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Fire Resistant Grease For Steel Plants

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Abstract

Steel plants require high performance lubricating greases to combat stringent operating conditions in applications like blast furnace, coke ovens, wire rod mills, continuous casters, hot units, etc. In continuous slab casters, molten steel enters formation chamberand is transformed into steel slabs of varying thickness and sizes emerging from the formation chamber with a thin skin of solidified steel holding together. These steel slabs are carried away from the formation chamber on suitable material moving devices. The temperature of these slabs in this section of the steel mill is typically very high in the range of around 900° C. The bearings fitted in these conveyer units are very costly and more over it is very difficult to replace bearings. Changeover /frequent unscheduled repair maybe a very costly affair for the steel plants. In steel plants, there are certain segments where specialty greases are also required like fire resistant greases. These are also known as self-extinguishing greases which catch fire but fire stops to propagate further within a few seconds and thus the costly bearing is saved, in addition to avoids costly breakdowns/shutdowns. The composition of grease is designed in such a way that it contributes to extinguish fire by selecting special thickener and base oil that controls fire by reducing availability of oxygen.

The authors at M/s Siddharth Grease & Lubes Pvt. Ltd, India have successfully developed Fire Resistant Greases using phosphate esters and a special fire retarding chemical. Thistechnical paper encompasses various stages of development of semi-synthetic fire resistant grease using suitable thickener, combination of selected base oils and additives.Properties of the developed grease have been compared to well established product arediscussed in this paper. Greases was tested for fire resistance and found to be comparable or slightly better than the existing products in use.

Keywords: Thickener, Fire Resistant Grease, Self-Extinguishing Grease, Semi- synthetic, continuous casters.

Introduction

In heavy Industries, grease fires can be costly in terms of loss of equipment, operational downtime and loss of life. It is highly desirable to have high-performance fire resistance greases which also reduce the incidence of grease fires [1]. Greases used in heavy industries play a key role in the performance of the equipment used. These may be mineral, semi-synthetic or synthetic in nature and are chosen by formulators based on their performance needs. Synthetic lubricants were developed for applications where petroleum products were inadequate to meet critical specification needs or where specialcharacteristics, such as long life, improved equipment efficiency or non-flammability wereneeded [2]. Among the synthetic lubricants, keeping non-flammability characteristics inview, phosphate esters are very low in volume. Fire resistant greases have beendeveloped for mining, die-casting, pressure casting machines, steam turbine control system, aviation, steel mill applications, etc. These greases have significantly higher temperatures or fire-resistant properties [1a]. This class of esters is widely used to conceptualize and incorporate fire resistance in lubricants or fire-resistant greases. Theseoils afford better fire protection over mineral oils. Polychlorinated Biphenyls were also themost effective fire resistant but due to toxicity they are no longer in use. [1b].

Greases of different base types (Calcium/Lithium/Aluminium/Polyurea/Clay base) with or without additives/fillers are used for the lubrication of different bearings and couplings in steel plants. Among the specialty greases that include aluminum complex, lithium complex, polyurea and calcium-sulfonate-thickened greases are designed to address the customers' needs through proven technology. Fire resistant greases have been developed by incorporating some special synthetic oils like phosphate esters and a special fire retarding chemical with high performance thickeners doping special additives that can work synergistically with the thickener under high temperature conditions.

SIGNIFICANT PROPERTIES OF FIRE RESISTANT GREASES

A grease composition can be designated as exhibiting fire resistance properties which possesses at least one of the two following qualities: (a) the grease composition will not spontaneously ignite (burn with flames) at the intended surrounding service temperature, that is the grease composition will not ignite, for example on contact with surfaces having temperatures of around 900°C; (b)Even if the grease composition does ignite, the flames will not propagate but will self-extinguish within a predetermined time. Unless otherwise specified, the predetermined period will be five minutes for the purposes herein [3].

Fire resistant grease should meet the following properties: (a) reduce wear and friction; (b) prevent rusting even in presence of water; (c) non-corrosive to bearing material; (d) resistant to pressurised water sprays and (e) should not disintegrate and exhibit fire retarding properties.

HOW TO EVALUATE FIRE RESISTANCE PROPERTY

As a natural phenomenon, all types of lubricating greases will catch fire after it attains a certain temperature but a grease with fire resistant property should burn with difficulty or after fire initiation, the fire does not sustain the flame for durations longer than five minutes as per a fire resistance test. The other characteristic may be that the grease component should come out of the costly bearing even after it catches fire and fire should not propagate further [3].

The fire-resistance of the greases may be evaluated by several tests, e.g. Wire Gauze Test (where the flammability of a layer of grease on a gauze is evaluated), fire point and flash point tests and spontaneous ignition test on a hot plate. In tests for fire-resistance, the grease was classified as "burning with difficulty" in a gauze test and did not ignite even at 650 °C in a spontaneous ignition test on a hot plate [6].

Few steel plants evaluate fire resistance property by simply applying direct fire generated through gas blower or welding flame blowing on grease and examine how soon the fire retards or stops. The sooner it extinguishes the fire, the better is the fire retarding property of grease.

Literature also indicates steel ball test for evaluating fire resistance property of the greases. This test includes a steel ball of diameter 19.05 mm heated for at least 15 minutes in a muffle furnace at 900° C, a cylindrical metal container having a circular bore of 67.5 mm and a depth of 5.0 mm. The metal cylinder is filled with the grease to be tested and the top surface of the grease is smoothed as flat as possible with spatula. The heated steel ball is quickly removed from the furnace and carefully dropped immediately on the sample grease surface into the centre of the sample. A stopwatch is started as soon as flame is generated in the grease sample. The time required for the flame to completely self-extinguish is recorded. If the flame does not extinguish within 5 minutes, the test is terminated. The above steps are repeated two more times using new grease samples as indicated above. The average time of the three test runs is reported [3].

Literature also indicates a modified oxygen index (OI) test performed on a 1.5-gram sample of grease (20 mm in diameter×10 mm high) that was subjected to a direct propaneflame for 5 seconds. The OI was recorded as the minimum percentage of oxygen in an oxygen/nitrogen environment required for the grease to ignite and sustain combustion. This test is a modification of ASTM D-2863 [8] for qualitative estimation but difficult to estimate quantitatively.
The vertical burn test evaluates the ability of the greases to resist combustion in a standard air environment when subjected to a direct flame for 30 seconds. A grease wasspread 1 mm thick evenly over a 2.54×12.70 cm steel mesh strip. The strip wassuspended vertically and a 1 inch propane flame was held at the base. The grease was observed for ignition. This test is a modification of ASTM D-3801 [7].

RECIPE FOR FIRE RESISTANT GREASE:

Though the literature reveals that fire-resistant property can be enhanced in a grease bymixing some amount of water but the water mixed grease will be prone to degrade additives and the phosphate ester may be subjected to hydrolysis in the presence of water leading to a premature degradation of the grease resulting in poor lubrication that will cause a reduction in the bearing service life [5], [3].
The base components of all types of greases are base oil, thickener, additives and fillers. If required, the components for fire resistance should be instilled in the grease without degradation of the necessary lubricating features [3]. In short, we can say that the grease recipe is selected based on the ease of consistent availability of raw material, ease of manufacture, storage stability and cost economics.

BASE OIL:

A fire-resistant grease composition should consist of a fire-resistant base oil having a kinematic viscosity of approx. 300 cSt at 40 °C with a high viscosity index, a flash point of above 270 °C and an auto ignition temperature of above 315 °C [4], [6], [7], [8].

It is difficult to make grease using phosphate esters alone but a blend of Group II mineral and synthetic oil is preferred. The choice is Group II mineral, synthetic PAO oil and phosphate esters. The hydrocarbon portion of the ester may be aryl, alkyl or a mixture of alkyl and aryl having 3 to 15 carbon atoms. Tri (alkyl aryl) phosphates may be particularlysuitable [6], [7], [8].

THICKENER:

The high performing grease thickeners may be organic such as polyurea; inorganic suchas clay or fumed silica; or a soap/complex soap such as lithium, aluminum or calcium sulfonate complex [3].
Most conventional grease thickeners are reasonably fire-resistant, particularly when the nature of the thickener requires the use of relatively high temperatures complex thickeners are preferred to process the grease.

ADDITIVES:

The additives may be anti-oxidant, anti-rust, anti-wear and extreme pressure but must becapable of working synergistically with the thickener and the oil to lead to a balanced and stable mixtures of the three distinct components [8]. A special fire retarding chemical has beenincorporated to enhance the fire resistance properties of the greases.

DEVELOPMENT WORK:

Development work was initiated by doping varying percentages of phosphate ester I (PE-I) and phosphate ester II (PE-II) in different thickener based greases without any additive having same base oil viscosity. All these greases were subjected to fire resistance tests. Optimised dosage of PE-I /PE-II was finalized based on the best results obtained in the fire resistance tests evaluation. Candidate batches were chosen and projected for further development work. Among the above blends, complex thickener based was rated the best one [Annex I & II].

Based on the above evaluation, batches were made to design a suitable and cost effective fire-resistant grease. Final product was developed based on the blend of base oil using Group II mineral, PAO and finalized dosage of phosphate ester. Required additives werealso incorporated. The key properties of the base oil blend are indicated in Table (1). The thickener used was a proprietary complex soap. The grease was first made at laboratoryscale and then scaled up further to bench scale and then to commercial level. The productwas made in open kettle and was kept slightly acidic at soap stage. After doping anti- oxidant, anti- wear and EP additives, the product was homogenized and finally deaerated.The consistency of final product was kept on softer side of NLGI 2; the product was evaluated for different properties as indicated in Table (2). The developed grease was evaluated for the fire resistance property comparing it with the product in use by steel plants [Annex III].

Table (1)

Properties of base oil blend

S. No	Characteristics	Test Method	Test Data
1	Color	ASTM D 1500	2.5
2	Base Oil KV at 40^{0}C, cSt	ASTM D 445	307
3	Base Oil KV at 100^{0}C, cSt	ASTM D 445	23.5
4	Viscosity Index	ASTM D 445	96
5	Flash Point ,^{0}C	ASTM D 92	235
6	Pour Point ,^{0}C	ASTM D 97	-12

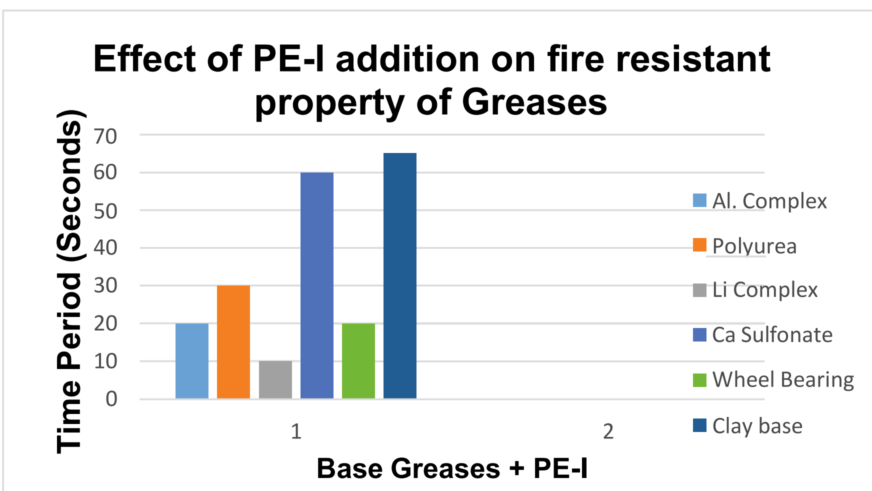
Table (2)

Properties of Developed Fire Resistant Grease

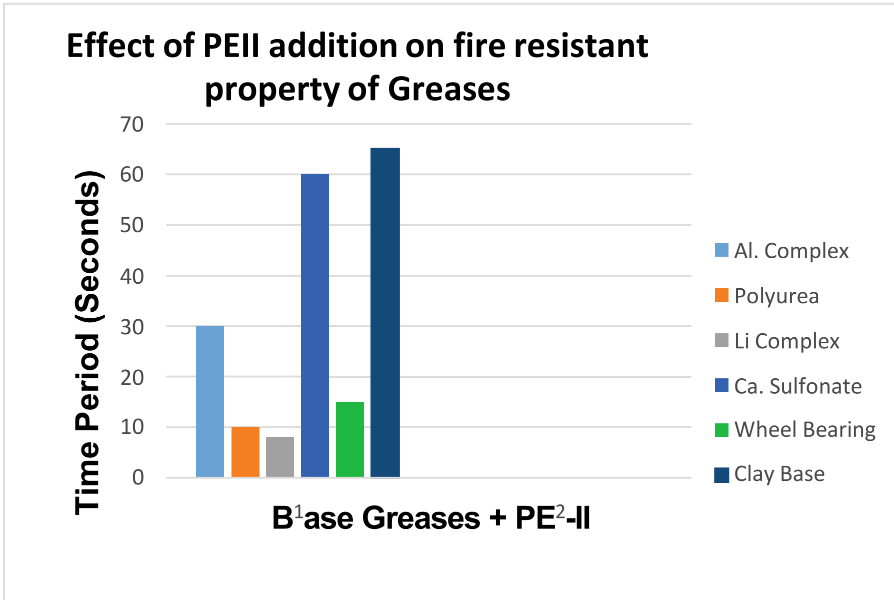
S. No.	Characteristics	Test Method	Test Results
1	Appearance	Visual	Smooth, free of agglomerates
2	Thickener Formula	Proprietary	Complex
3	Color	Visual	Light Brown

