introduction system and segmented array Charge couple Device (SCD) detector. Sample introduction system composed of sample tubing (PVC, 0.76mm), waste tubing (PVC, 1.4mm), Gemcone nebulizer (PEEK), cyclonic spray chamber (Quartz, 4mm baffle), and Injector tube (Alumina, 1.2mm). ICP acquisition parameters shown in the table are optimized to get the target repeatability and accuracy of each analyte (Na, Al, Li, Mo, Zn, P, Si). Data acquisition and processing were carried out using ICP equipment control software Qtegra (Ver 2.14).

2.3 Infrared and Raman Analysis

A. Fractionation of Grease components (Solvent reflux - Dialysis - Open Column)

Greases both soap (Li stearates) and non-soap (Silica, Poly urea, Li stearate with MoS2 and graphite) based are subjected to hexane solvent reflux (10g Grease / 100ml) for 2 hours followed by filtration (0.45u Mixed Cellulose Ester, Millipore, 45mm Filter). Residue is washed with hexane and air dried to get the thickener content. Filtrate is collected and hexane solvent recovered through rotavapor (Buchi). After complete removal of hexane solvent, quantitatively transferred to dialysis membrane and continuously soxhlet extracted for 5 to 6 hours for molecular weight separations. High molecular or non-permeable part is separated and weighed for quantitative estimation of polymer types. Permeable or low molecular weight (base oil and additives) part is further subjected to open column (30mm ID x 900mm length) with chromatography grade silica (60 -120mesh). Column washed with 100ml of hexane for two 2 or 3 times. Eluent flow should be set to 2ml / min and collect the 300ml of hexane fraction to 450ml of glass beaker. Remove hexane from the column effluent using rotavapor and weighed to get the base oil content. Sem-micro analytical balance with 0.1mg sensitivity (MSA-225S-100-DA, Sartorius, Germany) is used for all the weight measurements.

B. Characterization of Thickeners & Base Oils

Greases, thickeners and base oils are analyzed for FT-IR (Agilent, Cary 600, Singapore) using scan range 4000 - 400cm^{-1}, resolution 4cm^{-1}, and 30 no' of scans. Greases are presented to spectrometer as films on KBr / KRS5 (Circular window, 25mm x 4mm) and base oils are filled in demountable fixed path cells having 0.1mm optical path. Dried thickener samples (3-4mg) are mixed with 400mg dried (at 120°C) potassium bromide powder (IR spectroscopy grade, Merck) grounded to are pressed to 13mm KBr disc using hydraulic pellet press with 5ton pressure. Data acquisition and processing were carried out using FT-IR equipment (Fig 3) control software (IR Solution Ver 1.50) for base line, smooth, and peak wavenumber. Hydrocarbon type analysis (Ca, Cp, Cn) of base oils separated from greases performed on FT-IR spectrum recorded with 0.1mm optical path as per IS13155 & IP451. Non-soap thickeners (Graphite, MoS_2, Silica) separated from greases are analyzed by Raman (Horiba, LabRam HR Evo, France, Fig 3) microscope using 470nm / 530nm laser and 50x objective (FN26.5, long working distance) in the range 4000 - 200cm^{-1} with 20sec acquisition time. Data acquisition and processing were carried out using Raman equipment control software (Lab Spec 6) for base line, smooth, and peak wavenumber.

3. Results & Discussion:

3.1 Thermal Analysis

Thermal stability or weight losses measured by TGA are presented in Table 1 and corresponding thermogram of selected greases in Fig 1. TGA in nitrogen atmosphere shows major weight loss in the range 275 - 375°C. All the samples lost volatile or by-products of decomposition and no further weight loss seen in most of the greases after 600°C. The change in weight loss difference between 600°C and 700°C is not significant. TGA residue 6.4% for SPL#2 infers that thickener is inorganic type and it is directly revealing the exact content of inorganic type thickeners. Grease SPL#1 residue 0.4% at 700°C confirms the thickener is organic type and residue is due to presence of additives with metals. TGA thickener quantification for inorganic types (Clay, Graphite, MoS_2 type) is produces false positive results if the sample contains the additives with metals. Clay, Graphite, and MoS_2 type thickeners are highly stable up to 700°C or even higher temperatures under N_2 environment. Grease SPL#3 shows 4.0% residue and SPL#5 is with 1.4%. From Raman study (Fig 7), SPL#3 shows MoS_2 and Graphite where the IR (Fig 5 & Fig 6) confirms the presence of Li soap in both the samples (SPL#3 & SPL#5).

