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Assessment of Bearing Grease anti-corrosion performance using Emcor washout test rig

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1.0 Abstract:

Greases are designed to protect bearings from corrosion during operation. Bearing greases are supposed to withstand conditions of cooling water spray and washout. The SKF Emcor test is an age old standard test method used for the evaluation of Dynamic Anti-rust performance in bearings, however this evaluates the corrosion performance of greases with bearings remaining dipped in stagnant water. This may not be true representation of the severe conditions in plants where the cooling water constantly flows through the bearing housing and may lead to the grease being washed out and not being available for corrosion prevention.

To account for this aspect, the modified Emcor test rig with a water washout attachment was used to evaluate greases simulating conditions in laboratory closer to those present in a steel plant environment. The anti-rust performance of several greases was evaluated in Emcor testrig with and without water washout. A correlation was attempted based on these studies, and abetter understanding of the factors affecting grease corrosion performance was developed during these studies.

2.0 INTRODUCTION:

Greases offer significant benefits over oils in bearing lubrication. They provide inherent sealing properties thus keeping contaminations away from the surfaces to be lubricated. They also act to resist the washing effect of water in bearings and machine components. Greases can be used in open bearing components even in vertical orientations by virtue of its retentive properties. In bearings the reservoir of grease moved to sides/kept on sides take care of replenishment when the thin film existing earlier degrades or dries due to oxidation thus protecting components at all times. It is estimated that greases lubricated over 90% of all bearings, thus is the preferred choice for lubrication of bearings.Bearing lubrication presents several challenges to the grease formulators. They have to do a balancing act of working with minimal quantity lubrication coupled with long bearing life (the same as that of the bearing itself) as well as the above challenges of working to keep the contaminants out and also to be able to work with ingress of water. The performance demands on the grease include working at higher speeds, loads, and temperatures and for extended relubrication intervals.

This imposes severe demands on the grease used in such bearings. In this context it becomes a complex task to predict the lubricating life or the relubrication interval to prevent lubrication or bearing failure with uncontrollable like contamination with water. Greases of different chemistry behave differently on contact with water so their performance also vary differently.

In this context, to be able to formulate the right grease for the right application taking into consideration the requirements, the right testing methodology has to be worked out. Several standard tests are available for this purpose to guide the formulators to have the right product in place. Standard tests are available, but these suffer from limitations of not being able to correlate with the conditions encountered in service. In such a case, it is necessary to modify the test conditions on these standard equipments or develop new equipments altogether that simulate the conditions in a better way.

3.0 LITERATURE REVIEW:

Corrosion prevention is an important part of lubricant development. Any oil or grease used in service conditions ideal for corrosion of metallic parts has to be able to prevent corrosion of the surfaces to prevent premature failure of the same.

As per McKibben **[1]** relating to the relation of Humidity Cabinet life of lubricants to their service life, Corrosion is significantly dependent upon Humidity (H) and temperature (t). Corrosion proceeds at negligible rates at lower temperatures and humidity. So it is very necessary to look at corrosion problems where the temperatures are high and ingress ofmoisture and free flowing water occurs.

$$C=((H/23.4)-1.28) \times 2^{(t/18)}$$

It has been estimated in studies by bearing manufacturers like SKF and Timken [2,3] that even a small amount of water even less than 1% in the grease shortens the life of rolling element bearings. Lugt[4,5] has described that some greases perform well with water present, while some do not. Water ingress can occur due to number of reasons, some due to use of water as acoolant for bearings in steel plants, in some cases due to condensation of moisture in the bearings due to temperature changes, and sometimes due to machine malfunctions which cause water to reach inside the bearings. It is necessary to know how the grease structure that is primarly responsible for its performance changes with the ingress of varying quantities of water. Water with free electrolytes due to presence of various salts dissolved in it may lead to problems of galvanic potential leading to corrosion.

A white paper by Axel Christiernsson **[6]** reviews and gives insights into which greases are water resistant and do well under wet conditions when lubricating a bearing. This paper also gives an overview of the popular test methods used in industry for evaluating water ingress in greases in a bearing. A recent publication by the Leckner [7] of the same organization has documented the available industry methods to assess the ability of various lubricating greases with different thickener systems to perform when contaminated with water. This paper also tries to validate the laboratory field results with actual field data about the performance.

The failure modes due to the ingress of water in the bearing have been documented by Fitch [8]. These include the Hydrogen induced fractures due to hydrogen embrittlement and blistering. When water comes in contact with free metal in the microscopic fatigue cracks in balls and rollers, this occurs. Corrosion and rusting renders surfaces unusable due to rapid formation of etched and pitted surfaces. High temperatures and water ingress consume the antioxidants rapidly reducing the protection required causing corrosion, sludge, varnish etc. Other additives like AW, EP, Rust inhibitors etc. get depleted in the lubricants in the presence of water. Film strength of lubricants like greases and oils in bearings get impaired due to presence of water. Bearings work in EHD and boundary lubrication so the surface protection imparted by film strength gets impaired causing premature failure.

Folger et al [9] in their paper lists the top causes of bearing damage, and have indicated that as little as 1% of water in grease or oil can significantly shorten the bearing life. They indicate that moisture or water ingress in bearings leads to etching or corrosion in bearings. Even bearing surfaces left idle for long period are susceptible to corrosion in bearings, so greases should protect surfaces at all times during operation as well as storage.

Authier et al [10] has presented a study on use of Calcium Sulphonate chemistry grease as a water resistance grease which is able to successfully overcome problems due to water ingress in bearings even at high temperatures. This grease works well with water due to its inherent properties which is able to offer great performance in the laboratory tests as well as during field trials. The paper offers a comparison with other chemistries of greases and notes that under conditions of high temperatures and water ingress into bearings, Calcium sulphonate greases offer the best solution.

4.0 REVIEW OF TEST METHODS IN PRACTICE:

To be able to evaluate the water ingress effect on performance as well as corrosion resistance of greases, it is required to run tests on greases using the metallic components in contact with water. These tests give a directional indication of the properties of greases to prevent corrosion, however it would correlate with field performance if a dynamic test in the actual component being lubricated is run on the grease. It would also be useful to maintain the test conditions as close as possible to the actual field conditions as possible in terms of load, speed temperatures as well as the contact with the water or the process fluid as in actual service.

Various tests have been used and standardized by ASTM, IP, DIN and ISO over the years to assess the performance of greases in the presence of water. Some of these are listed below:

(a) DIN 51807 water resistance test is used to assess the grease's water resistance. In this test a thin layer of grease is applied to a glass plate and it is then dipped in hot water kept in a test tube and allowed to stand in there for three hours. A visual inspection after this static test assesses the change in the grease after the test, with 0 indicating no or little change and 3 means that grease has significantly dissolved or dispersed inwater.

(b) In the ISO 11009 Water washout test, the ability of the grease to withstand water under washout conditions. This dynamic test uses a SKF 6204 C3 bearing filled with 4 grams of the grease rotated at 600 rpm for an hour during which a jet of distilled water at the rate of 5 ml/sec is sprayed on the bearing shield. The temperature of 37.8ºC or 79.4 ºC (100°F or 175°F) is maintained depending upon specification requirements for the grease,also it is possible to use various fluids, salt water, sea water or process fluids depending upon the requirements. After the test the bearing is dried and amount of grease in the bearing is calculated. Values of washout below 10% are acceptable performance limits.

(c) ASTM D4049 Water spray off is a test used to evaluate the retentive stay in place ability of a grease on an open plate when subjected to a high pressure shower of water.In thisa Stainless steel plate is coated with a 0.8 mm thick film of grease. It is weighed and stationed at a specific angle ranging from 55º to 65º in the apparatus. The water is heated to 38 ºC and sprayed at the plate at a pressure of 276 kPa(40 psi) over the sample for 5 minutes. The plate is then dried and weighed to estimate the remaining amount of the grease. A grease should ideally achieve a value below 25%.