4	NLGI Grade	ASTM D 217	2
5	Worked Penetration (60 double strokes)		290
6	Change in Penetration after 10,0000 Strokes		35
7	Leakage by mass, gms	ASTM D 1263	3.5
	Other Observation		No Deposits
8	Dropping Point, □C	ASTM D 566	238
9	Oxidation Stability pressure drop, 99° C,100 hrs., Kg/cm2	ASTM D 942	0.25
10	Water Content % by wt.	ASTM D 95	NIL
11	Effect of Grease on Copper	ASTM D 4048	1b
12	Base Oil Viscosity at 40 □C, cSt	ASTM D 445	307
13	Water Resistance ,80° C, %	ASTM D 1264	3.5
14	Oil Separation, 24 hrs., 25° C, wt. %	ASTM D1742	1
15	Rust Protection, Rating	ASTM D 1743	Pass
16	Wear Protection (4 Ball Wear Scar Diameter), mm	ASTM D 2266	0.45
17	EP Performance (4 Ball Weld Load), Kgf.	IP 239	250
18	Heat Stability, % wt.	ASTM D 6184	1.6

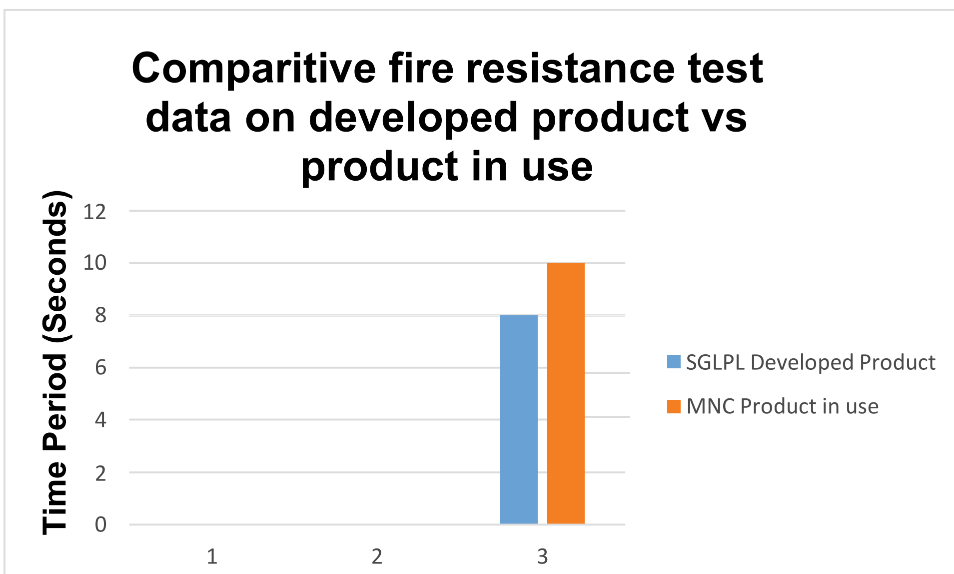
Annex -I



Annex -II



Annex –III



RESULTS & DISCUSSION:

Developed fire resistant grease was designed in VG 320 base oil having high VI and flashpoint. It was evaluated for various properties that are typically common in all types of greases. The penetration of the product was kept on the softer side of NLGI 2 so that theproduct must easily drip down on thermal exposure. Dropping point was found to be 238^{0}C which is high enough to sustain elevated temperature. Water washout evaluated as per ASTM D 1264 was 3.5% by weight low enough to show water resistance. The developed grease was found excellent in various properties like heat stability, oil separation, copper corrosion, EP & AW Properties. The fire-resistant properties were evaluated by gauze test and direct fire exposure through welding flame blowing on to thegrease. The results are encouraging in fire resistance properties.

CONCLUSION

- We at M/s Siddharth Grease & Lubes Pvt Ltd., India have developed Fire Resistant Grease.
- The grease when evaluated for fire resistant property was found to besimilar /better compared to the commercial greases available in the market.
- The product has been scaled up and commercialized for use steel plants and other heavy industries encountering grease fires.

ACKNOWLEDGEMENT

The authors are thankful to the management of M/s Siddharth Grease & Lubes Pvt Ltd, India for permitting us to present this technical paper.

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Lubricants and Impairment of environment

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Introduction

Lubricants both fresh and used can damage the environment considerably. It is estimated that about 40% of all lubricants are released into the environment by improper use, spillage and by way of disposal. The base oils and additives used for making various lubricants and greases and their oxidation products can be toxic to aquatic animals, plants & human beings. Although there might not be direct impact of these pollutants on human beings, but indirectly they harm us through our environment. From lubricant manufacturing, storage, transportation, application, and disposal of lubricants need to be considered for possible protection of living being, nature and the environment. Various lubricants i.e. Engine Oils, gear oil, process oils, coolants, metal Working fluids, industrial specialities lubricants, greases even biodegradable Lubricants are major contributors for environmental pollution if not handled carefully and properly. Environmental regulatory forces across the Globe are shaping the global lubricants markets. Spillage of automotive and other lubricants due to wrong applications, improper handling and leakage from vehicles and wrong practices of disposal are the main sources of impairment of environment. Growing awareness of vehicle emission, and threat endangered by these wrong practices, evolving new environmental regulations, which will force not only original equipment manufacturers across the globe to redesign or modernize the engines but also lubricant manufacturers to develop high performance lubricants, proper recommendations, follow good storage and handling and proper disposal of lubricants without damaging the environment. Thus the lubricant manufacturers will play an important role in protecting environment by adopting good manufacturing practices, developing long life high performance lubricants, following good storage and handling management and right recommendation of lubricants for desired applications for longer life of vehicles and equipment. In addition, more usage of biodegradable lubricants will also help in protecting the environment. Also proper reclamation/ reprocessing and disposal processes will substantially help in reducing the impairment of environment by lubricants

Environmental concerns

The increasing legislative norms has necessitated the lubricant manufacturers for adopting good manufacturing practices for developing high performance long life lubricants, following good storage and handling management and right recommendation of lubricants for longer life of vehicles and equipments. Discharge of small amount of lubricant into water can contaminate a large amount of water. Due to inadequate and unsafe technology of reprocessing tones of used oil is wasted. In addition to liquid lubricants, usage and disposal of lubricating grease is of great concern with the environmental issues. The disposal of used grease is more complex and difficult. As collection of used grease is very labourous and impossible. In order to reduce the consumption, associated labour cost for relubrication and disposal issues, the grease is required to perform for longer life. Thus the life of bearings and equipment can be enhanced and disposal can be minimised. Similarly, in steel plants, paper, mining, cement, etc. also there is a great demand of high performance long life grease where, water ingress is very high grease is wash away from the system and passes into sewage.

Environmental Aspects of Lubricants

More than 90% of lubricants manufactured are mineral oils based. In view of their low biodegradability and high eco-toxicity mineral oil-based lubricants pose substantial threat to impairment of environment. To identify lubricants with regard to their impairment of the environment manufacturing, application and disposal of lubricants should be considered. Health hazard aspects are characterized by endangering of living beings by fresh and used lubricants. The important aspects of health hazards by lubricants is their endangering potential and their toxicity. Health hazards to human beings are mainly considered when they come in direct contact with lubricants. Ecotoxicity and biodegradability governs the impairment of the environment by lubricants. Biodegradability means the tendency of a lubricant to be ingested and metabolized by microorganisms. Completely biodegradability indicates the lubricant has essentially returned to nature. Partial biodegradability usually indicates one or more component of the lubricant is not degradable. Materials with an LD50 value >1000 ppm/kg are low or non-toxic. Regarding the toxicological potential of lubricants, base oils and additives have to be considered. The acute dermic LD50 for rats was higher than 2000 mg/kg of mineral oils. For human beings no detrimental consequences are known for short-time dermal contacts. However, swallowing by accident low viscosity products may cause serious effects, because aspiration after vomiting can produce chemical pneumonitis. Skin irritation leading to dermatitis may occasionally occur from prolonged exposure to automotive lubricants. Inhalation of vapour or oil mist for short periods may cause mild irritation of the mucuous membranes of the upper respiratory tract. Due to the different fate of lubricants during their usage contamination by fuel and combustion products of engine oils— the toxicity of used lubricants may be significantly different than that of fresh oils.

Lubricants which are having good biodegradability, low toxicity and low bioaccumulation potential and not harmful to aquatic environment, compared to conventional lubricants are categorised in Environmentally Acceptable Lubricants. Environmentally acceptable lubricants should not harm the aquatic living beings and they should be fast biodegradable when enter in water. Environmentally acceptable lubricants should have zero water hazard classification and they should be fast biodegradable when enter in water. They should not harm the aquatic living beings.

Automotive Lubricants & Impairment of Environment

Used automotive lubricants particularly, engine oils form carbon sludge, oxidation products, metallic contaminants, complicated by products and liquid impurities. Engine oils like passenger car engine oils and heavy duty diesel engine oils constitute about 60% of total lubricants. In addition to these various other lubricants are disposed in environment. All these lubricants are used in loss lubrication frictional contacts. Presently about one-third of lubricants used is indiscriminately dumped or burned every year in the country, thus contaminating water, and polluting environment by releasing metallic oxides into the atmosphere. These metallic contaminants are generated from engine crankcase oils, transmission and gear oils and fuel additives. These oils commonly contain various detergents and extreme pressure additives such as polyvalent metal soaps as well as impurities which result from oxidation of the oil itself, water and fuels (diesel, gasoline).

Lubricating Greases & Impairment of Environment

Though total lubricating grease is used 6 to 10% of total lubricants but grease play a very important role in bearing lubrication system. Approximately 90 percent of all bearings are lubricated with grease. The steel industry is a major user of lubricating oil and greases followed by automotive sector. With the advancement in automotive sector and industrial revolution in industrial sector changes in the equipment design, higher operating speeds and temperature, heavier loads the development of high performance grease for longer relubrication interval or even filled for life concept is coming. Inautomotive sector fleet operators, state transport and heavy commercial vehicles where there is no control of load, relubrication of bearing is considered, a grease life is expected more than 100,000 KM. Apart from load factor the grease is required to have better water resistance properties as the vehicle drivers are unaware about the effect of water on grease. There is a frequent braking on road as a results temperature of grease goes up. The grease is required to have good thermal and mechanical stability. Many bearings fail prematurely due to contamination. Grease contamination can come not only from environmental contaminants such as dirt and water, but also cross-contamination from other greases. This is a major issue with greases because many gelling agents are incompatible sample.

Marine Lubricants & Impairment of Environment

The maritime environment is challenging to equipments. Long hours, heavy loads, extreme weather and the constant risk of contamination contribute to difficult operating conditions. The National Oceanic and Atmospheric Administration (NOAA) estimates over 2653,000 KL of petroleum products enter the environment each year, over half of which is through irresponsible and illegal disposal. It is estimated that 70% - 80% of hydraulic fluids leave systems through leaks, spills, line breakage and fitting failure. Base oils and additives used in marine applications should be selected for their environmental performance in the marine environment. There is growing concern regarding the environmental impact and associated costs of lost petroleum based fluids.

Environmental Legislation and regulations

Environmental regulatory forces across the Globe are taking the climate change and environmental concerns seriously. These issues are shaping the global lubricants markets. Growing awareness of vehicle emission, greenhouse gasses from various industries, which is the main source of air pollution, spillage of automotive lubricants due to improper handling and leakage from vehicles and wrong practices of disposal are evolving new environmental regulations, which will force original equipment manufacturers across the globe to redesign or modernize the engines and evolution of performance level of lubricants. This eventually follow additive suppliers and lubricant manufacturers for development of high performance lubricants for long drain interval.

Environmental and regulatory drivers for reducing the impairment of theenvironment

Due to increasing public awareness, government directive and regulations, globalization of markets ways and measures to reduce the impairment of environment by way of lubricants usage, spillage andemission caused by vehicles is growing rapidly. Vehicle manufacturers are putting great efforts in reducing the pollution by way of redesigning the engine, installing various after treatment devices in vehicles to reduce particulate matters and other pollutant gasses. At the same time additives manufacturers and oil manufacturers are working jointly for development of high performance lubricants and synthetic lubricants. Tight Environment Regulations are creating ways for developmentof Eco-Friendly Products. Health, safety and environmental regulations in industrial end-use markets are becoming more stringent. Regulations are becoming ever more restrictive with regard to contents, use and disposal of lubricants. There is mounting governmental pressure to establish environmentally sustainable products. Governmental policies and regulations facilitating the introduction of bio lubricants. In order to use lubricants for longer period demand of high performance lubricants is increasing. The shortcoming of conventional lubricants can be compensated by use of synthetic lubricants. Lowering tailpipe emissions, increasing fuel economy, and increasing the usage of low sulfur or zero sulfur fuel are some ways by which the environment can be protected and pollution can be reduced. Environmental concerns will also drive demand for re-refined base stocks and products derived from bio-based sources to conserve the natural resources. .