3.2 Elemental Analysis

ICP-OES thickener elemental data of selected greases for study given in Table 5. From ICP data, SPL#1 not showing any thickener elements (Li, Na, Al, Si, Ca, Ba) which confirms the organic type thickeners (Polyurea). SPL#2 shows the presence of Al, Na, Fe, and Si and confirms the thickener is inorganic clay (bentonite) based. Sample#3 shows Lithium and Molybdenum where as the sample#5 shows only Lithium. From Raman study (Fig 7), SPL#3 shows MoS_2 and Graphite where the IR (Fig 5 & Fig 6) confirms the presence of Li soap in both the samples (SPL#3 & SPL#4).

3.3 Infrared and Raman Analysis

A. Greases & Thickeners

IR spectra of greases and thickeners separated from greases are presented in Fig 5 & Fig 6. IR spectrum of SPL#1 & SPL#2 shows the presence of Lithium stearate type thickener and characteristic peaks appears about 1585 & 1555cm^{-1}. Both these IR bands are with high intensity and appears due to C=O vibration modes (asymmetric) of COO- functional groups present in complex soap types. IR band at 1400cm-1 is due to symmetric COO- vibrational mode. Grease SPL#3 is non-soap inorganic type and IR confirms clay (bentonite) due to presence of strong vibrational modes of SiO_4 tetrahedron (1100-100cm^{-1}, str), deformation mode of Al-O-Si (535cm^{-1}), and deformation mode of Si-O-Si (470cm^{-1}). Grease samples (SPL#4 & SPL#5) are non-soap and organic thickeners. SPL#4 IR confirms to polyurea based thickener due to presence of urea characteristic bands amide NH (3400cm^{-1}) and C=O (1600cm^{-1}). SPL#5 FT-IR clearly shows the presence of fluorinated thickener preferably and its exact component type is difficult to interpret without base oil separation. Type of base oil (SPL#1 to 4) in all the greases selected is not very clear due presence of thickener and additives characteristic IR bands. Base oil in SPL#5 is fluorinated and is confirmed due to absence of -CH_2- or -CH_3 characteristic bands (2900, 1450, 722cm^{-1}) which generally present in long chain hydrocarbons of thickeners and base oils. Raman spectrum of thickeners (MoS2 & Graphite) separated from greases presented in Fig 7.

B. Base oils

FT-IR spectrum of base oils separated from greases after hexane removal is presented in Fig 11. There is no base oil present in column fraction 1 due to wet packing method used for column preparation. All the base oil component of selected greases is eluted in hexane column fractions 2 to 4. There is no base oil seen in column hexane fraction 5. All the additives are eluted to polar fraction 6 with dichloromethane & methanol. Column fractions 2 to 4 mixed to get the base oil content and tested for FT-IR to check the purity of base oils obtained with proposed methodology. Based on the FT-IR functional groups, there is no characteristic peaks of commonly used additives present in the base oil fractions. Aromatic band of base oils is not interfering with the most of the grease additives and Ca (aromatic carbon) is reported using IS 13155. Carbon type (aromatic) of the selected greases is presented in Table 3 and varying from 6.4 to 11.4 %. This method is not applicable to synthetic base oils of Gr IV and Gr V or synthetic base oils blended with mineral type oils.

4. Conclusions:

Current methodology successfully applied for quantification of base oils and thickeners from clay, polyurea, lithium stearate greases. Sequence of fractionation methods should be strictly followed for getting the accurate results. Time of solvent reflux, soxhlet extraction (dialysis), and column elution is very important for effective separation of base oils and thickeners. Based on the current experiments 2 hours for solvent reflux and 6 hours for Soxhlet extraction (dialysis) achieves excellent separation. Residue content derived from TGA reveals that the thickener is inorganic or organic type. ICP-OES elemental analysis data helps to find out the thickener elements preferably inorganic. Organic thickener based greases not shows the significant amount (< 0.01%) of elements. FT-IR is a simple and quick technique for identification of thickener types in greases. Due to functional groups overlap in greases, accurate judgement of base oil types can be done after its separation from thickener (filtration) and additives (dialysis and column fractionation). Grease components (base oil and additives) produces strong fluorescence in Raman and difficult to produce raman signals using visible (470, 530, 633nm) and Near IR lasers (830nm). Inorganic type thickeners (Graphite and MoS_2) needs to be separated through solvent reflux for getting the raman signals. Study of similar type of protocol for Al, Ba, Na, Ca, PTFE thickener greases in progress.