(d) Another test that evaluates the performance of a grease in presence of water is the Mechanical stability in the presence of water. The change in the penetration is assessed due to the absorbtion of water in the grease. Grease is contaminated and thoroughly mixed with 10% of water and is subjected to 100000 strokes prolonged cone penetration as per ASTM D217 and the Roll stability as per ASTM D1403. The change in the penetration after these tests for greases with 10% water is assessed and reported.

(e) Emcor test is a widely used test for the assessment of the corrosion prevention propertyof the grease in a bearing. The test is done in an actual bearing filled with grease and kept immersed in water (distilled, synthetic sea water, tap water, or process water as per requirements). The test conditions are simulative of the ability of the grease to stay in place withstanding the shearing due to the action of the bearing rotation, as well asto prevent corrosion on the surface. The test was developed with the bearing running immersed in static water for a period of a week as per IP220, ASTM 6138, ISO 11007,DIN 51802 etc.

However it was realized that this test does not correlate with conditions of flowing water existing in many applications where the grease tends to be washed out. So a water washout option was developed and it is a part of the new ISO 11007 standard. Bearings after the test are rated for the corrosion on the inner side of the outer race of the test bearings and rated from 0 to 5, 0 standing for no corrosion to 5 being very severe corrosion. The rating procedure remains same for both the old Emcor test and the washout option on the Emcor machine.

5.0 PRESENT STUDY:

The present study was carried out since using the old Emcor test method using bearings immersed in water was no guarantee that the grease will perform well in service in bearings with a constant ingress of water. Some field analysis reveal that a 0 rating in this test did not mean that the grease will meet the requirements of plant performance especially in steel plant roll neck bearings in hot strip mills where a constant flow of cooling water passed through the jacket of the bearings. This caused the greases to get emulsified as well as washed away due to the action of the constant water.

So it was decided to evaluate several greases with known pass Emcor Test performance and evaluates the same on the modified Emcor test procedure. This would enable us to get an insight into whether there was any correlation between the two. Also a good assessment of the grease performance was possible, to separate out the good performers from the ones that could not stand the washout test. The water washout test data was also included for all these greases.

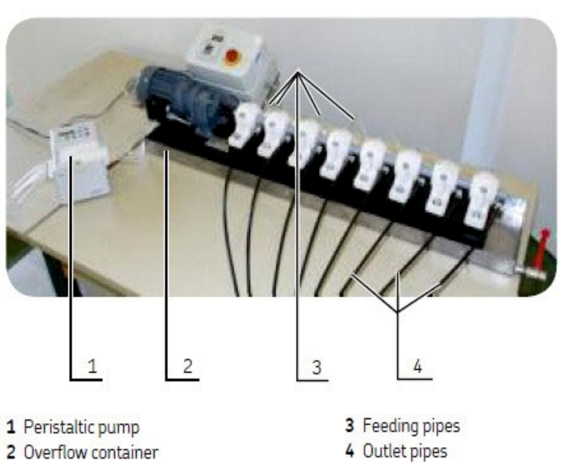
6.0 DESCRIPTION OF EMCOR TEST RIG

An Emcor rig is used for the the Dynamic Anti Rust test studies on various greases. This rig is popularly used to characterize the corrosion resistance properties imparted by the greases especially in conditions where water ingress occurs in bearings or there is condensation of moisture which ultimately gets deposited on the bearing parts. There is a requirement for the grease to prevent rusting of the bearing surfaces to maximize its bearing life. This test has been popularly used for over 40 years to measure the ability of a grease to protect a bearing from corrosion even in the presence of water. The test assesses the rust prevention ability of the parts that are lubricated by the grease such as the inner surfaces of the outer race of the bearing.

6.1 SF Grease Test Rig EMCOR: As shown in Figure 1, it consists of a ground plate (3) on which eight polyamide housings (5) are mounted. A shaft protected with a nylon coating (4) carries the test bearings (7) and is driven by an electric motor (2).

The test bearings are specially-treated 1306K/236725 double row self aligning ball bearings. The bearings are washed carefully, filled with the appropriate quantity of test grease and fitted on the shaft with the help of a nylon sleeve and nut. The seals are fitted and the specified quantity of water is introduced into the housings. The bearings are placed in the housings and the housings are closed and sealed. The test is run in the following sequence after charging of the water (10 ml on either sides of the bearing). The rotational speed of the shaft is kept at 80 rpm and no load is applied.

Fig 1: Standard Emcor test rig (picture courtesy SKF)



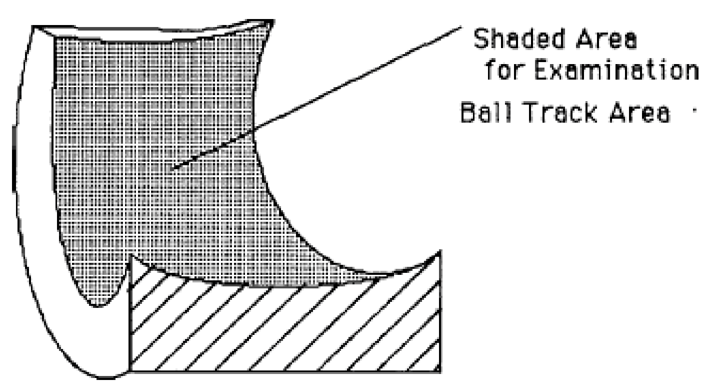


Fig 3: Outer ring of Test Bearing (double row self aligning ball bearing) examined for rust rating

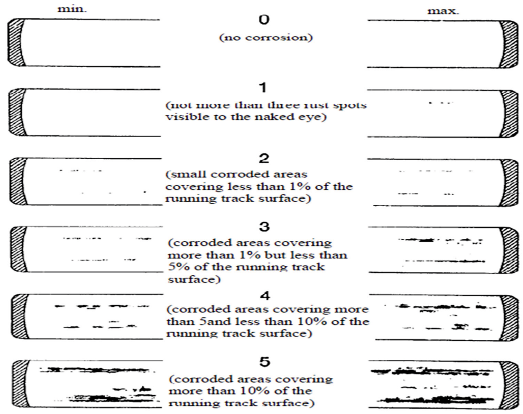


Fig 4: Emcor Corrosion Rating Chart (IP 220, ASTM D6138)

Fig 5: An example of rust rating during Emcor test

Day 1: 8 h run, 16 h stop
Day 2: 8 h run, 16 h stop

Day 3: 8 h run, then stop for 108 hours(over four days) after which the the bearings are dismounted, taken apart, washed, evaluated and rated. The rating is done on the inner surface of the outer race (ring) of the test bearing as shown in Figure 3 and Figure 4. An example of various ratings of the test bearings is shown in Figure 5.
The degree of rust is an indication of the corrosion-inhibiting property of a grease. This test method is standardised to the international ISO 11007, ASTM D6138 Germany DIN 51802 Great Britain BS 2000 pt 220 (IP 220) Sweden SIS 155130 and France NFT 60-135. The new international standard (published in 1996) contains contemporary, modified and internationallyapproved procedures to further increase test precision. The test can be run to test greases as well as oils, and variations can be made with regard to the test medium. Instead of water, brine(synthetic sea water simulation), tap water or process water can be used
Alternatively the machine can be slightly tilted to test the corrosion-inhibiting properties of a lubricant when water flows through the housings and so washes out the corrosion inhibitors – the so-called SKF EMCOR wash-out test (optional). This test as per the SKF standard method is for the determination of water washout rust prevention provided by a lubricating grease. This corrosion test is a useful guide to the protection provided by lubricating grease in the event of abearing becoming constantly contaminated with water with ingress. The use of flowing water inplace of the standard laboratory static test leads to the failure of greases with water-soluble corrosion inhibitors.

6.2 **SKF Grease Test Rig EMCOR with the wash-out test:** The test rig used is the same device as the standard EMCOR (as described before) with some options as shown in Figure 2 such as the peristaltic pump (1) feeding and outlet pipes (3) and (4) and overflowing container (2). The mechanics is inclined so that an angle from the horizontal of 1,5° is formed and placed in a overflow container (2) to collect test fluid if necessary. The peristaltic pump (1) pumps test fluid through the feeding pipes (3) into the plummer blocks. Via the outlet pipes (4), the fluid flows out of the plummer blocks. The test machine with the washout option has the following additional features to enable the running of the test.