Contribution of Lubricant Manufacturers

The lubricant manufacturers with support of OEM and additive suppliers will have to develop high performance long life lubricants to reduce impairment of environment and ultimately disposal. Though the initial cost of high performance and long life lubricants is high but in long run they are more cost effective and environmental safe. By making long life lubricants not only extend service life but also save equipment/vehicle shutdown time and labor cost. Development of low sulphated ash, phosphorous, and sulfur (SAP) oils and increased usage of 0W and 5W lower viscosity high performance engine oils that will last longer. By usage of such high performance engine oil, the efficiency of diesel engine can be increased many fold. This will lead to a greater need and usage of higher quality base stocks such as American Petroleum Institute (API) Group II, II+ and III oils, as wellas synthetic types. Which are more thermal stable than conventional mineral oils. These oils are useful at very low operating temperature also. Better quality base oils are necessary for lubricants to comply with the variety of new standards in the industry, like the new category of PCMO, API SN – 6. The oil will come in 0W 8, 16, 12, 20, 30 category. For heavy duty diesel engine oils also new high performance HDDEO has been developed, which falls in CK-4 and FA -4 category.

Development of high performance long life Grease

Protecting the health of production operators and reducing waste emissions are becoming key factors in future developments in grease production. For example, in the manufacture of polyurea grease, producers can now avoid the use of toxic amines and iso-cyanates by using pre-reacted raw materials. Similarly, manufacturers of aluminium complex grease now avoid the emission of isopropyl alcohol by using suitable chemical precursors. Environmental concerns associated with the use of lead as an extreme pressure agent have encouraged replacement by sulphur-phosphorus technology in greases, in combination with zinc compounds. But zinc itself is not completely acceptable from an environmental aspect and compounds of bismuth have received increasing technical and commercial focus. Ash less extreme pressure additives need to be used more. Water resistance properties and mechanical stability can be improved by the combination of Lithium and calcium soaps. Use of various types of high molecular weight polymers in grease formulations can improve water wash out and water spray-off resistance properties. It can improve mechanical stability and some reduction in soap contents also in greases. Usages of other high performance complexes greases such as aluminium complex, calcium complexes and calcium sulphonate complexes have increased the life of bearings and increased the re-lubrication interval in high temperature applications and high humid atmosphere. More usages of synthetic base fluids in grease formulation can widen the high and low temperature application and can improve pump ability of greases in centralised lubrication system and extending service life of grease and bearings. Additionally, these base fluids have better biodegradability when comes in contact of water due to spillage.

Eco-friendly process of reprocessing of used oils

Presently various processes are being adopted for the purification and reprocessing of used lubricating oils. Typically, the used oil is heated to drive off volatile hydrocarbons and water and to permit some of the solids to settle before adding a strong mineral acid which precipitates out a large portion of the oil as sludge. The supernatant oil is separated from the sludge, neutralized with a caustic and distilled or further treated with clay and filtered. This process is severe, altering the petroleum base composition of the lubricating oil and resulting in the loss of a substantial quantity of recoverable organic materials. Additionally, severe treatments of the acid or caustic type result in a substantial loss of diaromatic and polyaromatic polar materials from the oil. These higher molecular weight aromatics are generally associated with natural lubricity characteristics of the base oil and removal of these compounds would affect the performance of the lubricant. Likewise, the polar materials are responsible for natural resistance to oxidation, and selective removal of these compounds will contribute to poor oxidation stability of reprocessed lubricating oils. There is an urgent need of development of eco-friendly process for reprocessing/ re-refining of these used crankcase oils and lubricating oils. Re-refining extends the life of the petroleum resource indefinitely. Re-refining is preferred because re-refined used oils takes only about one-third of the energy than making lubricating oil from refining crude oil. Recycling is the most efficient and economical way of managing used oil. Re-refining saves money by preventing costly clean ups and to protect environment.

Use of more Biodegradable Lubricants

There are many ways that lubricants enter the environment. Environmentally acceptable lubricants means lubricants that are “biodegradable” and “non-toxic” and are not “bio-accumulative. ASTM 6064 has defined biodegradable as a function of degree of degradation, time, and test methodology. The two widely used designations for biodegradability are readily and inherently. Readily biodegradable is defined as degrading 80% within 21 days. Inherent biodegradation is defined as having the propensity to degrade with no indication of timing or degree. Biodegradability tests are performed by ISO 14593 and in OECD 301B methods.

Summary

Environmental regulatory forces across the Globe are shaping the global lubricants markets. Growing awareness of vehicle emission, greenhouse gasses from various industries, which is the main source of air pollution, spillage of automotive lubricants due to improper handling and leakage from vehicles and wrong practices of disposal are evolving new environmental regulations, which will force original equipment manufacturers across the globe to redesign or modernize the engines and evolution of performance level of lubricants. The lubricant manufacturers will play an important role in protecting environment by adopting good manufacturing practices, developing long life high performance lubricants, following good storage and handling management and right recommendation of lubricants for longer life of vehicles and equipments. In addition to this proper reclamation and disposal processes will help in reducing the impairment of environment by lubricants nad greases.

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Characterisation of Solid lubricants based Lubricating Greases by Horizontal Attenuated Total Reflectance Spectroscopic (HATR) Methodolgy .

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Abstract :

In recent years, there is a ever growing demand of lubricants in both Industrial and Automotive applications with variety of products available to end users. With the advent of newer technological development both in machinery as well as end applications , many lubricants based on various combinations of additives & base oils are available to meet stringent & extreme application of high load and high temperature conditions . Additives are of two categories - one category modifies physical parameters such as viscosity, tackiness , pour point , foaming tendency etc. and second category - enhances performance characteristics such as friction reduction , antiwear and extreme pressure properties, oxidation stability, rust & corrosion etc . Antiwear (AW) additives, are used in lubricants to prevent metal-to-metal contact between moving parts by film formation. Extreme Pressure (EP) additives are chemically bonded to metal surfaces thus preventing metal to metal contact even at high pressure /high load conditions,. In addition, a special type of chemical compounds commonly known as solid lubricants are also used to take care of extreme conditions of heavy and shock loads .The most widely used is molybdenum disulphide , graphite , PTFE etc. in very fine powder form.
In the present study , an attempt has been made to characterise the lubricating greases containing the solid lubricant component such as molybdenum disulphide and graphite powder by using Horizontal Attenuated Reflectance (HATR) spectroscopic methodology. Optical Spectroscopic techniques has limitation of analysing lubricants with dark black / grey color because of poor transmission properties and conventional wet chemical method is time consuming and involves hazardous solvent & organic acid . These limitations can be overcome by using Horizontal Attenuated Total Reflectance technique. HATR technique has been used to characterise solid lubricant containing superfine powder of graphite & molybdenum disulphide in different lubricating greases for the chemical composition. In the present study, samples of different lubricating grease with graphite powder , lubricating grease with molybdenum disulphide powder and Lubricating grease with mixed graphite & molybdenum disulphide powders were taken for quantitative estimation of solid lubricants using HATR technique. The effect of consistency of lubricating greases , type of grease on the quantitative estimation of solid lubricants were also studied . The information obtained from the above study shall be useful in both qualitative and quantitative estimation of solid lubricants in different lubricating greases. The methodology adopted is rapid with the results obtained are comparable with wet chemical method.

Introduction

With advent of newer technology ,various changes in machinery & equipments were observed in both industrial and automotive applications. This has made significant requirements on various lubricants to meet the conventional to stringent, extreme and specialized applications. In order to meet the above challenging conditions , wide range of base fluids , additives , solid compounds such as solid lubricants are available to the manufacturers to manufacture lubricants to meet the desired requirements . Solid lubricants are solid chemical materials, which reduce coefficient of friction and wear of rubbing parts preventing direct contact between their surfaces even under high loads. The mode of action of solid lubricants may be present in the friction area in forms of either dispersed particles or surface films. The characteristic properties of solid lubricant are their ability to work under high loads , high thermal stability, diversity of application forms such as dry powder, liquid coating forms and semisolid form such as in lubricating greases. Graphite and molybdenum disulfide (MoS2) are the predominant materials used as solid lubricant. In the form of dry powder these materials are effective as lubricant additives due to their lamellar structure. A typical area of applications where sliding or reciprocating motion are involved such as gear and chain lubrications , high temperature and oxidizing atmosphere environments , extreme contact pressures-the lamellar structure of the solid lubricant orient parallel to the sliding surface resulting in high bearing-load combined with a low shear stress and as compatible additive to plastic and ceramics applications.

It is widely known that solid lubricant -graphite and molybdenum disulfide (MoS2) based lubricants are dark ,grey/black , opaque in appearance with very poor transmission . It is observed that a very few analytical methods are reported in the literature . Limitation of conventional Optical Transmission Spectroscopic Techniques such as FTIR etc . to analyse the lubricants containing these solid lubricants. It was felt that multiple reflection spectroscopic technique such as Horizontal Attenuated Total Reflectance (HATR) would find useful in characterising the lubricating greases containing graphite and molybdenum disulfide based solid lubricants. Horizontal Attenuated Total Reflection (ATR) is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid or liquid state without further preparation.. HATR uses a property of total internal reflection resulting in an evanescent wave. A beam of infrared light is passed through the HATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample. This reflection forms the evanescent wave which extends into the sample. The penetration depth into the sample is typically between 0.5 and 2 micrometres, with the exact value being determined by the wavelength of light, the angle of incidence and the indices of refraction for the ATR crystal and the medium being probed. The number of reflections may be varied by varying the angle of incidence. The beam is then collected by a detector as it exits the crystal. Most modern infrared spectrometer - FTIR can be converted to characterise samples via HATR by mounting the HATR accessory in the spectrometer's sample compartment. The accessibility of HATR-FTIR has led to substantial use by the scientific community.

In the present study , an attempt has been made to characterise the lubricating greases containing the solid lubricant component such as molybdenum disulphide and graphite powder by using Horizontal Attenuated Reflectance (HATR) spectroscopic methodology. Optical Spectroscopic techniques has limitation of analysing lubricants with dark black / grey color because of poor transmission properties and conventional wet chemical method is time consuming and involves hazardous solvent & organic acid for total solid lubricant content in lubricating greases. These limitations can be overcome by using Horizontal Attenuated Total Reflectance Accessory attached to FTIR instrument . HATR technique has been used to characterise solid lubricant containing superfine powder of graphite & molybdenum disulphide in different lubricating greases for the chemical composition. In the present study, samples of different lubricating grease with graphite powder , lubricating grease with molybdenum disulphide powder and Lubricating grease with mixed graphite & molybdenum disulphide powder were taken for quantitative estimation of solid lubricants using HATR technique. The effect of consistency of lubricating greases , type of grease on the quantitative estimation of solid lubricants were also studied . The information obtained from the above study shall be useful in both qualitative and quantitative estimation of solid lubricants in different lubricating greases. The methodology adopted is rapid with the results obtained are comparable with wet chemical method.

EXPERIMENTAL

Chemicals : All chemicals employed for analysis were of Analytical Reagent Grade Hexane , Toluene and Acetic Acid, , Anhydrous Sodium Sulphate, Graphite and Molybdenum

Disulphide super fine powder forms of Purity 99.9%

Labware : Standard glassware of Borosil make were used for analysis. Beaker 250ml & 500 ml capacity, Glass rods .Filter Papers

Instruments : Thermo Nicolet make Fourier Transform Infrared Spectrometer model iS10 (FTIR) with Horizontal ATR accessory with Zinc Selenium Trough with angle 45^0.

PROCEDURE :

Samples of Solid Lubricant –graphite & molybdenum disulphide containing different known lubricant greases such as simple Lithium 12 hydroxy stearate grease, Lithium Complex, Sulphonate Complex grease and Non Soap based greases such as Polyurea grease & Silica based grease were taken and subjected to Horizontal ATR spectral analysis :

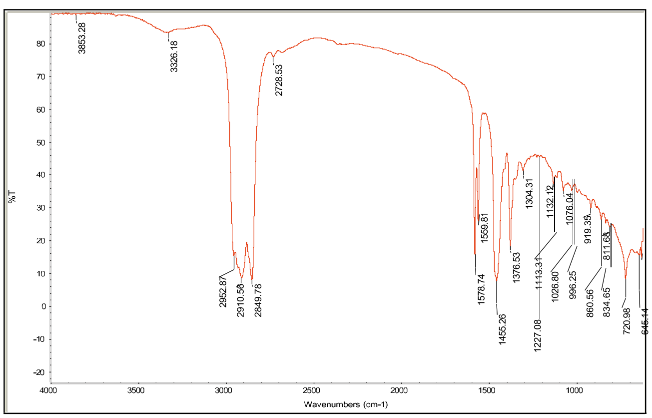
I Sampling Procedure for Characterisation of Lubricating greases containing solid lubricants - About 2 to 2.5 gm of each of the lubricating greases containing graphite and molybdenum disulphide was spread on the Zinc Selenium Crystal with angle 45^0 ATR trough for recording IR spectrum through ATR accessory attached FTIR Instrument . Standard Instrumental condition used : Resolution 4 cm^{-1}, Scan range : 4000cm-1 to 650cm-1 , Number of Scans : 32. Before recording the IR spectrum of each of the samples of Lubricating greases , background of blank HATR accessory with cleaned Zinc Selenium trough was recorded . IR spectrum of sample obtained through background correction .. Lubricating greases with Solid Lubricant of consistency NLGI 2 & 3 were taken for study .