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Fig 1: Methodology for Grease Components Separation

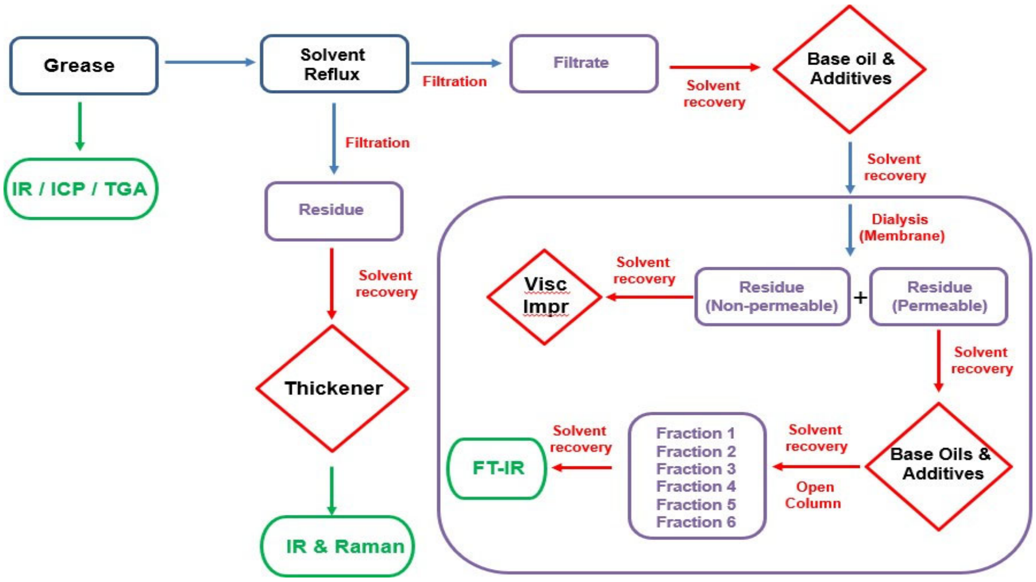


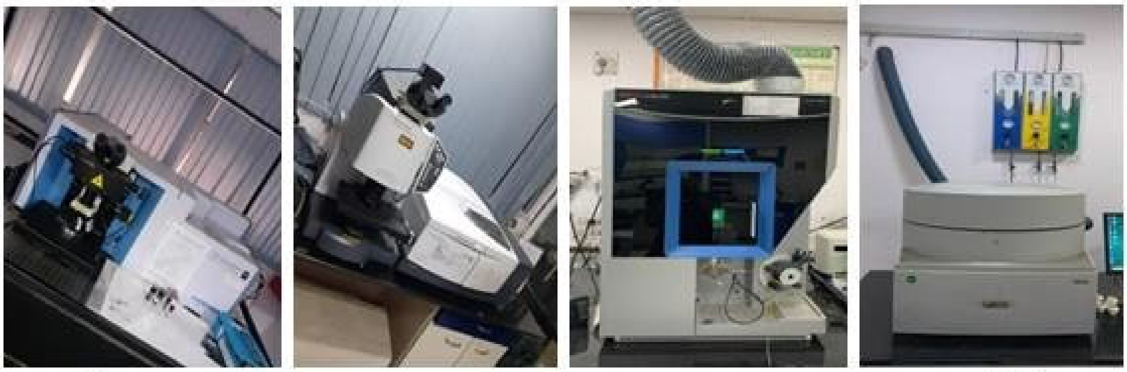
Fig 2: Equipment's used for Separation of Grease components