1. Peristaltic pump : It should be calibrated to ensure flow rate of 2.08 ml per minute (1 litre for 8 hour period,or 3 litres during the entire running phase of test)in each channel.
2. Fit adaptors to the bearing housings and ensure drain is free from contamination.
3. Fill the peristaltic pump lines with test fluid and prepare sufficient reservoir of supply test fluid and drainage for the test.
4. The test procedure remains the same except that each test bearing filled with grease will be exposed 3 litres of test fluid over running time of the entire test procedure

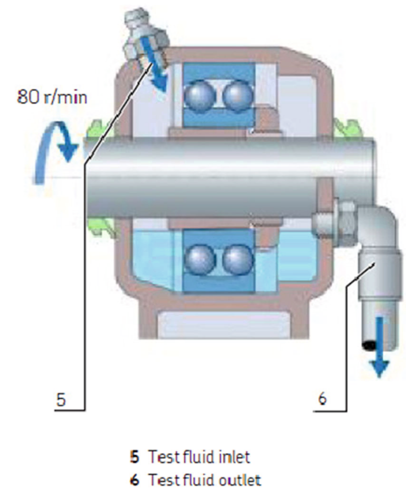


Fig 2: Schematic Emcor rig with a water washout option(Pictures courtesy: SKF)

during the running of the motor, as opposed to just 20 ml test fluid with the static test without the washout option. The rotational speed of the shaft is kept at 80 rpm and no load is applied. The rating procedure remains the same.

7.0 OBSERVATIONS AND ANALYSIS OF TEST RESULTS:

Seven different greases were selected for Emcor studies without and with water washout. Distilled water was used for the present studies. The selection of these commercial products was done varying various factors like base oil viscosity, type, soap chemistry and presence of corrosion inhibitors. Most of the greases were selected so that the standard Emcor IP220 test yielded a pass result, and one of the grease was selected with a marginal fail result to assess if its water washout result varies due to the effect of the washout. The post test analysis of water was carried out to get information about the mechanism of corrosion protection during thetest.

Emcor test with water wash out is reported to be more severe test due to presence of larger quantity and fresh charge of water. It is expected in case of a test with water washout, the following will be differences as compared to a standard IP 220 Emcor test which affect the performance significantly.

(1) In case of a standard Emcor test, it is expected that a corrosion inhibiting film that forms during the initial phase of test remains intact preventing the water and the presence of metallic ions that may cause galvanic corrosion to not have any detrimental effect on the surface causing corrosion. The strong film that forms during the initial phase of the test may be enough to protect the surfaces.

(2) In case of a water washout test, since significant amount of fresh water flows continuously through the bearing, due to the mechanical shearing as well as the leaching of the additives and washing out of the oil film, it is expected that corrosion inhibition additive or the oil film that forms may have to be constantly replenished for the grease to give a good performance in this test.

Keeping this into consideration the greases were evaluated on the Standard IP 220 Emcor Test and Modified Emcor test with water washout. The table with the test results of the Emcor test and the grease composition and the post test analysis data is given below.

TABLE 1: GREASE TEST RESULT SHOWING PHYSICOCHEMICAL PROPERTIES AND EMCOR TESTRESULTS.

Property	Grease 1	Grease 2	Grease 3	Grease 4	Grease 5	Grease 6	Grease 7
Soap	Lithium complex	Lithium base	Lithium base	Polyurea	Sulphonate complex	Lithium base	Lithium complex
Base oiltype	Semi-synthetic	Mineral	Mineral	Mineral	Mineral	Mineral	Mineral
Base oil Viscosity at40° C (cSt)	220	210	135	460	320	110	220
Consistency	2	3	2	1	2	3	2
Corrosion inhibitor	No	Yes	Yes	Yes	Yes	No	No
Emcor test rating (average)							
Without water	0	0	2	0	0	0	0
With water	5	3	2	0	0	3	5
pH of water							
IP 220 without washout	5.90	6.32	6.55	6.02	6.60	6.80	7.06
IP 220 withWater washout	5.12	7.59	6.32	5.90	10.46	6.95	7.76
Appearance of water collected after IP 220 test with washout	Milky	Milky (Tur-bid)	Clear	Milky	Milky	Clear	Milky

7.1: ANALYSIS OF TEST RESULTS

Lithium complex greases (No. 1 & 7) -These greases do not contain any corrosion inhibitor. Emcor value for both Lithium complex greases were found to be (0,0) without water wash out. It seems that the film formation due to heavy base oil can protect surfaces in the Emcor Standard IP 220 test. However, significant corrosion was found in Emcor test with water wash out test i.e rating of (5,5), which suggests that the film does not remain intact in the constant ingress of water causing corrosion.

Lithium Base Greases (No. 2, 3, & 6) - Grease No. 2 & 6 with similar consistency of 3 exhibited similar behavior in Emcor test conducted without (0,0) or with water wash out (0,3), indicating that this higher consistency plays a role. Grease No 2 had Corrosion inhibitor, whereas Grease No 6 had none. Among Lithium base greases, only grease No. 2 was in NLGI grade 2, Emcor results for this grease remained same with or without water wash out i.e (2,2), which was not satisfactory.

Polyurea (Grease 4) and Sulphonate Complex Greases(Grease 5) – Both of these greases are known to have excellent anti-corrosion properties, which is verified by their identical Emcor ratings (0,0) with or without water wash out. Their mechanisms of corrosion protection are on account of their intrinsic chemistry. In case of polyurea Grease 4, the absence of metal ions is reported to be responsible for corrosion protection, which inhibits the galvanic potential formation leading to corrosion. In case of Calcium Sulphonate grease, the basic chemistry is responsible for corrosion protection. This grease is manufactured using water which enables its structure to be developed. The grease is reported to have excellent corrosion protection as well as retention of mechanical stability when evaluated in the presence of water.

To explain above findings following parameters can be considered –

a) Consistency of the grease – Higher the consistency of the grease better will be the film formation on the surface. Therefore, better results in static Emcor test can be expected for harder greases. Typical case of Lithium base greases No. 2, 3, & 6.

b) Base oil viscosity – Greases prepared with heavier base oil viscosity will result in better film formation on the surface, ensuring better performance for Emcor test both in the static and with water wash out.

c) Type of the soap and presence of the anti-corrosion additive at the site of application – Most of the soaps are polar in nature. Therefore, they compete for metal surface with polar additives. Secondly, some soaps are known to perform better in the presence of water [10] , for example Sulphonate and Polyurea greases in this case. Increase in pH of water after the Emcor test for Sulphonate grease is an indicator of strong interaction of water with sulphonate grease. However, it should also be kept in mind that presence of other additives such as EP, AW and AO can also react with water or may leach out and can alter pH of water significantly. In the case of Grease 5 (Calcium sulphonate) the effect of the basic chemistry of grease's strong interaction with water overshadowedthe effect of other additives.

8.0 CONCLUSIONS:

(1) Emcor Water washout test is comparatively much severe than the Standard IP 220 Emcor Test.

(2) The test is able to distinguish between different greases which offer mild to moderate corrosion protection to those that offer high degree of protection.

(3) The results obtained in the test correlates well with the field performance in terms of the greases which are known to give good performance in field conditions like Calcium sulphonate and the Polyurea greases.