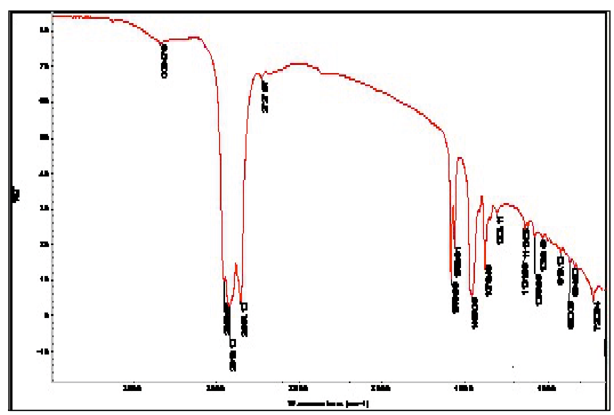
Figure 1 and 2 shows Horizontal Attenuated Total Reflectance (HATR) Accessory and Horizontal Zinc Selenium Crystal with angle 45 ^{0} ATR trough.

Figure 1 HATR Accessory

Figure 2 Zinc Selenium Angle 45 ^{0}Trough

For Qualitative Analysis ,from the recorded IR spectrum , identified the type of soap /non soap thickener present in the lubricating greases as well as type of solid lubricant whether it is graphite based or MoS_2 based or mixed solid lubricant (Graphite & MoS_2) type .Figure 3 shows a typical IR Spectrum obtained (plot of %T/ % Reflectance R against wave number cm^{-1})





Lubricating Grease with Solid Lubricant Molybdenum Disulphide Lubricating Grease with Solid Lubricant -Graphite

Figure 3 IR Spectrum of Lubricating Greases with Solid Lubricant Molybdenum Disulphide & Graphite by HATR Accessory

II Methodology adopted for Quantitative Analysis of solid lubricant Graphite & MoS2 content in lubricating greases containing solid lubricant using HATR accessory attached to FTIR :

Lubricating grease samples containing only graphite, molybdenum Disulphide only and mixed graphite & Molybdenum disulphide were taken for quantitative estimation of solid lubricant in the lubricating grease . In present study ,base grease - simple lithium 12-Hydroxy stearate grease with consistency NLGI 2 and 3 were used for calibration of solid lubricant in the base grease. Separate calibration was constructed for solid lubricant molybdenum disulphide with varying amount 0.75%, 1.5% 3.0% &
4.5 % in both the consistency of base grease Lithium 12-hydroxy stearate . Similarly, separate calibration was

constructed with solid lubricant –graphite with varying amount of graphite 2.5% , 5.0%. 7.5% and 10.0% in both the consistency of lithium 12- hydroxy stearate grease . Lithium 12 –Hydroxystearate grease IR spectrum of each of the standard was also recorded by using ATR accessory and measured % Transmittance . % Transmittance (T) of base lithium 12 –hydroxyl stearate grease of both the consistency were also measured as a blank with no solid lubricant .Calibration plot was obtained by difference as %ΔT (%T(Blank Grease – %T Grease with % Solid Lubricant) . IR spectra of unknown lubricating grease samples containing only molybdenum disulphide , only graphite and mixed solid lubricants both graphite and were recorded in a similar manner using ATR accessory and measured their transmittance . Lubricating greases of different types containing solid lubricants such as molybdenum disulphide and graphite such as Lithium Complex (LICOM) grease , Sulphonate Complex High Temperature (SCHT) grease , Non soap thickener based grease such as Silica based and Polyurea based were also taken for study in similar manner .

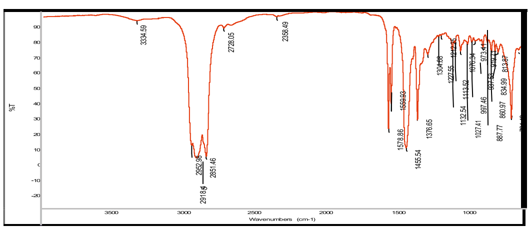
Results and Discussions :

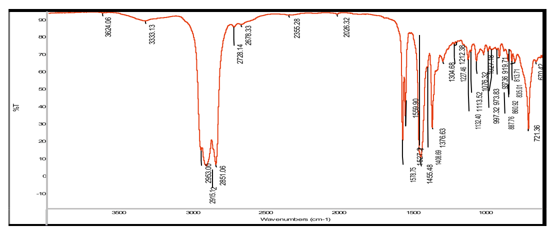
I **Characterisation of Lubricating greases containing Solid Lubricant by HATR accessory with FTIR : Table 1** shows for qualitative analysis ,from the recorded IR spectrum of lubricating greases as such and without lubricating greases in HATR accessory , identified the type of soap /non soap thickener present in the different lubricating greases

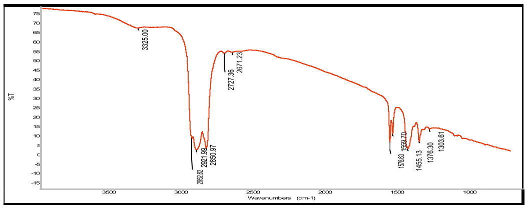
Table 1

S.No.	Sample Description	Thickener Type / Base Oil	Solid Lubricant Type	Characteristics Peaks of Thickener in Lubricating Grease By ATR Accessory / FTIR
1	A	Lithium 12-Hydroxy Stearate / Mineral oil	---	**3334**cm^{-1}, bifurcated peaks **-1578 cm^{-1}& 1558**cm^{-1}, 1132cm^{-1},1076cm^{-1}, 973cm^{-1}&**721**cm-1
2	B	Lithium 12-hydroxy Stearate / Mineral oil	MoS_2	**3334cm^{-1}, bifurcated peaks -1578 cm^{-1}& 1558cm^{-1}**, 1132cm^{-1},1076cm^{-1}, 973cm^{-1}&721cm-1
3	C	Lithium 12-hydroxy Stearate /Mineral oil	Graphite	**3334cm^{-1}, bifurcated peaks -1578 cm^{-1}& 1559cm^{-1}**, 1132cm^{-1},1076cm^{-1}, 973cm^{-1}&721cm-1
4.	D	Lithium complex / Mineral Oil	---	**3333cm^{-1}, bifurcated peaks -1579 cm^{-1}& 1559cm^{-1},** 1132cm^{-1},1076cm^{-1}, 970cm^{-1}&721cm-1
5	E	Lithium complex / Mineral Oil	MoS_2	**3333cm^{-1}, bifurcated peaks -1579 cm^{-1}& 1558cm^{-1}, 1132cm^{-1}**,1076cm^{-1}, 970cm^{-1}&721cm-1
6	F	Lithium complex/ Mineral Oil	Graphite	**3334cm^{-1}, bifurcated peaks -1579 cm^{-1}& 1559cm^{-1},** 1132cm^{-1},1076cm^{-1}, 970cm^{-1}**& 721cm-1**
7	G	Sulphonate Complex Grease /Mineral Oil	----	**3639cm^{-1},3356cm^{-1}, 1576cm^{-1},broad peak 1450cm^{-1} - 1350cm^{-1}**,1193cm^{-1},1068cm^{-1},1014cm-1,**884cm^{-1}** 721cm^{-1}
8	H	Sulphonate Complex Grease /Mineral Oil	MoS_2	**3639cm^{-1},3356cm^{-1}, 1576cm^{-1},broad peak 1450cm^{-1} 1350cm^{-1},1193cm^{-1},1068cm^{-1} ,884cm^{-1} 721cm^{-1}**
9	I	Sulphonate Complex Grease /Mineral Oil	Graphite	**3639cm^{-1},3356cm^{-1}, 1575cm^{-1},broad peak 1450cm^{-1} 1350cm^{-1}**,1193cm^{-1},1068cm^{-1}, **,884cm^{-1}** 721cm^{-1}
10	J	Polyurea grease /Mineral Oil	-----	**3269cm^{-1}, Trifurcated peaks- 1632cm^{-1},1609cm^{-1} 1582cm^{-1}** 1515cm^{-1},1193cm^{-1},1068cm^{-1}, **,884cm^{-1}** 721cm^{-1}
11	K	Polyurea grease /Mineral Oil	MoS_2	**32696cm^{-1}, Trifurcated peaks- 1632cm^{-1},1609cm^{-1} 1582cm^{-1}** 1515cm^{-1},1193cm^{-1},1068cm^{-1}, **,884cm^{-1}** 721cm^{-1}
12	L	Polyurea grease /Mineral Oil	Graphite	**3269m^{-1}, Trifurcated peaks- 1631cm^{-1},1609cm^{-1} 1573cm^{-1} 1515cm^{-1},721cm^{-1}**
13	M	Silica Grease / Silicon Oil	----	**3698cm^{-1}**, 2940cm-1, 2904cm^{-1} **1257cm^{-1},Broad bifurcated peaks -1046 cm^{-1}, 986cm^{-1},864cm^{-1},& 798cm^{-1}**
14	N	Silica Grease / Silicon Oil	MoS_2	**3699cm^{-1}**, 2940cm-1, 2903cm^{-1} **1257cm^{-1} ,Broad bifurcated peaks -1046 cm^{-1}, 986cm^{-1}**,864cm-1, & 798cm^{-1}
15	O	Silica Grease / Silicon Oil	Graphite	**3698cm^{-1}**, 2940cm-1, 2904cm^{-1} **1258cm^{-1} ,Broad bifurcated peaks -1046 cm^{-1}, 986cm^{-1},864cm-1, & 798cm^{-1}**

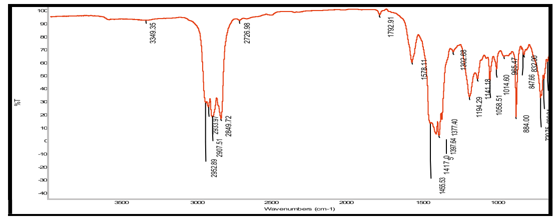
it was observed from the recorded IR spectra of lubricating grease containing solid lubricant using HATR accessory depends on the type of solid lubricant used MoS_2 or graphite .The fall in percentage transmission is more fall in graphite based lubricating grease than MoS_2 based grease with similar content of solid lubricant . It is also observed that increase in solid lubricant content , the drop in percentage transmission is more prominent in graphite based lubricating grease than in molybdenum disulphide lubricating grease . With increase in high content of graphite in lubricating greases , IR spectrum shows poor transmission with information on thickener with number of peaks reduces .This information provides dosage level & type of Solid Lubricant used in the unknown sample .Lubricating grease with mixed type containing both graphite and molybdenum sulphide shows similar pattern as that of graphite based lubricating grease . The effect of consistency of lubricating grease with solid lubricant in the percentage transmission in the IR spectrum recorded in HATR accessory was also studied . It was observed that lubricating grease containing solid lubricant with NLGI 2 consistency shows better % transmittance than lubricating grease containing solid lubricant with NLGI 3 consistency. This is applicable to both the solid lubricants- Graphite and MoS_2 containing lubricating greases. This observation was taken into consideration for quantitative estimation of solid lubricants subsequently. Figure 3 shows IR Spectra of some of lubricating greases with and without solid lubricants recorded by HATR accessory .


Lithium 12-Hydroxystearate grease

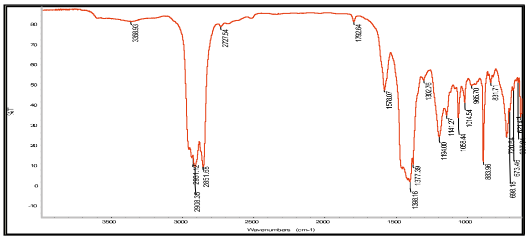

Lithium 12-Hydroxystearate grease with SL- MoS_2



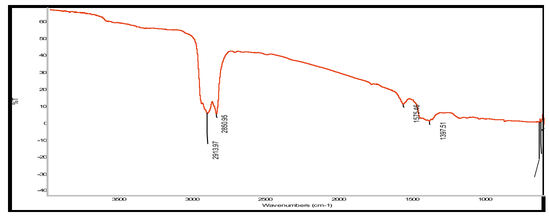
Lithium 12-Hydroxystearate grease with SL- Graphite



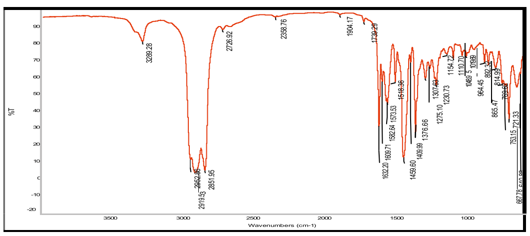
Sulphonate Complex Grease



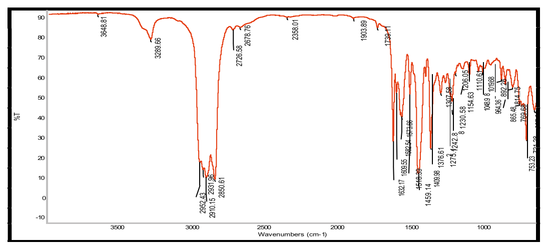
Sulphonate Complex Grease with SL- MoS_2



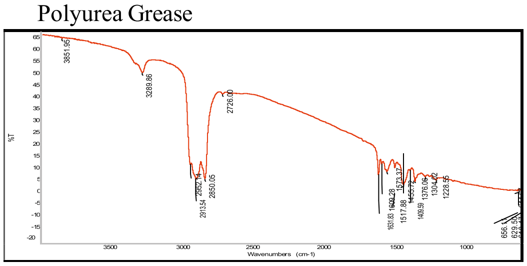
Sulphonate Complex Grease with SL- Graphite



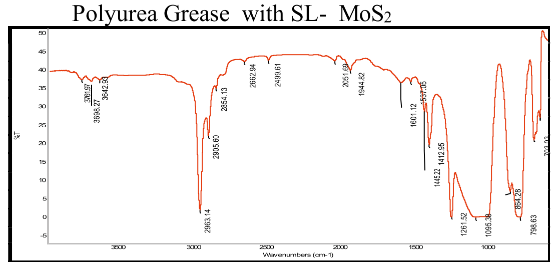
Polyurea Grease



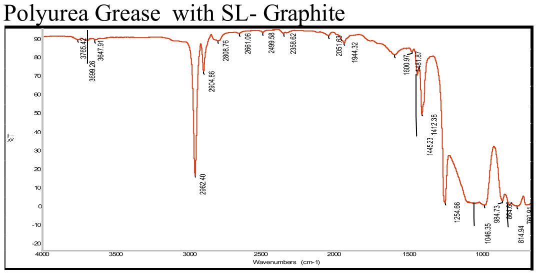
Polyurea Grease with SL- MoS_2



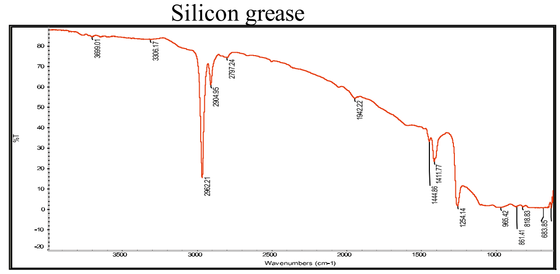
Polyurea Grease with SL- Graphite



Silicon grease



Silicon grease with SL- MoS_2



Silicon grease with SL- Graphite

Figure 3 IR Spectra of Lubricating greases with and without solid lubricants recorded by HATR accessory with FTIR.