Filtration

Dialysis

Open Column

Fig 3: Equipment's used for characterization of greases and grease components


Raman

FT - IR

ICP-OES

TGA

Fig 4: TGA Thermogram of Greases

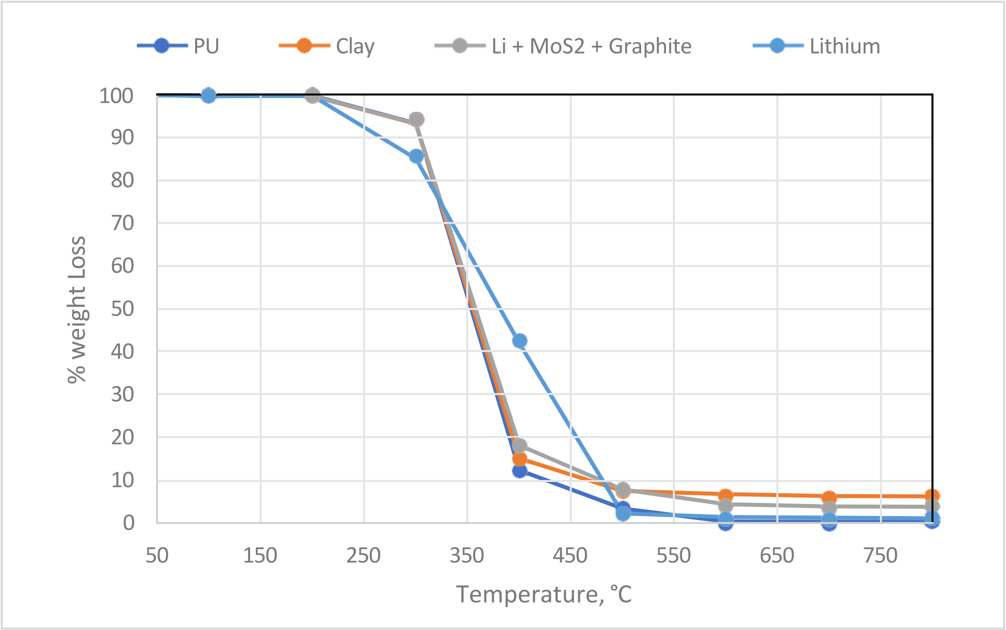


Fig 5: FT-IR spectrum of Greases

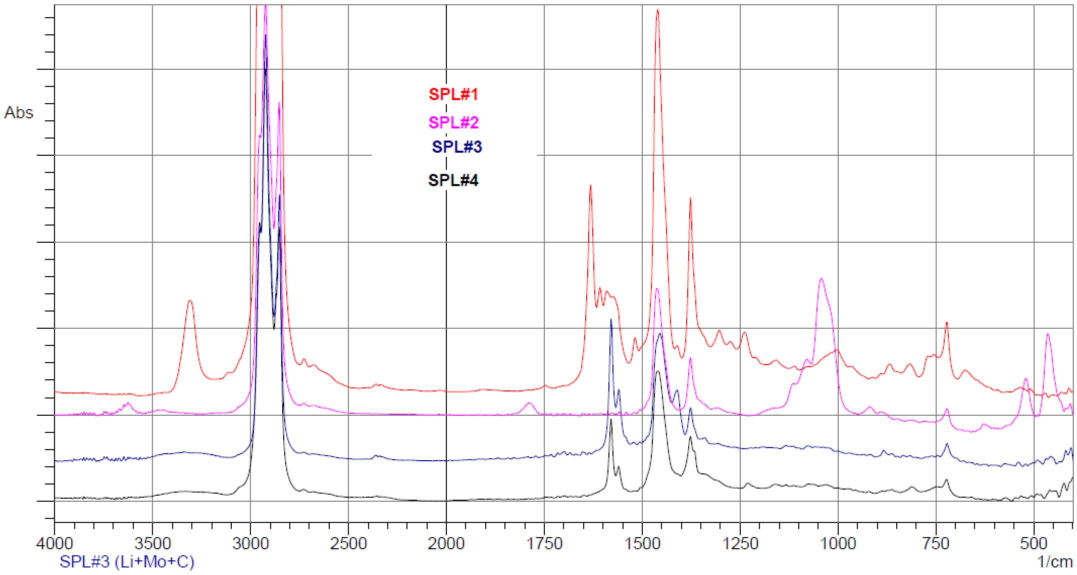


Fig 6: FT-IR spectrum - Hexane in-soluble parts of Greases (Filtration)