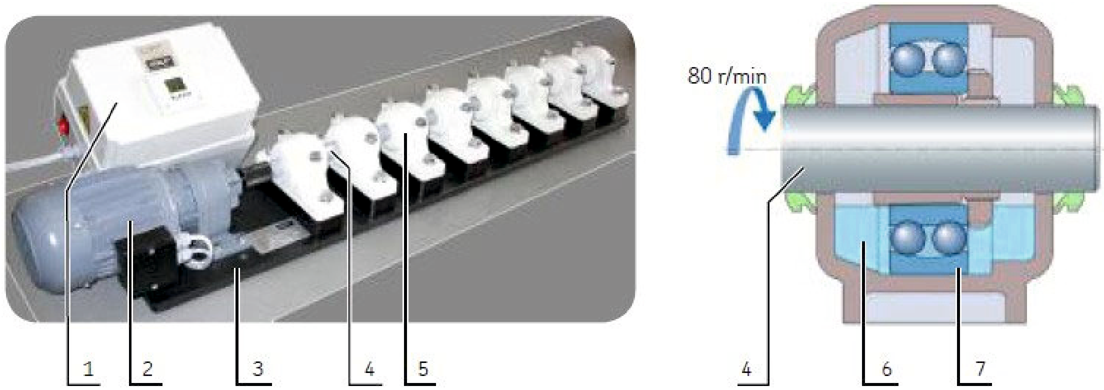
(4) The mechanism of corrosion protection varies from grease to grease based on various factors. The study yields a good insight into the factors that should be borne in mind for formulation of a grease to meet the performance requirements whenever there isingress of water or moisture in the rolling element bearings. Primary Factors such as the instrinsic chemistry of the grease and corrosion inhibitor additives play a key role, but it is necessary for greases to be fortified by secondary factors like higher base oil viscosity, mechanical stability retention in presence of water etc.

(5) Calcium Sulphonate and Polyurea chemistries work well in offering good corrosion protection in a static Emcor test and a water washout Emcor test. This may be due to their inherent chemistries. Calcium Sulphonate is known to work well as a Corrosion inhibitor, whereas Polyurea greases offer corrosion protection since these do not have any metallic ions which could promote the galvanic effect.

(6) There was a sharp increase in basicity of the Calcium sulphonate grease during washout test, which explains the good corrosion performance. In case of the others, the changeof pH was not so significant(ranging from weak acids to weak base), and may also be due to the depletion effect of other additives present in the grease such as Antiwear, EP or Antioxidants.

(7) The test methods used may not fully correlate with conditions present in a hot rolling mill bearings where the grease lubricated bearings are subjected to high temperature conditions which may increase the severity of test. The Polyurea and Calcium Sulphonate grease are also known for their high temperature performance, so the correlation with field conditions was still valid. However, this could be a future course of action for a study.

9.0 FIGURES



1 Control unit with digital clock
2 Electric motor
3 Base plate
4 Shaft with protective nylon coating
5 Eight polyamide housings
6 Distilled or demineralised water, salt water or synthetic sea water
7 Test bearing and teasting grease/oil

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Study of thermal and oxidation stability of various lubricating greases.

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ABSTRACT

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

Introduction

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

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

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

EXPERIMENTAL :

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

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

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

PROCEDURE :

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

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

Thermal Analysis (TGA) of Lubricating Greases – The sample preparation procedure is given below:

The instrument was calibrated with known standard before analysing the samples. Initially, tared the weight of blank ceramic cup followed by weighing about 40-60 mg of each of grease sample in the ceramic sample cup and placing it in a sample chamber in a furnace .The sample was heated at a heating rate of 10 ^{0}C / minute from 50 ^{0}C to 900 ^{0}C and the mass loss was recorded against temperature in the form of thermogram (TGA graph) of the sample. Any variation due to type of base oil (major constituent) used in the grease as well as soap structure is reflected in the inflexions / plateau in the thermogram. All the samples were subjected to analysis by adopting above procedure. Recorded simultaneously Differential Thermal Analysis **(DTA)** study of Lubricating Greases temperature was obtained in the form of DTA graph for each sample of lubricating grease under similar conditions.

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

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


Fig 1

Fig.2

Fig.1 shows Stainless Steel cylindrical pressure vessel in which a Stainless Steel rack with provision of grease sample taken in glass dish
The combined stack of grease-filled dishes are then inserted into a cylindrical pressure chamber and then placed on a stainless steel rotating base and entire vessel with rotating base inserted into the unit with sealing gasket which is bolted with three nuts
slowly so that no leakage is observed. The oxygen of purity 99.9% was introduced into the pressure chamber with pressure set at an initial pressure of around 95 - 100 pounds per square inch (PSI = 690 kPa) and room temperature which is then increased to 99 ±0.5°C. Under this increased temperature, the oxygen pressure is carefully released through a vent available in the unit to maintain pressure inside the chamber in running condition not more than 110 ±2 PSI). The unit was rotated at a standard rpm required for the test. The test continued for 100 hours . The pressure PSI at regular intervals of 12 hours were taken for study although the instrument has provision of continuously recording pressure change with time. After 100 hours completion of the test , the final pressure displayed was noted and pressure vessel was cooled to room temperature with rotation stopped with rotational controller in the unit and with the help of vent the oxygen was released from the pressure vessel. Nuts were opened and the pressure vessel with tray filled with grease was taken out. The grease after the test was drawn , collected and subjected to FTIR Spectral analysis. Repeated the procedure for each of the grease samples in a above similar conditions.

Fourier Transform Infrared Spectral Analysis of Lubricating Greases :

Infrared spectra of each of the samples before and after the oxidation test were recorded directly as such in Potassium Bromide cell windows in a IR Demountable cell.The instrumental conditions are spectral range 4000cm-1 to 400 cm-1, 32 number of scans and resolution of 4 cm-1. The changes if any in the IR Spectra fresh grease against grease after oxidation test will indicate oxidation resistivity/ stability of the lubricating greases .

Results and Discussions :

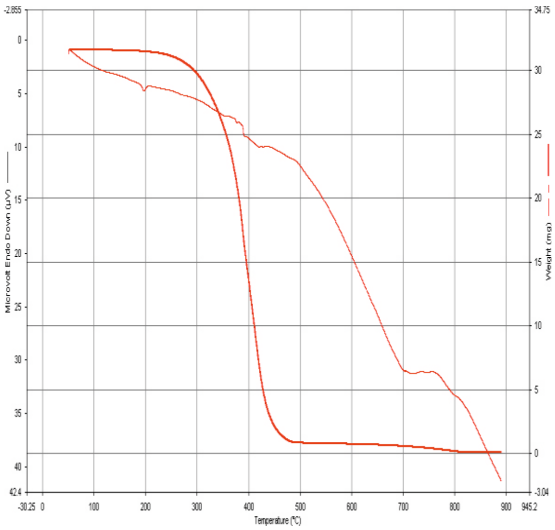
Dropping Point determination of Lubricating greases : Table 1 shows the results of dropping point of the greases under study as per standard test method ASTM D 566.

Table 1

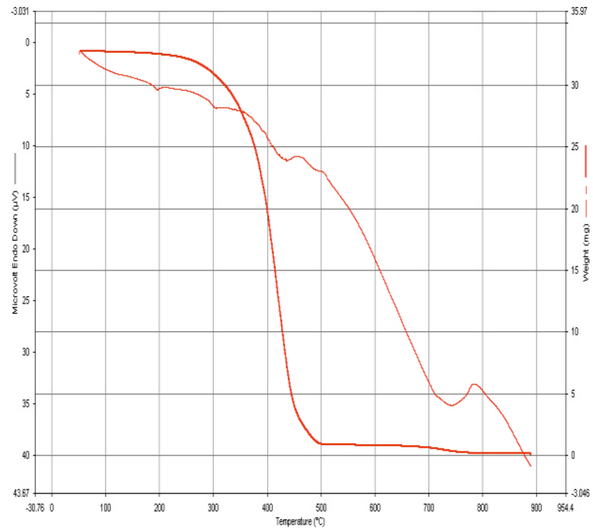
S.No.	Sample Description	Thickener type	Base Fluid	Drop point ^0C
1	A	Lithium	Mineral Oil	203
2	B	Lithium	Synthetic Base fluid	194
3	C	Lithium complex	Mineral Oil	245
4	D	Lithium complex	Synthetic Base fluid	265
5	E	Aluminium Complex	Mineral Oil	240
6	F	Aluminium Complex	Synthetic Base fluid	260
7	G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