II Methodology adopted for Quantitative Analysis of Solid Lubricant Graphite & MoS2 content in Lubricating Greases containing solid lubricant using HATR accessory attached to FTIR :

Basis on qualitative analysis as mentioned above , the type of lubricating grease is obtained . As observed in study,

% T obtained from IR spectrum of lubricating grease containing solid lubricants depended on consistency of the lubricating grease. Quantitative methodology adopted by taking consistency of grease into consideration .The present study is restricted to Lithium Grease of consistency both NLGI 2 & 3 by constructing a separate calibration plot - **% age difference ΔT (%TBlank - %T with SL)** vs % age Solid Lubricant -Molybdenum disulphide & Graphite .Four separate calibration plot were obtained for both the consistency with two solid lubricants - MoS2 & Graphite.

Unknown lubricating grease samples containing solid lubricant either MoS2 or Graphite or mixed type , were subjected to same instrumental condition as that carried out with standards and recorded IR spectrum of the sample. %T was measured from the recorded IR spectrum. Using the calibrations plots , % age solid lubricant content either MoS2 or Graphite contents is obtained . Attempt has been made to study few type of lubricating greases such as Licom grease with and without solid lubricants , Sulphonate complex grease with & without solid lubricants, Polyurea grease with & without solid lubricants and Silicon grease with & without solid lubricants. The study also cover quantitative estimation of mixed solid lubricants in lubricating greases containing both the solid lubricants . From the above plot , samples of lubricating greases with unknown MoS2 content were determined .The results was compared with standard method for estimation of Total Solid Lubricant by toluene acetic acid method & by AAS/ICPOES methods .

Table 2 shows Lithium 12-Hydroxystearte Grease NLGI 3 with varying amount of Solid Lubricant Molybdenum Disulphide for calibration plot

Table 2

Sl. No.	Sample Description	%MoS_2 in Grease	%T	ΔT ($\%T_{Blank}$-$\%T_{with\ SL}$)
1	Base Grease Blank	0	95.37	-----
2	Standard 1(Base Grease + MoS_2)	0.75	94.32	0.95
3	Standard 2(Base Grease + MoS_2)	1.5	93.52	1.85
4	Standard 3(Base Grease + MoS_2)	3.0	90.52	4.85
5	Standard 4 (Base Grease + MoS_2)	4.5	89.20	6.17

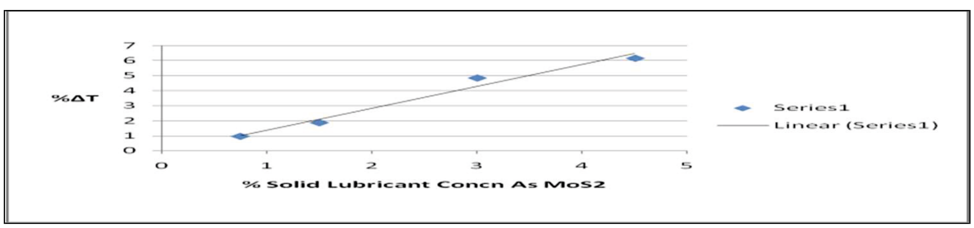


Figure-4 Calibration Plot -Lithium 12-Hydroxystearate Grease with NLGI-3 consistency with varying amount of Solid Lubricant –MoS_2

Table 3 shows samples of different Lubricating Greases with unknown concentration of Solid Lubricant - MoS_2

Table 3

Sl. No.	Sample Description	Grease without Solid Lubricant MoS_2 ($\%T_{WO\ SL}$)	Grease with Solid Lubricant MoS_2 ($\%T_{with\ SL}$)	ΔT ($\%T_{WO\ SL}$- $\%T_{with\ SL}$)	**Results (%) HATR Method**	**Results (%) Toluene Acetic Acid Method**
1	Sample A (Lithium Grease)	95.37	94.12	1.25	1.01	1.12
2	Sample B (Lithium Grease)	95.37	90.86	4.71	2.92	3.09
3	Sample C(Sulphonate Complex)	94.40	92.44	1.96	1.59	1.54
4	Sample D (Licom Grease)	96.28	91.24	3.99	2.47	2.65

Table 4 shows Lithium 12-Hydroxystearate Grease with NLGI-2 consistency with varying amount of Solid Lubricant -MoS_2

Table 4

Sl. No.	Sample Description	%MoS_2	%T	ΔT (%T $_{Blank}$ -%T $_{with\ SL}$)
1	Base Grease (Blank)	0.0	90.87	-----
2	Standard 1(Base Grease + MoS_2)	0.75	89.54	1.335
3	Standard 2(Base Grease + MoS_2)	1.5	88.77	2.095
4	Standard 3(Base Grease + MoS_2)	3.0	86.42	4.45
5	Standard 4 (Base Grease + MoS_2)	4.5	82.53	8.34

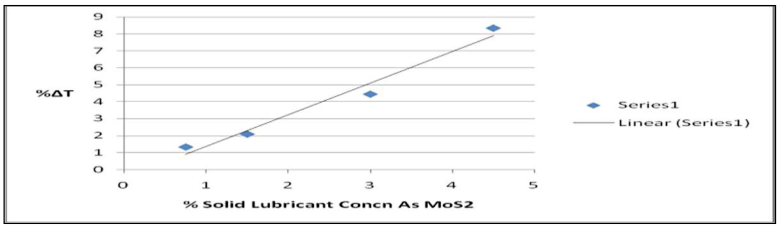


Figure-5 Calibration Plot -Lithium 12-Hydroxystearate Grease with NLGI-2 consistency with varying amount of Solid Lubricant –MoS_2

Table 5 shows samples of different Lubricating Greases with unknown concentration of Solid Lubricant MoS_2

Table 5

Sl. No.	Sample Description	Grease without Solid Lubricant MoS_2 (%T$_{WO\ SL}$)	Grease with Solid Lubricant MoS_2((%T$_{with\ SL}$)	ΔT (%T$_{WO\ SL}$ - %T $_{with\ SL}$)	**Results (%) HATR Method**	**Results (%) Toluene Acetic Acid Method**
1	Sample A (Lithium Grease)	90.87	87.01	3.87	2.61	2.52
2	Sample B (Lithium Grease)	90.70	89.08	1.62	1.17	1.21
3	Sample C(Sulphonate Complex)	92.65	89.18	3.67	2.47	2.56
4	Sample D (Licom Grease)	93.10	88.75	4.35	2.93	3.01
5	Sample E (Polyurea Grease)	93.59	89.75	3.85	2.59	2.54
6.	Sample F (Silicon Grease)	94.23	91.02	3.21	2.17	2.42

From the above Table 5 shows the results obtained from different type of lubricating Greases of MoS_2 is close agreement with wet gravimetric chemical method . Generally ,Lubricating grease with solid lubricant MoS_2 contains MoS_2 in the range of 0.5% to 3.0%.

Table 6 shows Lithium 12-Hydroxystearte Grease NLGI 3 with varying amount of Solid Lubricant - Graphite for calibration plot

Table 6

Sl. No.	Sample Description	%Graphite	%T	ΔT (%T $_{Blank}$ - %T $_{with\ SL}$)
1	Base Grease (Blank)	0	**95.01**	-----
2	Standard1(Base Grease +Graphite)	2.5	**76.59**	18.42
3	Standard1(Base Grease +Graphite)	5.0	**67.43**	27.59
4	Standard1(Base Grease +Graphite)	7.5	**55.57**	39.44
5	Standard1(Base Grease +Graphite)	10.0	**45.33**	49.68

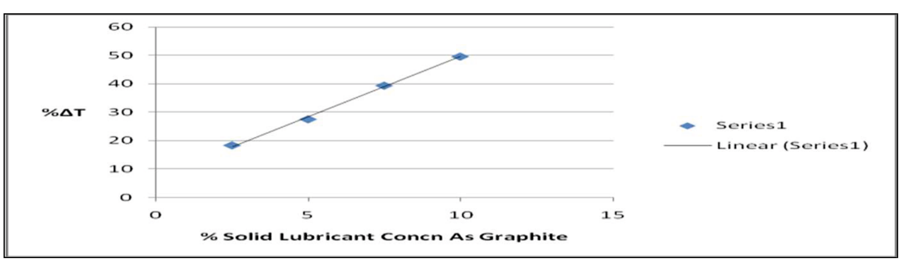


Figure-6 Calibration Plot -Lithium 12-Hydroxystearate Grease with NLGI-2 consistency with varying amount of Solid Lubricant -Graphite

Table 7

Sl. No.	Sample Description	Grease without Solid Lubricant-Graphite ($\%T_{WO\ SL}$)	Grease with Solid Lubricant -(Graphite) ($\%T_{with\ SL}$)	ΔT ($\%T_{WO\ SL}$- $\%T_{with\ SL}$)	Results (% Graphite Content) HATR Method	Results (% Graphite Content) Toluene Acetic Acid Method
1	Sample A (Lithium Grease)	95.01	74.12	20.89	2.83	2.98
2	Sample B (Lithium Grease)	95.17	62.16	33.01	6.23	6.18
3	Sample C(Sulphonate Complex)	94.40	69.25	25.15	4.60	4.93
4	Sample D (Licom Grease)	96.28	64.50	31.78	5.76	6.01

From the above **Table 7** shows the results obtained solid lubricant graphite content from different type of lubricating greases containing graphite is close agreement with wet gravimetric chemical method . Generally ,lubricating grease with solid lubricant graphite contains graphite content in the range of 0.5% to 10.0%.

Table 8 shows Lithium 12-Hydroxystearte Grease NLGI 2 with varying amount of Solid Lubricant - Graphite for Calibration Plot

Table 8

Sl. No.	Sample Description	%Graphite	%T	ΔT ($\%T_{Blank}$ - $\%T_{with\ SL}$)
1	Base Grease (Blank)	0	95.45	-----
2	Standard1(Base Grease +Graphite)	2.5	84.31	11.14
3	Standard1(Base Grease +Graphite)	5.0	76.19	19.26
4	Standard1(Base Grease +Graphite)	7.5	68.17	27.28
5	Standard1(Base Grease +Graphite)	10	59.44	36.00

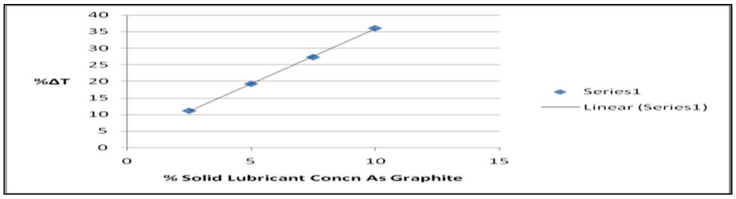


Figure 7 Calibration Plot -Lithium 12-Hydroxystearate Grease with NLGI-2 consistency with varying amount of Solid Lubricant – Graphite

Table 9

Sl. No.	Sample Description	Grease without Solid Lubricant Graphite(**%T$_{WO\ SL}$**)	Grease with Solid Lubricant Graphite (**%T$_{with\ SL}$**)	**ΔT (%T$_{WO\ SL}$ - %T $_{with\ SL}$)**	**Results (% Graphite content) HATR Method**	**Results (% Graphite content) Toluene Acetic Acid Method**
1	Sample A (Lithium Grease)	95.45	75.62	19.83	5.14	5.06
2	Sample B (Lithium Grease)	95.45	81.82	13.63	3.04	2.97
3	Sample C(Sulphonate Complex)	88.65	66.5	22.15	6.09	6.25
4	Sample D (Licom Grease)	92.60	70.75	21.85	5.67	5.91
5	Sample E (Polyurea Grease)	93.50	70.85	22.65	6.23	6.41
6.	Sample F (Silicon Grease)	96.10	83.42	12.68	2.84	3.06

Table 10

Sl. No.	Sample Description	Grease without Solid Lubricant - Mix (**%T$_{WO\ SL}$**)	Grease with Solid Lubricant-Mix (**%T$_{with\ SL}$**)	**ΔT (%T$_{WO\ SL}$ - %T $_{with\ SL}$)**	**Results (% Mix content) HATR Method**	**Results (% Mix content) Toluene Acetic Acid Method**
1	Sample A (Lithium Grease Nlgi 3) 3.0% MoS_2+6..0 % Graphite	95.01	51.56	43.45	8.78	8.97(9.0 %)
2	Sample B (Lithium Grease Nlgi 3) 3.0% MoS_2+3 % Graphite)	95.01	75.91	19.10	3.04	6.18
3	Sample C (Lithium Grease Nlgi 3) 1.5 % MoS_2+6..0 % Graphite	95.01	56.86	38.15	7.31	7.74
4	Sample C (Lithium Grease Nlgi 3) 3.0% MoS_2+ 1.5 % Graphite)	* 95.37	88.86	18.56	4.74	4.62

* Estimation of total solid lubricant using calibration plot of Solid Lubricant MoS_2 in Lithium grease NLGI 3 consistency

Table 10 show the results of total solid lubricant content (MoS2 & Graphite together) using calibration plot of solid lubricant in Lubricating greases whichever solid lubricant content is high . It was observed that sample with higher graphite content in Lubricating grease ,calibration plot of Graphite is taken for the estimation of total solid lubricant. Individual solid lubricant content in mixed solid lubricant in lubricating greases cannot be obtained as %T is summation of transmission from respective solid lubricant content in lubricating greases . Further work is in progress.