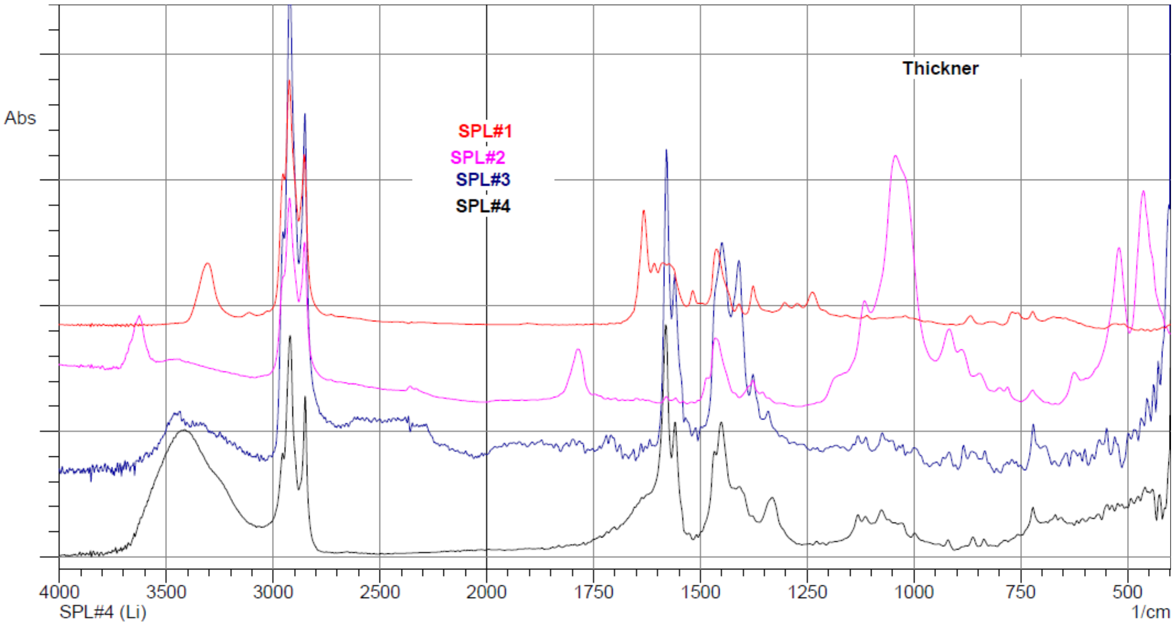


Fig 7: Raman spectrum - Hexane in-soluble part of SPL#3 (Filtration)

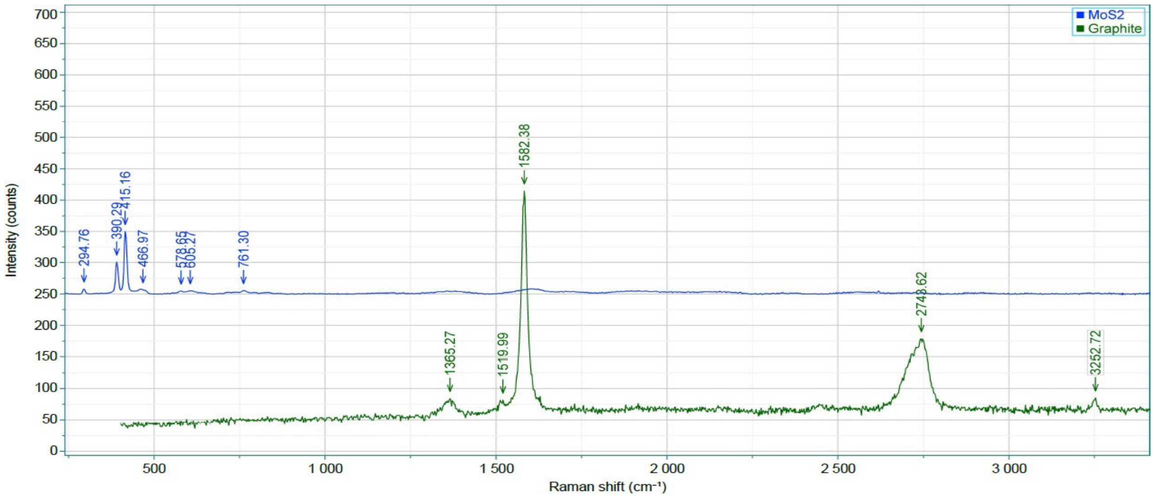


Fig 8: FT-IR spectrum - Hexane soluble parts of Greases (Filtration)