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

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



A



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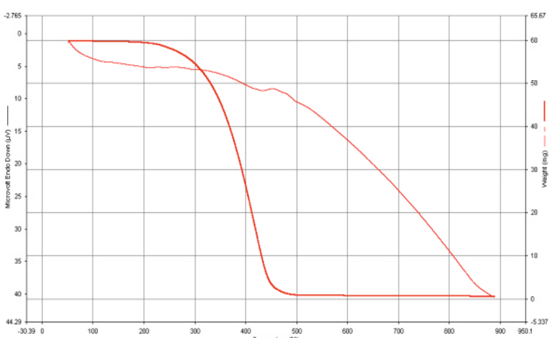

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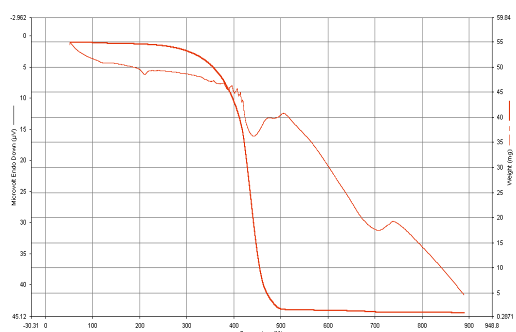

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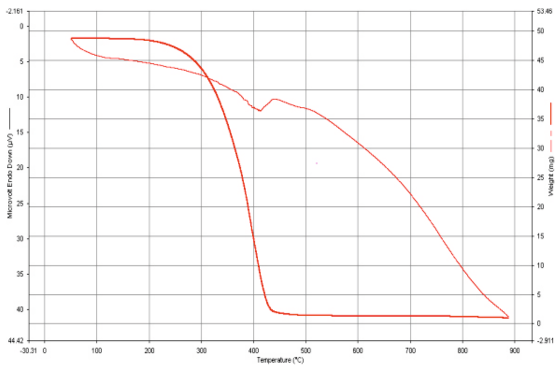

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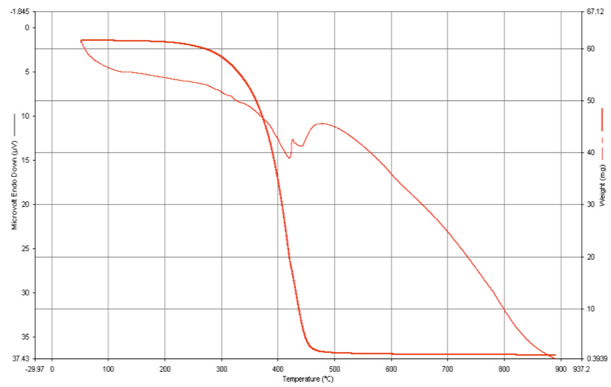

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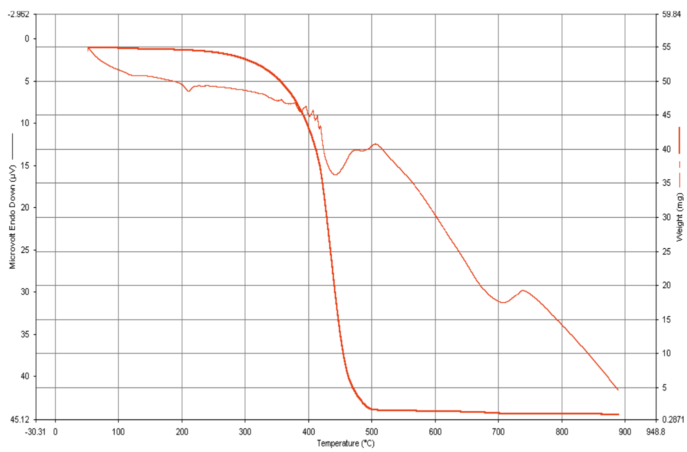


G

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

It was observed that the samples under study have shown two types of thermal decomposition pattern (Differential thermograms) when the sample is heated. Out of the samples analysed, Sample **‘B’** , Sample **‘D’** and Sample **‘F’** have indicated one particular type of thermal decomposition pattern with two inflexion points/humps at high temperatures (at around 430 ^{0}C and around 470 ^{0}C) (Figure 3 Thermogram **‘B’ , ‘D’ & ‘F’**). All the remaining lubricating grease samples **‘A’, ‘C`, ‘E’** have shown conventional type of decomposition pattern with single peak at 420 deg.C.
Sample ‘G’ having have shown different thermal degradation behavior although grease is b mineral oil based . This may be attributed to type of thickener used.
This difference is mainly attributed due to different thermal degradation of base oil being used .The synthetic base oil shows higher thermal stability behavior as
compared to conventional mineral oil based as Sample **‘B’ ‘D’, ‘F’** uses superior synthetic base oils with better thermal stability .

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

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

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

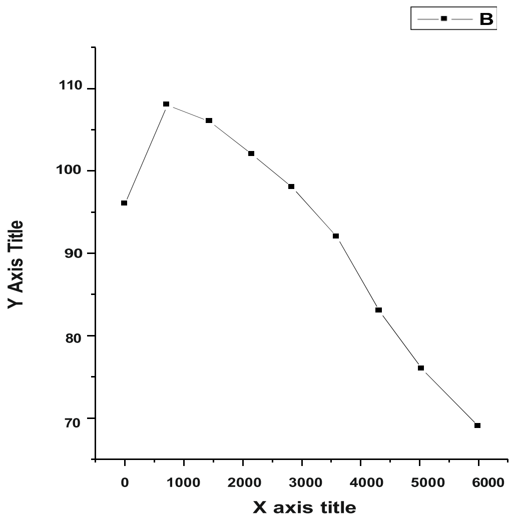
Table 2 shows the recorded pressure in PSI of oxidation chamber at mentioned regular time intervals of lubricating greases being tested by RBOT Test . Initial pressure of oxidation chamber of all the lubricating greases under study was around 96 PSI

Table 2

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

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

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



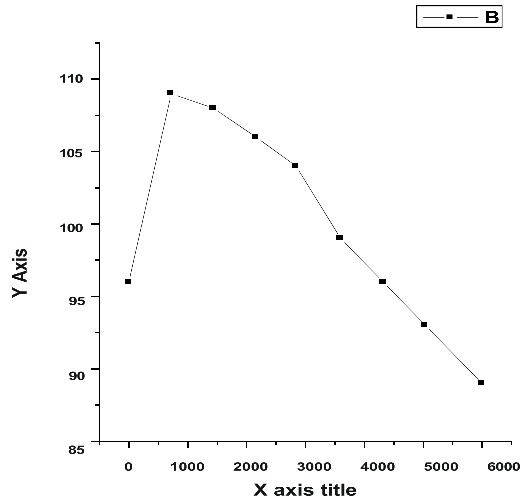


Figure 4 Sample A

Figure 5 Sample G

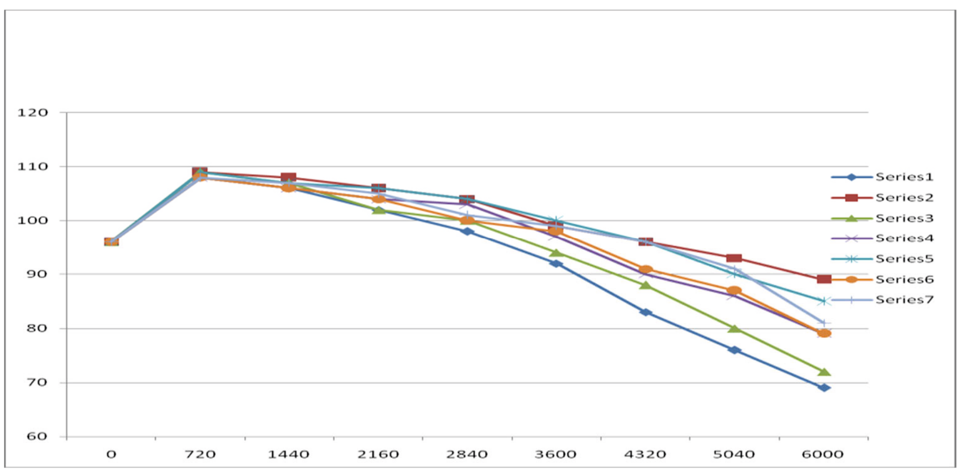


Figure 6 Oxidation Chamber Pressure PSI Vs Time Duration in minutes

Fourier Transform Infrared Spectral Analysis of Lubricating Greases :

Infrared spectra of each of the samples before and after the oxidation test were recorded directly as such in Potassium Bromide cell windows in a IR Demountable cell and compared for any spectral changes .