Conclusions :

In the present study, attempt has made to use instrumental technique such as Horizontal Attenuated Total Reflectance (HATR) accessory attached to FTIR to characterize strongly absorbing solid lubricants such as Molybdenum disulphide (MoS2) and Graphite containing lubricating greases . HATR technique is an alternative technique which overcomes the limitation of conventional optical IR spectroscopic tool using potassium bromide cell windows for characterizing solid lubricant based lubricants. HATR technique is fast and easy which requires minimum time for sample preparation .
For qualitative analysis, the characterisation of different lubricating greases with and without solid lubricant can be studied with ease from recorded IR spectrum using HATR accessory with FTIR .

IR spectrum of solid lubricant based lubricants depends on the solid lubricant content in both MoS_2 and graphite based lubricating greases. Both the lubricating greases containing solid lubricant shows different IR Spectral pattern with same content of respective solid lubricant MoS_2 and Graphite . %Transmittance drop is high in graphite than in Molybdenum disulphide for same amount of solid lubricant in lubricating greases

For Quantitative analysis of solid lubricant content in lubricating greases , consistency of the lubricating grease is important parameter for creating calibration plot . Secondly, %T of fresh grease without solid lubricant as a blank along with %T of solid lubricant containing lubricating grease to be measured and the difference %ΔT of % T blank grease & %T with solid lubricant is plotted against known % age amount of solid Lubricant in the lubricating grease keeping in mind consistency of lubricating grease . Separate calibration plot were made for Solid Lubricant -MoS_2 and Graphite . Solid lubricant MoS_2 or graphite content in different solid lubricant based lubricating greases having unknown content of solid lubricant was determined from the calibration plot of same consistency of the grease anlaysed . The results were found to be in close agreement with expected values which is determined by conventional wet chemical gravimetric -Toluene - Acetic Acid method.

The developed method is extended to lubricating greases containing both the solid lubricants graphite and MoS_2 and results were found to be encouraging by selecting suitable calibration plot and in agreement with conventional wet chemical method. Work is in progress.

Work is in progress to analyse market samples of lubricating grease with solid lubricants with unknown content.

The information obtained from the above analytical study will be useful in characterizing the solid lubricant based lubricating greases with type of soap used and nature of solid lubricant whether MoS_2 or graphite or both .This study also used rapidly estimating the solid lubricant content in lubricating greases using HATR with FTIR technique .The method is fast and easily adoptable for laboratory with minimum sample preparation time.

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Life Performance Assessment of Greases Using Test Rigs

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INTRODUCTION:

Bearing lubrication using greases has been revolutionized due to the demanding and challenging requirements from the operational and efficiency stand point of view of modern day machinery and equipment. The greases are expected to enhance the efficiency of the machinery as well as to reduce the maintenance cost. The increased efficiency of the machinery or equipment make them available for their effective usage.

The demanding conditions like high speed, high temperature and increased life expectancy of greases calls for use of high performance greases like greases based on semi synthetic/ synthetic base oil, complex thickeners like Lithium Complex, Calcium Sulphonate complex and Polyurea which are also fortified with good anti oxidant and extreme pressure additives. There are many factors like type of thickener, quality of base oil used, selection of suitable additives which influence the ability of the grease to lubricate during long service, under severe conditions. Various studies have been published to understand and explain the mechanism of grease lubrication and failure in rolling element bearings and the relationship between failure and the bulk properties of the greases. Most of the studies conclude that the failure is due to lack of lubricant or lubricating film due to reduction of lubricant at the contacting surfaces. The various Chemical and Physical change attributes responsible for the lack of lubrication are:

1. Greases are subjected to Chemical changes which results in
   a) Oxidative degradation of both oil and thickener
   b) Loss of antioxidants due to thermal degradation
   c) Formation of low volatile components.
2. Greases also undergo Physical changes as under
   a) Bleeding and leakage from the system/ bearings
   b) Breakdown of thickener structure
   c) Evaporation due to high temperature and volatility

During a product development approach, the evaluation of the greases is done using the normal Physico - Chemical tests. The validation of performance of the greases is being done using various test rigs which are expected to give some insight into grease performance in the field or in actual machinery. These evaluations or assessments of greases are used to select the right candidate for undertaking any product for trial at the customer place.

The present study was carried out on the life of high performance Lithium Complex Greases using FAG FE 9 Test Rig (DIN 51821) and High Temperature Wheel bearing Test Rig (ASTM D 3527). Lithium Complex Greases made using different complexing agents as well as base oils (Mineral & Synthetic) were taken for the assessment of their life performance study using FAG FE 9 and ASTM D 3527 test rigs.

The results of the study presented here throw some insights into the usefulness of such test rigs in selecting the right candidate greases for the intended applications.

TEST RIGS AND THEIR SALIENT OPERATING FEATURES.

FAG FE9 Test rig:

The FE-9 test bench has five test heads, so five test bearings can be tested under the same testing conditions until grease failure. All running times reached are entered on a Weibull chart, so that the probabilities of failure can be read out. The grease service life F_{10} and F_{50} are obtained at a 10% and 50 % failure probability.

The FE-9 test-bench consists of 5 test heads identical in construction. Each unit comprises one test bearing and one auxiliary bearing with same dimensions. The auxiliary bearing is provided with lubricating oil for lubrication while the test bearing is lubricated by the Grease under study.

Test parameters

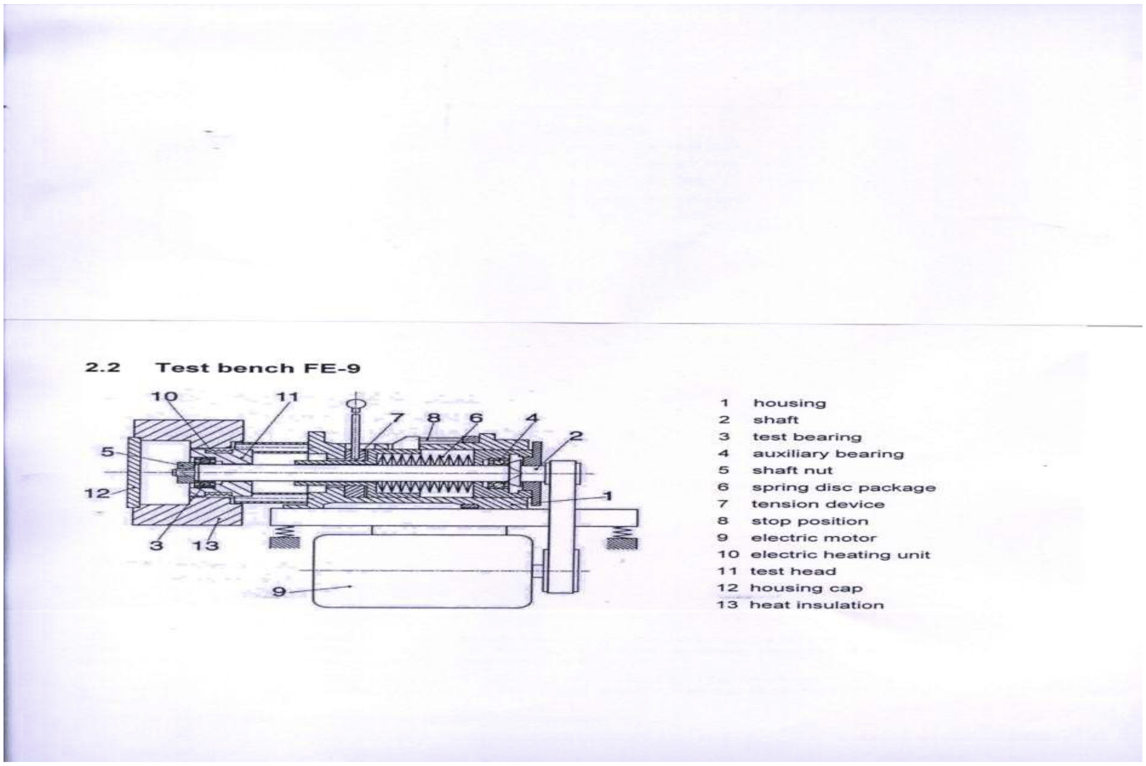
Test parameters according DIN 51821 Load: 1500 N

Shaft speed: 6000 RPM Temperature: 120□ C, 140° C, 160□ C Capacity of grease: 2 cm^3

Measurement Categories

During the whole test run, the temperature of the outer ring of the test bearing is acquired, recorded and put to the temperature control. To end the test run, the power output of the electric motor has to be acquired. If the motor power output increases double the persistent output, for more than 6 sec the test run is terminated .

All measurement installations work separately for each test head.



HIGH TEMPERATURE GRESE LIFE TESTER (AS PER ASTM D 3527):

High Temperature Wheel Bearing Grease Tester evaluates the high temperature stability of automotive wheel bearing greases in a modified automotive front wheel hub-spindle-bearings assembly. The ASTM D3527 Life Performance test employs severe conditions 25 lbf (111N) thrust load, 1000rpm, 160°C spindle temperature to induce grease deterioration and failure. The test continues in a 20/4 hour on/off cycle until grease breakdown causes measured drive motor torque to increase past an established steady state value (end point). The number of hours to failure is the test result.

The equipment consists of a modified front wheel hub-spindle-bearings assembly housed in a constant temperature oven and coupled to a ¼ hp variable-speed drive motor. Equipment controls test functions automatically and provides continuous digital display of motor torque, RPM, chamber temperature, spindle temperature, time cycle and elapsed time.

Development of Greases for evaluation:

Six Lithium Complex Greases developed as per the following scheme:

Designation	Thickener Type	Base oil Type	Additives	Base oil Viscosity at 40 Deg C
Grease A	Lithium Complex – Boric Acid	Mineral Oil	AO/ EP	ISO VG 220
Grease B	Lithium Complex – Sebacic Acid	Mineral Oil	AO/EP	ISO VG 220
Grease C	Lithium Complex – Boric Acid	Mineral/ PAO	AO/ EP	ISO VG 220
Grease D	Lithium Complex – Sebacic Acid	Mineral /PAO	AO/EP	ISO VG 220
Grease E	Lithium Complex – Boric Acid	PAO	AO/EP	ISO VG 220
Grease F	Lithium Complex – Sebacic Acid	PAO	AO/EP	ISO VG 220

Evaluation of Physico- Chemical Properties of the Developed Greases:

Sl No	Characteristics	GREASE A	GREASE B	GREASE C	Test Method
1	Worked penetration 60X	280	275	272	ASTM D 217
2	Drop Point, Deg C	281	286	286	ASTM D 2265
3	Cone Oil separation %	2.4	2.5	2.6	ASTM IP 121
4	Rust preventive property	Passes	Passes	Passes	ASTM D 1743
5	Copper corrosion at 100 □ C	1b	1b	1b	ASTM D 4048
6	Four ball wear scar dia, mm	0.54	0.57	0.55	ASTM D 2266
7	Four ball weld load, kgf	315	280	315	IP 239
8	Pressure oil separation	2.4	2.2	2.2	IP 181

Sl No	Characteristics	GREASE D	GREASE E	GREASE F	Test Method
1	Worked penetration 60X	275	277	280	ASTM D 217
2	Drop Point, Deg C	288	278	270	ASTM D 2265
3	Cone Oil separation %	3.2	2.2	2.8	ASTM IP 121
4	Rust preventive property	Passes	Passes	Passes	ASTM D 1743
5	Copper corrosion at 100 ° C	1a	1a	1b	ASTM D 4048
6	Four ball wear scar dia, mm	0.57	0.56	0.51	ASTM D 2266
7	Four ball weld load, kgf	315	280	280	IP 239
8	Pressure oil separation	2.6	2.1	2.4	IP 181

Assessment of Life of grease using FAG FE 9 Test (DIN 51821):

All the six greases were tested for life of the grease using FE 9 test equipment. The following conditions were used for the assessment of performance.