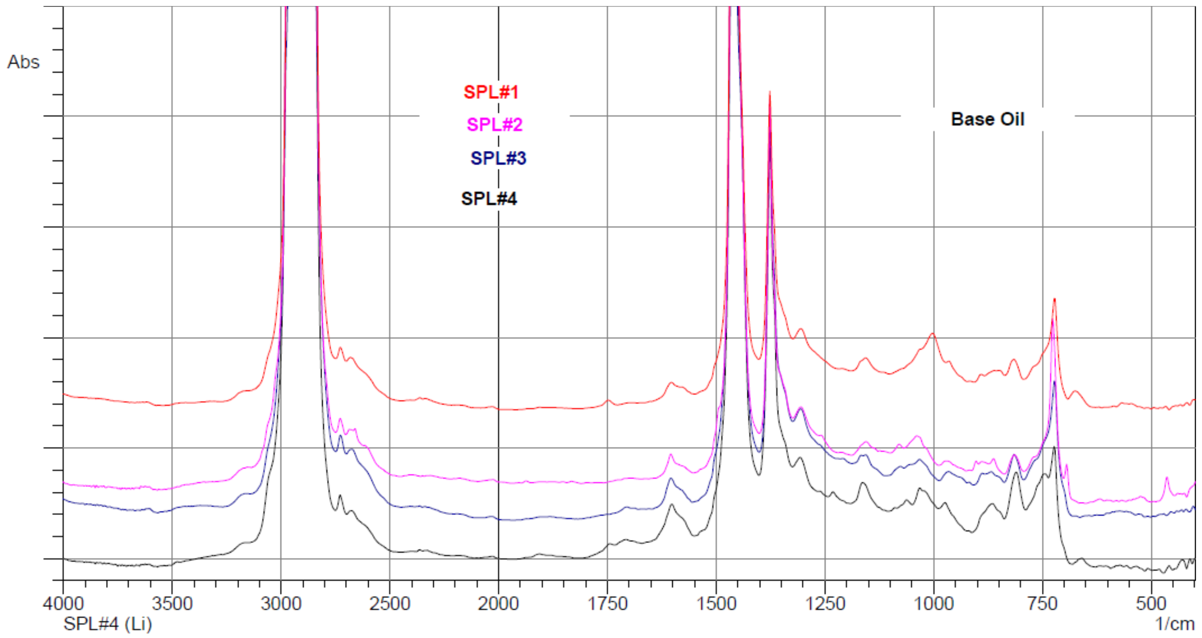


Fig 9: FT-IR spectrum – Solvent Reflux Experiments of SPL#4 Grease

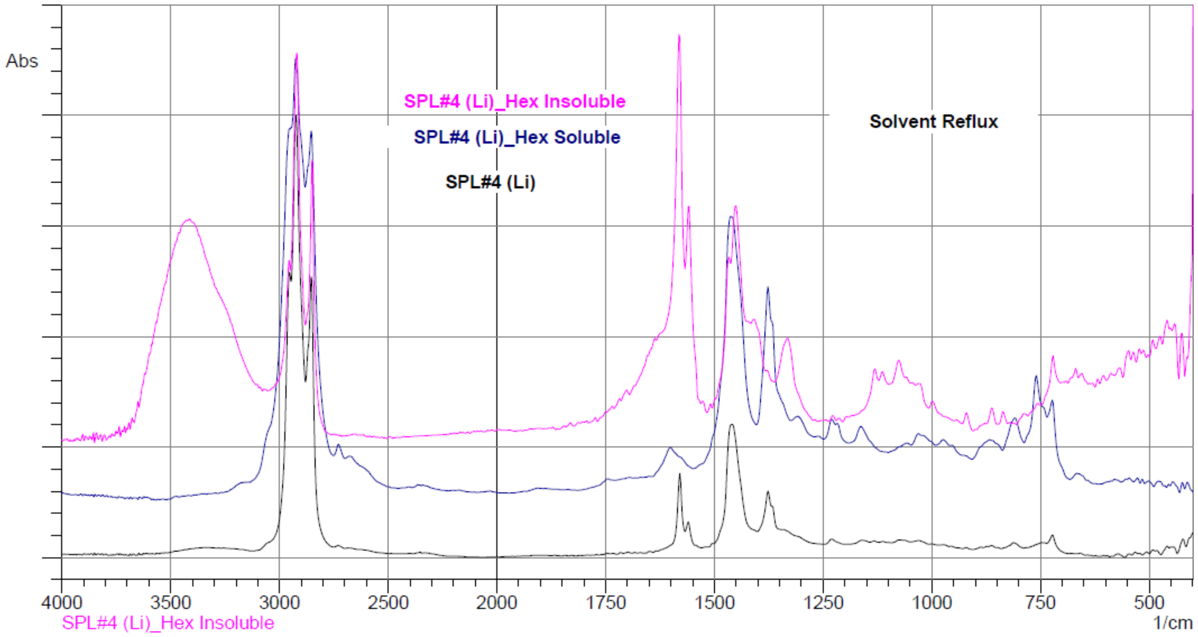