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

Table 3

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

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

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

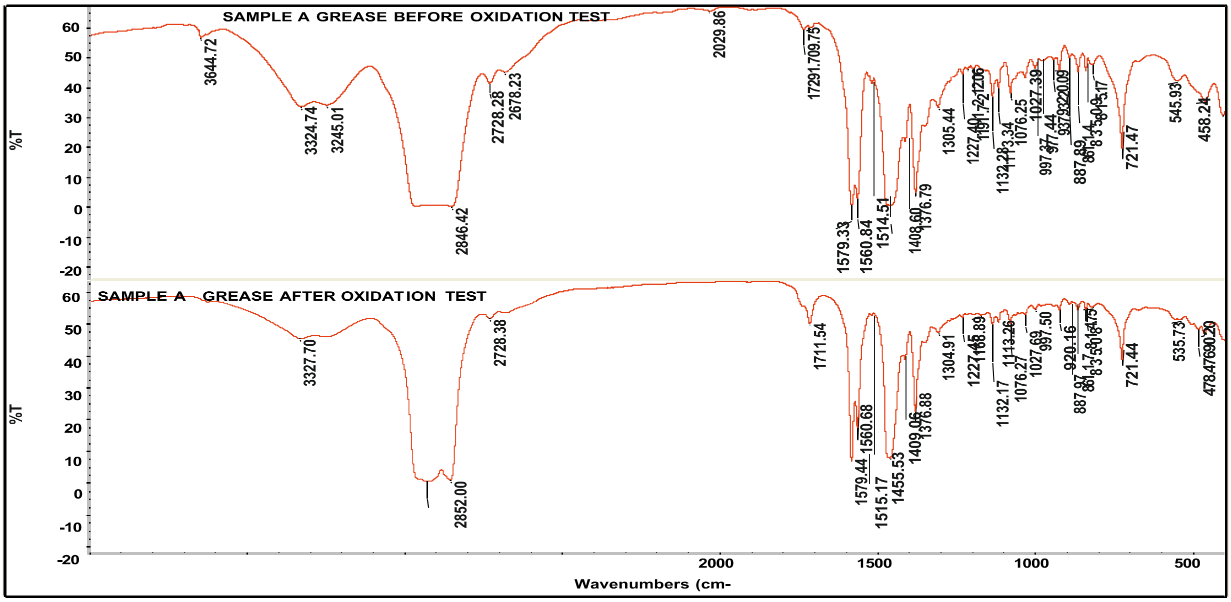


Figure 7 IR Spectral comparison of Sample A before and After Oxidation Test

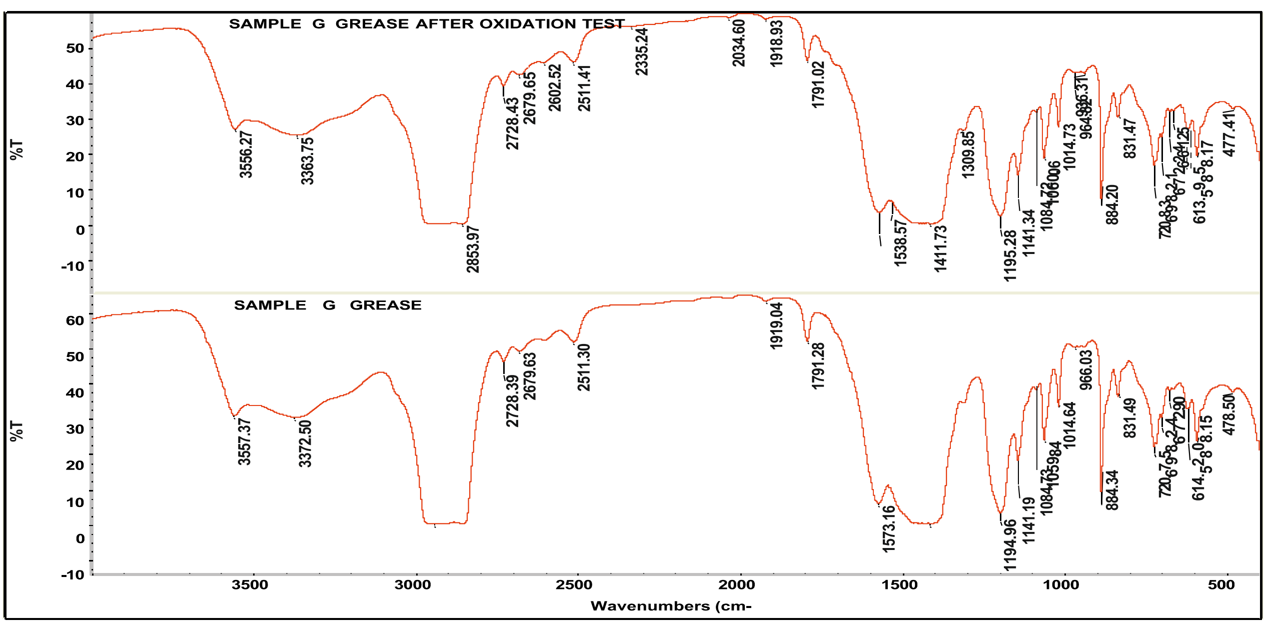


Figure 8 IR Spectral comparison of Sample G before and After Oxidation Test

Conclusions :

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

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

Thermogram (TGA) and its differential thermogram (DTA) of each of the lubricating greases were recorded and analyzed for their thermal degradation behavior pattern. Sample **'B'** , Sample **'D'** and Sample **'F'** have indicated one particular type of thermal decomposition pattern with two inflexion points/humps at high temperatures (at around 430 ^{0}C and around 470 ^{0}C) (Figure 3 Thermogram **'B' , 'D' & 'F'**). All the remaining lubricating grease samples **'A', 'C`, 'E'** have shown conventional type of decomposition pattern with single peak at 420 deg.C.

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

This difference is mainly attributed due to different thermal degradation of base oil being used .The synthetic base oil shows higher thermal stability behavior as compared conventional mineral oil based as Sample **'B' 'D', 'F'** uses superior synthetic base oils with better thermal stability . Sample 'G' which is high temperature grease with different type complex thickener based has shown hump with no clear thickener peak.

Oxidation Stability Test of lubricating greases under study by (RBOT) indicated that sample **'A'** has shown lowest pressure PSI after 100 hours test and sample **'G'** being highest among the lubricating greases under study which indicates that oxidation stability of Lubricating grease **'A'** is lowest and highest for sample 'G' . Among the four lithium based lubricating greases **'A', 'B', 'C'& 'D'** ,Lithium complex greases **'C' and 'D'** have better oxidation stability than simple lithium based lubricating greases . As expected, among the lubricating greases under study , greases based on synthetic base fluid **'B' ,'D' and 'F'** have better oxidation stability than the greases based on Mineral oil origin **'A', 'C' and 'E'**

Infrared spectra of each of the samples before and after the oxidation test were recorded and compared for any IR spectral changes. The base oil in the lubricating greases is prone for oxidation of hydrocarbon with formation of carboxylic acid indicated by the presence peak at 1710 cm-1. The intensity of this characteristic peaks indicative of oxidation stability of the grease .Higher the intensity less the oxidation stability of lubricating grease and vice versa.

It was observed that sample **'A'** has shown strong oxidation whereas sample 'G' has shown the least among the lubricating greases under study.