1. Load : 1500 N
2. Speed : 6000 RPM
3. Temperature of the test: 120° C, 140° C and 160° C

The number of hours to failure at each test bearing head is determined and the Weibull chart is obtained for F_{10} and F_{50} values.

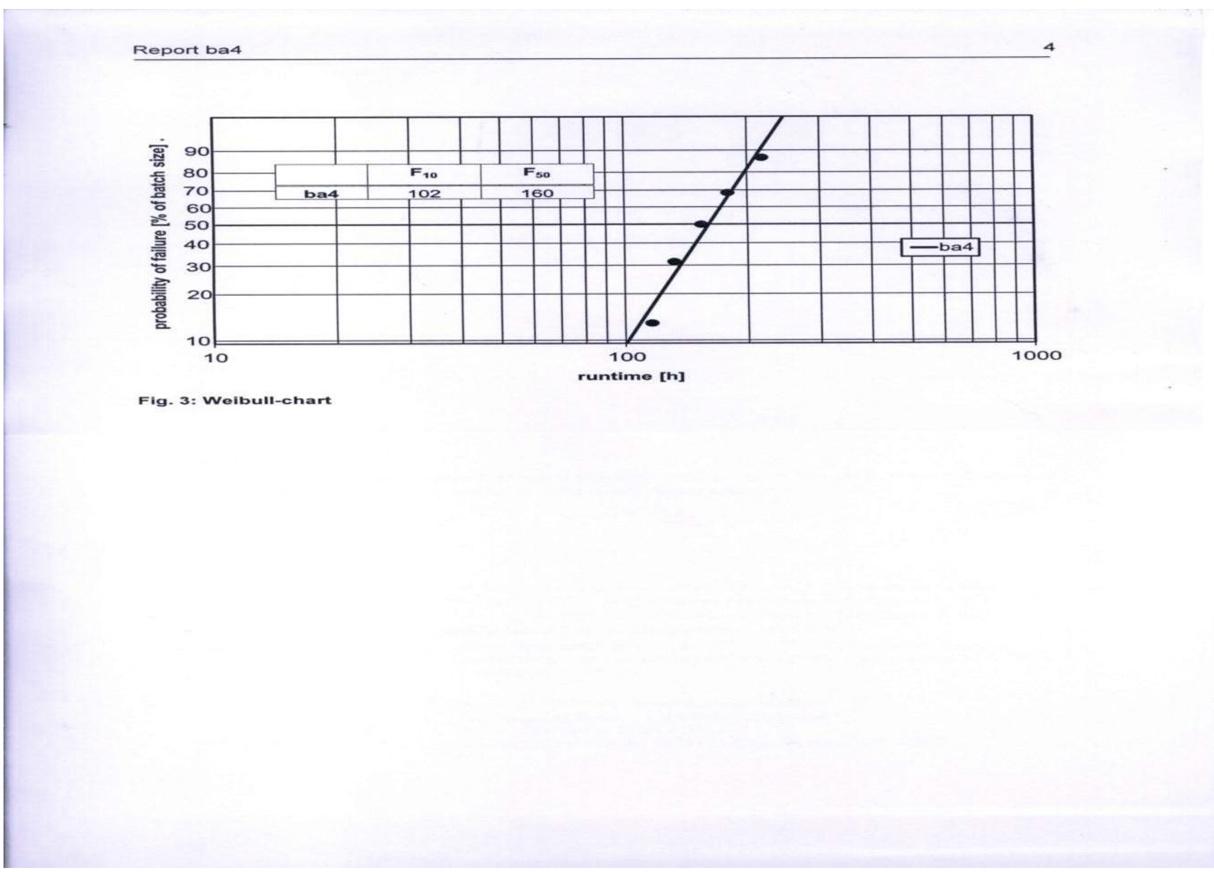


Fig. 3: Weibull-chart

The following are the results obtained:

	Time of Failure (in hours) at the 5 bearing Heads									
Temperature	**Grease A**					**Grease B**				
120 Deg C	100	130	80	110	95	139	173	101	155	90
140 Deg C	71	58	42	89	52	71	107	97	127	82
160 Deg C	33	30	18	32	20	34	30	18	29	19

	Weibull Results			
Temperature	**Grease A**		**Grease B**	
	F_{10} (Hours)	**F_{50} (Hours)**	**F_{10} (Hours)**	**F_{50} (Hours)**
120 Deg C	70	102	122	159
140 Deg C	40	53	65	98
160 Deg C	22	24	46	29

	Time of Failure (in hours) at the 5 bearing Heads									
Temperature	**Grease C**					**Grease D**				
120 Deg C	103	138	80	118	94	185	230	135	155	118
140 Deg C	74	63	51	89	60	95	143	131	169	109
160 Deg C	41	36	27	32	25	67	82	71	101	56

	Weibull Results			
Temperature	**Grease C**		**Grease D**	
	F_{10} (Hours)	**F_{50} (Hours)**	**F_{10} (Hours)**	**F_{50} (Hours)**
120 Deg C	73	108	163	212
140 Deg C	45	68	87	131
160 Deg C	22	33	52	78

	Time of Failure (in hours) at the 5 bearing Heads									
Temperature	**Grease E**					**Grease F**				
120 Deg C	179	116	132	217	155	355	374	286	243	331
140 Deg C	172	106	96	152	131	134	153	101	112	166
160 Deg C	43	68	51	60	37	39	57	48	70	44

	Weibull Results			
Temperature	**Grease E**		**Grease F**	
	F_{10} (Hours)	**F_{50} (Hours)**	**F_{10} (Hours)**	**F_{50} (Hours)**
120 Deg C	102	160	230	332
140 Deg C	86	134	91	135
160 Deg C	38	52	34	52

Assessment of Life of grease using High Temperature Wheel Bearing Tester (ASTM D 3527):

All the six greases were evaluated for number of hours to failure as per ASTM D 3527 test method. The following conditions were used for the assessment of life performance of the greases.

1. Speed – 1000 RPM
2. Load – 111N thrust load
3. Temperature – 120 Deg C, 140 Deg C & 160 Deg C

The results obtained in the above test are given below:

	Time of Failure (in hours)					
Temperature	**Grease A**	**Grease B**	**Grease C**	**Grease D**	**Grease E**	**Grease F**
120 Deg C	144	168	168	216	216	264
140 Deg C	72	72	96	120	120	172
160 Deg C	48	48	72	78	96	144

Results and Discussions:

Life performance in FE 9 test rig:

The mineral oil based greases designated as Grease A and Grease B have shown the least numbers of failure hours (F10 & F50) at all the temperatures compared to other four greases which are based on semi synthetic and fully synthetic oils which is the expected lines. By changing the thickener type (Complexing Agent) from boric acid to sebacic acid, some improvement could be achieved (B is better than A). Since both the greases Grease A & Grease B have same type of base oils and additives, the shorter life can be attributed to Boron present in Grease A which promotes oxidation. When the base oil combination was changed to semi synthetic (mixture of mineral oil and PAO), substantial improvement in the life of grease in the case of 120 Deg C,140 Deg C and 160 Deg C tests with the use of Sebacic acid could be obtained (Grease D is better than Grease A)

When the base oil is changed to fully synthetic oil (PAO), in both grease E and Grease F, substantial improvement in grease life hours with the use of sebacic acid could be obtained at 120 Deg C and 140 Deg C. However at 160 Deg C, the change of thickener (Complexing agent) in fully synthetic base oil has no appreciable improvement in life of the grease.

Upper service temperature Limit:

As per DIN 51825, the upper service temperature (K Value) limit of any grease is the temperature for which the F_{50} Value is above 100 hours as determined from FE 9 test Rig. Based on the F_{50} values for the six candidate greases, the upper service temperature can be declared as below:

	F 50 (120)	**F 50 (140)**	**F 50(160)**	**Upper Service temperature**
Grease A	102	53	24	120 Deg C
Grease B	159	98	29	120 Deg C
Grease C	108	68	33	120 Deg C
Grease D	212	131	78	140 Deg C
Grease E	160	134	51	140 Deg C
Grease F	332	135	52	140 Deg C

For Grease A and Grease B, the upper service temperature remained at 120 Deg C even with change of thickener. However for grease B the failure hours at 140 Deg C is just below 100 Hours (98), indicating that there could be improvement in life for this grease which is with sebacic acid complexing agent.

Among the semi synthetic oil based greases (Grease C & Grease D), by change of the thickener we could increase the upper service temperature by 20 Deg C. In other words boric acid thickener in Grease C promotes faster degradation at higher temperatures as compared to sebacic acid in Grease

D. This is further substantiated by more than doubling of the failure hours at 160 Deg C for Grease D compared to Grease C. Since both the greases have same type and level of AO additive, it is clear that the selection of thickener is important to enhance the service life in Semi synthetic oil based Lithium Complex Greases.

However in Synthetic lithium Complex Greases (Grease E and Grease F), there is no increase of upper service temperature by change of thickener type as indicated by the number of hours to failure remaining the same in both 140 Deg C & 160 Deg C tests. None the less at a lower service temperature of 120 Deg C, the increase in failure hours by more than double can attribute some improvement in life of the grease at 120 Deg C with change of the thickener.(Grease F is better than Grease E)

Life performance in D 3527 test Rig:
At 120 Deg C test in all the three category of Base oil combinations, Mineral, Semi Synthetic and Fully Synthetic, change of thickener (Complexing Agent) to sebacic acid has resulted in improvement in Grease Life.
At 140 Deg C while some improvement in the life can be observed for semi synthetic and (Grease C vs Grease D) synthetic base oil greases (Grease E vs Grease F) by change of thickener to sebacic acid, the mineral oil greases (Grease A & Grease B) with both boric acid and sebacic gave same life.
At 160 Deg C test only fully synthetic base oil based Grease (Grease E vs Grease F) showed some improvement in grease life hours by change of complexing agent to sebacic acid. Other two versions mineral and semi synthetic oil based greases have shown practically no improvement by change of complexing agent.
As expected the change of base oil from mineral to semi synthetic to fully synthetic version has shown improvements by using both boric acid and sebacic acids.

Scatter in performance of greases by FE 9 test:

Grease A (Mineral/ Boric Acid/ EP)						**Difference between low / high**	**Scatter Percentage**
	1	**2**	**3**	**4**	**5**		
120 Deg C	100	130	80	110	95	50	38.46%
140 Deg C	71	58	42	89	52	47	52.81%
160 Deg C	33	30	18	32	20	15	45.45%

Grease B (Mineral/ Sebacic Acid/ EP)						**Difference between low / high**	**Scatter Percentage**
	1	**2**	**3**	**4**	**5**		
120 Deg C	139	173	101	155	90	83	47.98%
140 Deg C	71	107	97	127	82	45	35.43%
160 Deg C	34	30	18	29	19	16	47.06%

Grease C (Mineral/ PAO/ Boric Acid/ EP)						**Difference between low / high**	**Scatter Percentage**
	1	**2**	**3**	**4**	**5**		
120 Deg C	103	138	80	118	94	58	42.03%
140 Deg C	74	63	51	89	60	38	42.70%
160 Deg C	41	36	27	32	25	16	39.02%

Grease D (Mineral/ PAO/ Sebacic Acid/ EP)						**Difference between low / high**	**Scatter Percentage**
	1	**2**	**3**	**4**	**5**		
120 Deg C	185	230	135	155	118	112	48.70%
140 Deg C	95	143	131	169	109	74	43.79%
160 Deg C	67	82	71	101	56	45	44.55%

Grease E (PAO/ Boric Acid/ EP)						**Difference between**	**Scatter**

	1	2	3	4	5	low / high	Percentage
120 Deg C	179	116	132	217	155	101	46.54%
140 Deg C	172	106	96	152	131	76	50.00%
160 Deg C	43	60	51	60	37	23	38.33%
Grease F (PAO/ Sebacic Acid/ EP)						**Difference between low / high**	**Scatter Percentage**
	1	**2**	**3**	**4**	**5**		
120 Deg C	355	374	286	243	331	131	35.03%
140 Deg C	134	153	101	112	166	65	39.16%
160 Deg C	39	57	48	70	44	31	44.29%

From the above results of the failure hours for the individual bearing heads at each of temperatures and greases, a large scatter (difference between lowest failure hours and highest failure hours for the same grease and at the same temperature) in the values for all the three different temperatures has been observed. The percentage scatter between the lowest and highest failure hours varies between about 35.03 to 52.81. This large scatter in the results for the same conditions of the test makes conclusion on the right selection of product for the applications difficult.

Conclusions:

1. Grease life in terms of no of hours to failure has been studied using the well known test rigs like FAG FE 9 (as per DIN 51821) and High temperature wheel bearing tester (as per ASTM D 3527).
2. The difference in the performance of various versions of Lithium Complex greases using different thickener/ complexing agents, base oil combinations by FE9 and ASTM 3527 test rigs was established.
3. Among the various base oil combinations, improvement in life of grease can be obtained by moving from mineral oil to semi synthetic and fully synthetic oils.
4. Improvement in upper service temperature (as per DIN 51825) by change of thickener for semi synthetic and fully synthetic base oil combinations can be obtained as per FE 9 test at 120 Deg C and 140 Deg C. However at 160 Deg C no substantial improvement was possible with change of thickener.
5. Boric acid when used as complexing agent tend to promote oxidation as compared to sebacic acid in all the base oil combinations. This trend is observed in both FE 9 and ASTM D 3527 tests.
6. The improvement in life of the grease in terms of number of hours to failure as obtained by ASTM D 3527 shows similar trend as FE 9 test rig values

Acknowledgements:

The authors wish to thank the management of Balmer Lawrie & Co Ltd for granting permission to present this study.