Fig 10: FT-IR spectrum - Dialysis Experiments of SPL#4 Grease

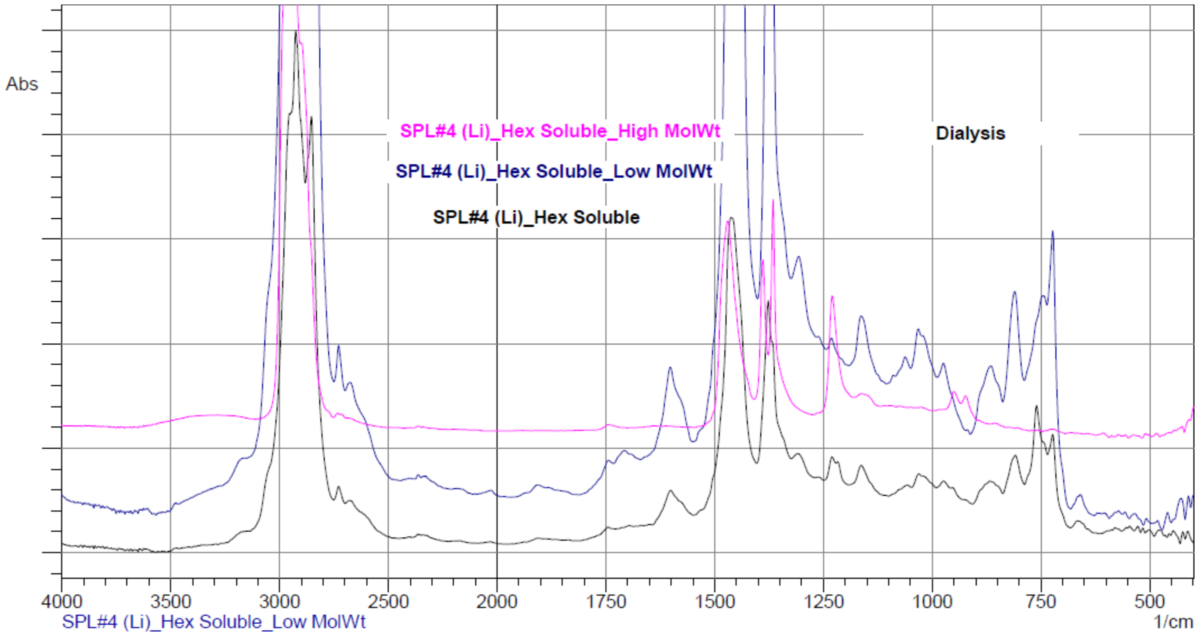


Fig 11: FT-IR spectrum - Column fractionation of low molecular weight from Dialysis