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

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Development of Cheminformatics Software for Evaluating Biodegradability of Lubricants and Greases

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Abstract

Biodegradation and green chemistry are increasingly becoming relevant today. This is reflected in changing regulatory frameworks as well as an increasing awareness of social responsibility by chemists. Thus one of the most pertinent challenges today is to develop formulations that meet these environmental expectations. To reduce cost of screening potential formulations, cheminformatics is a promising new aid and is increasingly being used by several industries. The possibility of creating and utilising the same to estimate the biodegradability of greases as per ISO 7827 test standards is explored herein.
The software is a simulation process consisting of a compilation of relevant information (microbial compositions of the medium as specified by the CEC standard and the general production amounts of biodegrading enzyme and the kinetics of these microbes). The programme calculates the possibility of using various chemicals in a formulation as substrates for microbial degradation, taking InChI codes as input. This is done by identification and categorisation of functional groups and bonds followed by accessing enzyme information to calculate the probable biodegradability of the molecule at the end of 28 simulated days or with 99% biodegradation (whichever is earlier).

Introduction:

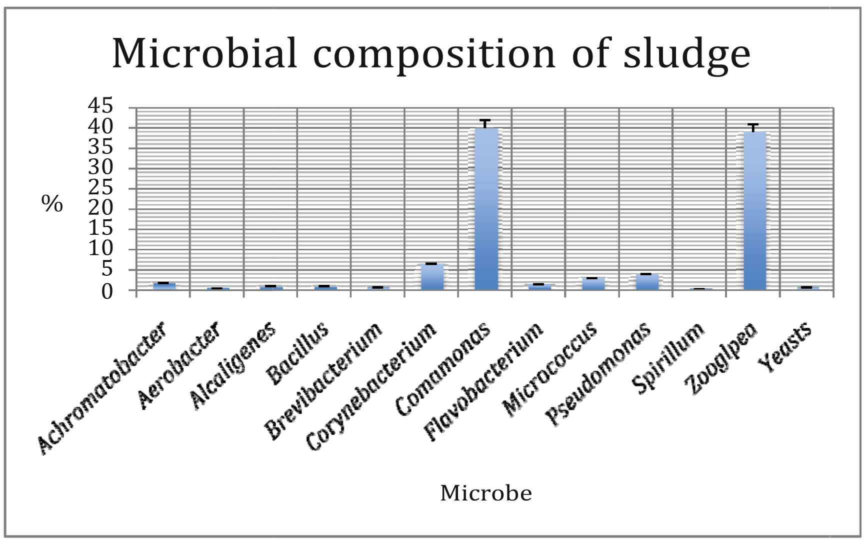
Cheminformatics and computational chemistry can extensively be used to simulate chemical reactions and processes, and aid viability studies before going on to resource intensive laboratory research. This makes it increasingly relevant in screening tests before embarking on expensive developmental experiments[1]. Among various applications of computational tools, this paper outlines an attempt to create a simulated study of biodegradation as per the International Standards Organisation (ISO) 7827 standards[2]. Briefly, the procedure outlined by these standards is as follows: 1 ml of inoculum extracted from activated sludge (municipal sewage) with 10^5-10^7 colony forming units is added to a mineral medium containing the test solution. The biodegradation may be evaluated in terms of dissolved organic carbon (DOC) at the end of 28 days.
To simulate the above test, the chemical and biochemical processes were enumerated, reviewed and modelled. The software, in its entirety will be made available for download after complete debugging as an executable file on http://sarbilabs.in.

Biological background of microbial degradation:

Biodegradability is caused primarily by microbes, though plants and larger animals contribute to a smaller extent. Dumping grounds and waste areas are breeding grounds for these microorganisms, as many of the dumped and discarded wastes are ric in nutrients[3]. To make use of these nutrients, microbes need to secrete enzymes and other secondary metabolites to degrade or otherwise make these chemicals available in a consumable form[4]. The kinetics as well as properties of the enzyme varies between strains of microorganisms as well as species [5].

To simulate a particular process (here biodegradation under standardised conditions), the composition of the inoculum and the identification of enzymes and their properties needed to be undertaken. The microbial composition of activated sludge presented below has been taken from the study conducted by Dias and Bhat[6].

Figure 1: Microbial composition of sludge. *Results are expressed as percentage ofpositive isolates from 7 sludge samples.



The typical enzymes produced by organisms commonly found in sludge and their function is summarised below[7-9]:activated

Enzyme	Function
Peptidase	Breakdown of peptide linkage
Esterase	Breakdown of ester bond
Phosphatase	Removal of phosphate groups
Lipase	Lipolyis
Amylase	Breakdown of glycosidic linkages
Glucosidase	Cleavage of glycosyl residues
Alkyl hydroxylase	Breakdown of hydrocarbons

Table 1: Functions of major enzymes in biodegradation

The averaged values of the kinetic parameters have not been included as they constantly change as the database is continuously updated.

Modelling and simulation:

On the basis of a literature survey, the microbes found in activated sludge were identified and the enzymes commonly produced by these microbes were listed along with enzyme activity in terms of units and kinetic parameters (this list is being constantly updated). It was assumed that perfect reaction conditions were never present and that the velocity of reaction (V) was taken randomly between $0.65V_{max}$ to $0.75V_{max}$ over 28 simulated days.

Chemical constituents were run through this database to estimate biodegradation by matching functional groups with enzyme function. The maximum and minimum biodegradation value was selected to estimate the biodegradation range for the selected substrate.

To begin the simulation, an input of any organic chemical was taken in the form of an InChI code [11] (an attempt to adapt the program to read Markush structures for more generalised analysis is the next step). Due to the variation of mineral base oils, an idealised base oil was generated with two InChI code inputs: 1S/C6H6/c1-2-4-6-5-3-1/h1-6H (benzene at 10%) and 1S/C12H26/c1- 3-5-7-9-11-12-10-8-6-4-2/h3-12H2,1-2H3 (dodecane at 90%). For other molecules, their actual InChI codes were searched online. The additive package was ignored due to its insignificant amount, variability and complexity. A screenshot from the program running the dodecane structure on QBASIC is given in Figure 2(a). Figure 2(b) shows the result of the simulated biodegradation,taking one only one set of parameters into consideration.