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Role of Inductively Coupled Plasma Optical Emission Spectroscopy during development and performance monitoring of Greases

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Abstract: Greases contains metals in the form of thickner and performance boosting additives. Most of the greases are classified based on the thickner metal type viz Li, Na, Ti, Ca etc. Other inorganic metals / non-metals viz Zn, Mo, P, S, Sb are from additives in the form of organo-metallic / organo-non-metallic compounds viz Zinc Dialkyl Dithio Phosphates, Molybdenum Sulphide, Sullfurized Iso Butylene etc. Grease development involves the need of quantification of metals either as thickner type or additive metals for its target performance in various applications. Food grade / Pharmaceutical grade greases for intended applications needs to be tested for carcinogenic metals residues viz As, Hg, Pb, Cd, Cr (USP 232: Elemental impurities in finished pharmaceutical products - Limits) which causes the adverse health effects as per pharmaceutical and food regulatory bodies. Periodic monitoring of greases for wear metals as per the ASTM 5185 required for assessing the in-service greases performance and fixing the changing intervals. Inductively coupled plasma optical emission spectrometry (ICP OES) based methodology is well known for metals analysis as well non-metals viz B, C, S, P, halogens. Based on the type metals and non-metals to be analyzed, different sample preparation should be adopted for ICP OES. Microwave assisted acid digestion sample preparation technique having the advantageous over conventional ashing method for retaining low boiling non-metals (sulphur) and metals (As, Hg, Pb, Sb etc.) in acid solution. Present study describes the sample preparation following ICP OES quantification protocol for the target metals in finished greases and in-service greases.

1.0 Introduction

Greases mainly contains the mineral type or synthetic base oils along with thickening agent. The thickening agent may be soap, an inorganic gel, or an organic substance. Other performance improving additives for inhibit oxidation and corrosion, wear are added to the greases. The fluid component is the more important lubricant for clearances between parts that are relatively large, but for small clearances the molecular soap layers provide the lubrication. Synthetic grease may consist of synthetic oils containing standard soaps or may be a mixture of synthetic thickeners, or bases, in petroleum oils. Silicones are greases in which both the base and the oil are synthetic. Synthetic greases are made in water-soluble and water-resistant forms and may be used over a wide temperature range. The synthetics can be used in contact with natural or other rubbers because they do not soften these materials. Special-purpose greases may contain two or more soap bases or special additives to gain a special characteristic.

Metals or non-metals in Grease analysis by ICP OES need proper dissolution prior to sample introduction. Several digestion / dissolution methods are reported in the literature viz sulphated ashing, micro emulsion and microwave acid digestion among which microwave digestion is having added advantageous over other two sample preparation methodologies. Dry or sulfated ashing procedures involves heating in muffle furnace followed by open vessel acid digestion results in contamination (Al, Fe, Na, K, Si) and loss of volatile elements (Hg, As, Pb, Cd, S). Literature reported Micro-emulsion methodology needs the optimization of stable emulsion formation for each type of grease. Even though draw-backs in dry / sulphated ashing procedure is solved in micro-emulsion method, getting a stable emulsion for desired analysis time is a challenging task. Emulsion stability seriously effects the required level of sensitivity and repeatability. Microwave digestion procure solves all the problems assisted with both dry / sulphated ashing and emulsification method. Grease samples prepared in microwave digestion procedure for grease sample preparation effectively removes the organic matter through oxidation and effectively dissolves the metal / non-metals. Present study successfully demonstrates the microwave digestion sample preparation methodology for the analysis of fresh greases (thickner elements, additive elements, toxic metals) and in-service greases (wear elements) using ICP OES.

2.0 Experimental

2.1 Materials

Suprapure hydrochloric acid and nitric acids are mixed for the preparation of aquaregia (3:1 HCl & HNO_3) in 500 ml volumetric flask. All the glass ware and digestion vessels are thoroughly washed with metals free surfactant followed by MilliQ water and 5% Hydrochloric acid. Required 1ppm and 10ppm level calibration standards are prepared by transferring the multi-element (0.05 ml & 0.50 ml) and single element standards (0.05 ml & 0.50 ml) to 50ml volume. SRM traceable to NIST CRM should contain thickner elements (Ca, Li), additive elements (Zn, P, S, Mo, Sb), toxic elements (As, Pb, Cd, Hg), and wear elements (Al, Ag, Cr, Cu, Fe, Ni). Calibration standards are prepared in 50ml volume with 8ml of aquaregia. SRMs used are Multi element standard (1000ppm IV M/s Inorganic ventures USA) and single element standards (1000ppm Hg, S M/s Inorganic ventures USA). Three numbers of in-house developed fresh greases and in-service (used) greases are selected for the thickner (Ca, Li), additive (Zn, P, S), toxic metals (As, Hg, Pb, Cd), and wear (Al, Cr, Cu, Fe, Ni, Pb) metals analysis.

2.2 Methods

2.2.1 Microwave Digestion Method

0.25g grease sample is quantitatively transferred to 55ml Teflon tube and added with 8ml of aquaregia. Prepare the minimum 2 no's of blank with 8ml aquaregia. Vessels are placed with protective PTFE pellet before closing with outer cap. All the sample vessels are placed in rotor and inserted into the microwave digestion cavity (Model - Mars 6, Make - CEM corp). Microwave digestion parameters are set to 200degC using 1600w microwave power. Ramping time for required temperature is 30min and 90 min hold time. Wait till the completion of digestion program and vessels temperature indication to 30 - 40degC. Remove the rotor from the microwave digestion cavity and transfer the contents to 50ml volumetric flasks with thorough washings. Cooling of Teflon vessels in ice bath will reduce the pressure developed in-side effectively and element losses in vapour form.

2.2.2 ICP OES

Inductively Coupled Plasma Optical Emission Spectrometer model 5300V from PekinElmer Inc. equipped vertical torch, Gemcone nebulizer and baffled cyclonic spray chamber. All the analysis were performed using WinLab32 software – manual analysis control window. Instrument parameters used for the calibration and analysis of samples is given in Table 1. Characteristic wavelengths for the desired metals are chosen from the data provided by the instrument manufacturer. ICP OES performance is checked before proceeding to multi-element calibration and samples analysis. The parameter chosen for the performance verification are Align view, UV-Vis detector calibration, Mercury lamp alignment and Detector calibration. All these parameters checked as per the equipment manufacturer guideline provided in instrument manual.

3.0 Results & Discussion

3.1 Detection Limits & Quantitation Limits

Detection limits and quantitation limits should be established based on the concentration of elements present in calibration blank or sample blank. Analyze the blank with 10 No's of replicates using the two point calibration (blank and 10ppm). This will produces the concentrations of desired elements in concentration units (ppb / ppm). Standard deviation of the calibration / sample blank level concentrations is multiplied with 3.3 for Detection Limits

(DL) whereas the 10 multiplication factor for Limit of Quantification (QL). DL and QL level concentrations determined are with reference to calibration of the instrument where as which needs to be multiplied with dilution factor (25 ml / 0.25g) for DL & QL sample level. DL & QL sample level should be understand that the concentration below is reported as BDL / BQL. Calculated DL & QL at calibration level & sample level are given in Table 2.

3.2 Samples Analysis

Instrument calibration is performed using the standards 0, 1, 10ppm of multi-element standard with minimum of 2 replicates. Once the calibration completed all the calibration statistics (slope, Intercept, correlation) along with correlation chart will be provided by the WinLab32 software. Characteristic atomic emission lines are given in Fig 3 and correlations between the concentration and intensities are given in Fig 2. Correlation statistics of the 3 point calibration is given in Table 3. All the samples are analyzed against the developed calibration. Element concentration levels of samples should be within the calibration standards concentration. Any element concentration above the calibration range should be further diluted with proper addition of acid level similar to calibration standards. Three number of fresh in-house developed greases are analyzed for thickner elements, additive elements, and toxic metals. Additive metals reported by the current methodology are within the in-house specifications of finished grease. No toxic element levels are seen in the fresh samples above the sample level DL & QL.

4. Conclusions

Proposed microwave digestion sample preparation for greases with aquaregia produces the target metals or non-metals in aqeueous medium. Grease types both fresh and used selected for the study are Lithium and calcium thickner based. Additive elements viz Zn, P and S are determined with required accuracy and repeatability. Detection and quantitation limits are established for the toxic metals requirement as per USP Chapter 232 and wear metals as per ASTM D5185. Reporting limits based on the dilution are calculated from the DL level concentration. With the current dilution, reporting limits achieved for Cadmium, Lead, Mercury, and Arsenic are 2, 10, 10, and 20ppm respectively. Even though toxic metals reporting limits are still higher side than the cited concentrations in USP 232, superior reporting limits can be achieved only with ICP-MS. There is no such CFR regulatory guidance for limiting metal residues in greases for food grade / pharmaceutical applications. Toxic metals profiling (As, Cd, Hg, Pb) in finished greases will helps the Wear metals reporting limit for Al, Cr, Cu, Fe, & Ni is 2, 2, 1, 2, & 5ppm respectively. The reporting limits achieved for wear metals are in-line to in-house wear metals specifications in used grease samples. Proposed Microwave digestion methodology is successfully applied for metals / non-metals grease developmental needs as well in-service grease monitoring purposes.

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Table 1: Instrument Operating Parameters

Plasma Argon Flow	16 L/min
Auxiliary Argon Flow	0.40 L/min
Nebulizer Argon Flow	0.66 L/min
Sample in-take	1.1 ml/min
Nebulizer type	Gem cone PEEK
Spray chamber type	Quartz cyclonic baffled
Injector tube	Alumina
View mode	Radial at 0 mm
Torch	Quartz - 3 slots
Detector	
Replicates	3 No’s
Calibration levels	3 No’s
Read delay	60 sec

Table 2: Detection Limits and Quantitation Limits for Toxic and Wear metals

Element	STDEV ppm	STDEV ppb	Calibration Level		Sample Level		Reporting
			DL ppb	QL ppb	DL ppm	QL ppm	ppm
Al	0.006	5.6	18.3	55.5	1.8	5.6	> 2
As	**0.056**	**56.3**	**185.8**	**563.0**	**18.6**	**56.3**	**> 20**
Cd	**0.003**	**3.2**	**10.5**	**31.9**	**1.1**	**3.2**	**> 2**
Cr	0.004	4.0	13.1	39.8	1.3	4.0	> 2
Cu	0.002	1.7	5.6	16.9	0.6	1.7	> 1
Fe	0.004	4.4	14.4	43.5	1.4	4.4	> 2
Ni	0.012	12.0	39.5	119.7	3.9	12.0	> 5
Pb	**0.026**	**26.0**	**85.7**	**259.7**	**8.6**	**26.0**	**> 10**
Hg	**0.022**	**21.5**	**71.1**	**215.4**	**7.1**	**21.5**	**> 10**

Table 3: Linearity experiment for Samples Analysis by ICP OES

S.No.	Element	λ, nm	Algorithm	Intercept	Slope	Correl.
1	Al	394.401	Lin, Calc Int	36.2	3671	> 0.9999
2	As	188.979	Lin, Calc Int	-0.7	69.43	> 0.9999
3	Ca	317.933	Lin, Calc Int	27.9	3049	> 0.9999
4	Cd	228.802	Lin, Calc Int	24.8	2494	> 0.9999
5	Cr	267.716	Lin, Calc Int	14.7	1911	> 0.9999
6	Cu	327.393	Lin, Calc Int	170.1	9365	> 0.9999
7	Fe	238.204	Lin, Calc Int	18.4	1902	> 0.9999
8	Hg	253.652	Lin, Calc Int	-1.1	527	> 1.0000
9	Li	670.784	Lin, Calc Int	225.8	54620	> 1.0000
10	Ni	231.604	Lin, Calc Int	5.9	542.4	> 0.9999
11	P	213.617	Lin, Calc Int	1.0	51.96	> 0.9999
12	Pb	220.353	Lin, Calc Int	-4.4	208.9	> 0.9999
13	S	181.975	Lin, Calc Int	1.3	25.12	> 0.9999
14	Zn	206.200	Lin, Calc Int	6.0	391.0	> 0.9999

Table 4: Metals Analysis in fresh and in-service Greases

Grease type		Fresh			In-service		
Element		A	B	C	A	B	C
Soap	Ca	-	0.84%	0.80%	-	0.61	0.35%
	Li	0.21%	-	-	0.36%	0.1	-
Additive	Zn	0.06%	0.12%	-	-	0.14	-
	P	0.06%	0.13%	-	-	0.54	-
	S	0.68%	0.93%	0.22%	0.80%	0.61	0.25%
Toxic	As	< 20	< 20	< 20	< 20	< 20	< 20
	Cd	< 5	< 5	< 5	< 5	< 5	< 5
	Hg	< 10	< 10	< 10	< 10	< 10	< 10
	Pb	< 10	< 10	< 10	< 10	< 10	< 10
Wear	Al	< 2	< 2	< 2	474	154	235
	Cr	< 2	< 2	< 2	< 2	6	< 2
	Cu	< 1	< 1	< 1	< 1	16	< 1
	Fe	< 2	< 2	< 2	24	161	37
	Ni	< 5	< 5	< 5	< 5	< 5	< 5
	Pb	< 10	< 10	< 10	< 10	< 10	< 10