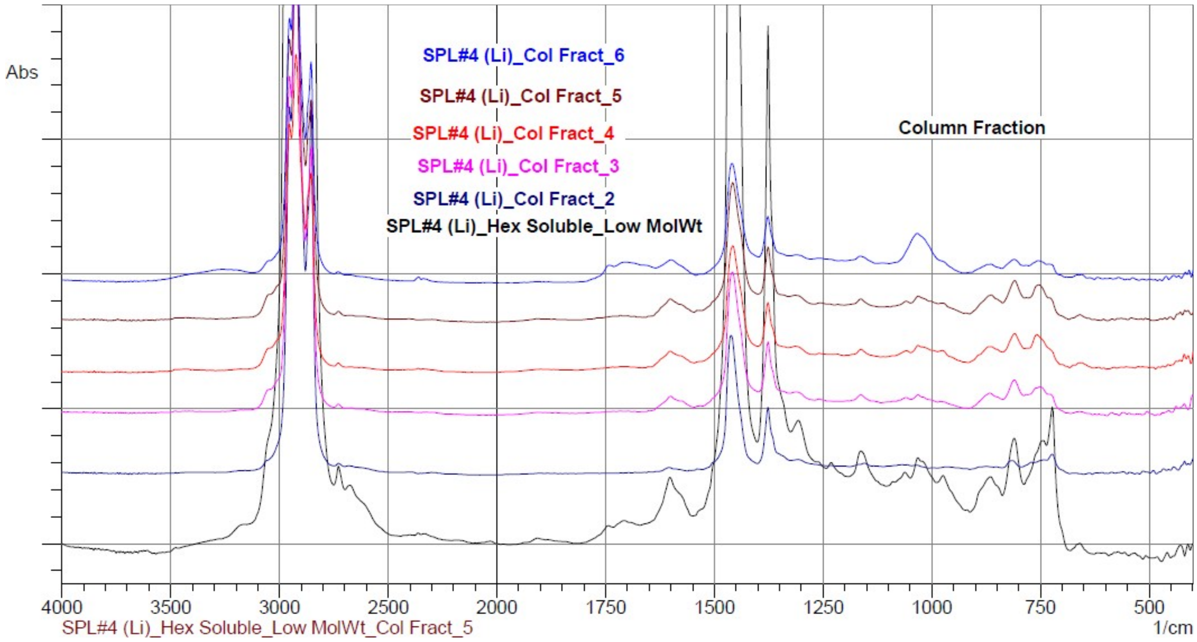


Table 1: Optical Emission Spectrometer - Acquisition Parameters

Parameter	Set value
Atomic Lines	Li, Na, Al, Fe, Si, Mo
Read delay time (s)	60
Replicates (Nos)	3
Plasma gas (Ar, L/min)	16.0
Auxiliary Gas (Ar, L/min)	1.20
Nebulizer Gas (Ar, L/min)	0.44
Purge Gas (Detector)	Nitrogen
Shear gas (Plume out)	Air
Nebulizer type	Gemcone (PEEK)
Spray Chamber type	Cyclonic (Quartz, 4mm
Injector tube type	Alumina (1.2mm ID)
Cooling Water (Chiller)	15°C (4L/min)
RF generator (MHz)	40
RF Power (watts)	1350
View Distance (mm)	15.0
View Mode	Radial
Peristaltic Pump Rate (ml/min)	0.74 (Sample flow)
Peak Algorithms (points / peak)	7 (Area)
Calibration Equation	Lin, Calc Int

Table 1: Weight Loss % by TGA

Grease	25°	100°	200°	300°	400°	500°	600°	700°
SPL#1	100	99.8	99.8	93.3	12.4	3.5	0.4	0.4
SPL#2	100	99.8	99.7	93.2	15.2	7.5	6.8	6.4
SPL#3	100	99.8	99.7	93.3	18.3	7.9	4.5	4.0
SPL#4	100	99.8	100.0	99.7	85.4	13.8	0.0	0.0

Table 2: Elemental (Thickener) Analysis by ICP-OES

Grease	Li	Mo	Al	Na	Fe	Mg	Si
SPL#1	< 0.01%	< 0.01%	< 0.01%	< 0.01%	< 0.01%	< 0.01%	< 0.01%
SPL#2	< 0.01%	< 0.01%	0.74	0.05	0.22	0.10	3.8
SPL#3	0.36	0.57	< 0.01%	< 0.01%	< 0.01%	< 0.01%	< 0.01%
SPL#4	0.16	< 0.01%	< 0.01%	< 0.01%	< 0.01%	< 0.01%	< 0.01%

Table 3: Grease components by Filtration - Dialysis - Column followed by IR / Raman

Grease	Base oil type	% Base Oil (column)	%Thickener (filtration)	Thickener type (IR / Raman)	Ca, % (IS131155)
SPL#1	Mineral	89.8	9.2	PU	6.4
SPL#2	Mineral	90.6	7.8	Clay	9.2
SPL#3	Mineral	84.7	13.4	Li + MoS_2 + G	11.2
SPL#4	Mineral	88.2	11.0	Li	11.4