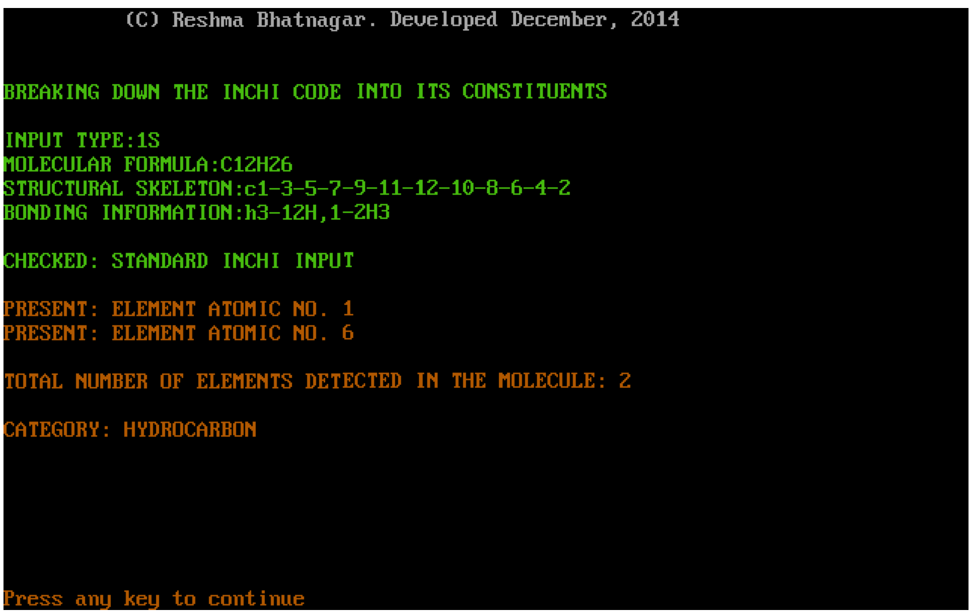


Figure 2(a) Analysing the InChI code in QBASIC

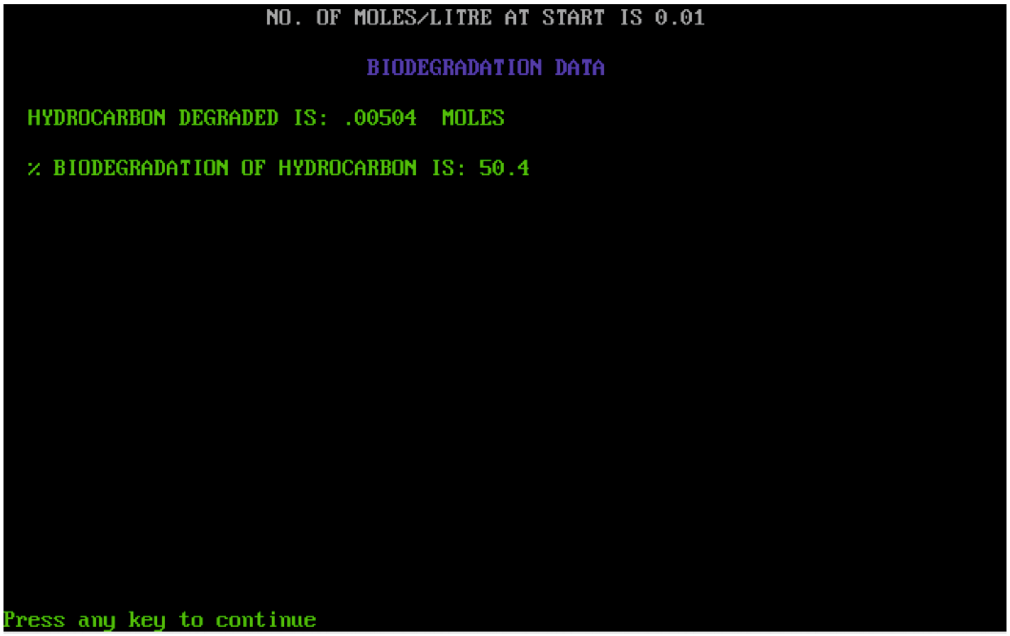


Figure 2(b) Determining biodegradation of InChI data in QBASIC.

The molecular characteristics viz. the chemical formula, structure, bonding and functional groups were extracted from the code as follows:

1. The positions of the forward stroke divisions were stored to break down the InChI into its layers.
2. From the main layer, the number and varieties of elements were found.
3. The structural skeleton was parsed by assigning the highest number to the non-carbon element with the highest atomic number.
4. Cyclicity and aromaticity was determined by identifying overlapping normalised numbers from the extracted skeleton.
5. Saturation and further structural characteristics were determined by taking into account the hydrogen atoms sub-layer.
6. From the structural data, relevant functional groups were identified.

The first enzyme of the database was then compared with the functional group/bond data in conjunction with other extracted information. If the functional group/bond was found to be susceptible to the enzyme, the biodegradation would be evaluated from kinetic parameters for 28 days or until 99% was reached.

Results:

A test simulation for a synthetic and mineral oil based grease formulation was run on a laptop running OS X 10.9.2 on a 2.5 GHz i5 processor with 4GB RAM on Matlab and QBASIC.

The mineral oil based grease showed a total degradation of a mean value of 50% with standard deviation of 9, sample size 9 represented in Figure 3(a), failing the test criteria, while the vegetable oil based grease showed 96% mean biodegradation with a standard deviation of 3% as seen in Figure 3(b), passingthe test. The sample size for the latter was 9 as well.

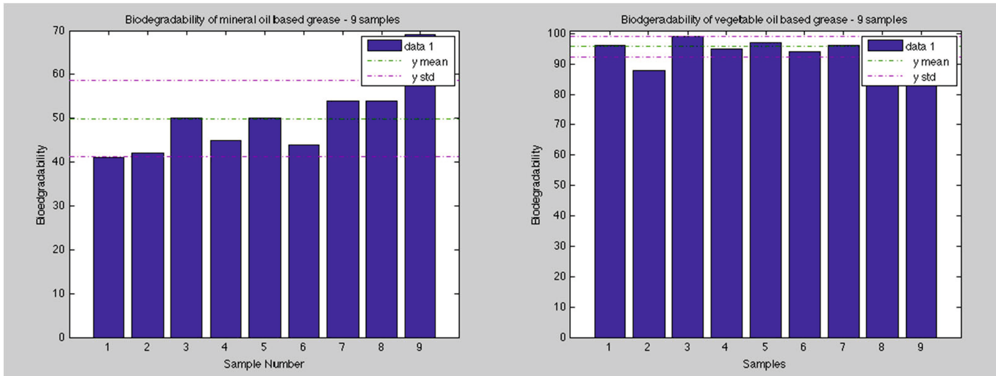


Figure 3(a) (left) biodegradability of mineral oil based grease, (b) (right)biodegradability of vegetable oil grease generated using Matlab

The computed biodegradation of individual grease components is tabulated below.

Lithiumgrease with mineral base oil:		Total degradation = 41 - 69%
Name	Amount	Biodegradation
Base oil	88%	30-65%
Lithium Soap	11.5%	90-99%
Additives*	0.5%	-

Sodium grease with palm oil base:		Total degradation=88 - 99%
Name	Amount	Biodegradation
Base oil (palm)	88%	90-99%
Sodium soap	11.5%	90-99%
Additive*	0.5%	-

Table 2: Calculated biodegradability at the end of 28 days. Biodegradation is represented in terms of percentage derived from a range of kinetic parameters of enzymes accessed randomly. *The biodegradability of additives was not estimated.

Discussion:

The model is currently a preliminary one and is very dependent upon the enzyme database generated manually on the basis of a literature survey, rather than experiment. Hence errors or variation may be to an extent, a result of this.Indeed, a large variation in biodegradation ranges is seen, especially in the lithium mineral oil based grease with degradation ranging from 54 – 7% over 28 days. Considering that the base oil has been hypothetically standardised, the variation can be attributed to the vast difference in degradation kinetics of various microbes. Accuracy in biodegradation estimates may be improved with respect to local laboratory readings if kinetic parameters in the program areoverwritten by experimental determination of the same using local sludge cultures. That said, the variation here does reflect real-world variation and seems to coincide with biodegradability values of these substrates in literature [12][13].

To obtain more accurate results, the database can be optimised and improved upon by collecting more data on the enzymes to obtain better statistical value, use of machine learning algorithms for optimisation and selection of kinetic parameters and by making more realistic predictions by using specific 3D structure docking.
To increase accuracy, the database is indeed being constantly updated. Artifical intelligence algorithms will become relevant and added to the current version once more parameters, coupled with real experimental data are collected. However, at the moment, future upgrades to enzyme docking have not been considered due to the computationally intensive nature of 3D protein modelling and docking. While open 3D protein structure prediction tools are extensively available online, due to the aim of creating an independent simulation software.
Due to simplifying assumptions, there are certain limitations of the software: A major limitation is that the simulation takes each chemical individually, and not the formulation as a whole. While this may give relatively accurate information on biodegradation of the constituents of various substances, it does not take into consideration the interaction of materials within the blend and the environment. For example, there may be materials and products formulated such that one material may be enveloped in another, making it inaccessible to degrading enzymes, hence leading to inaccuracies.
Another limitation is the need to input specific layered InChI codes for bond identification, a difficult task due to the variability of possible input compositions, such as base oil from mineral sources. While it is unlikely that there should be major variation in degradation of a similar class of molecules, and hypothetical InChI may be generated, taking as input a generalised hydrocarbon would probably be more convenient.

That said, the biodegradation software is very versatile and can be used for estimating biodegradation of virtually all compounds under these standards. Indeed, by changing, modifying or replacing the enzyme database, many other processes can be modelled or simulated. It is fast, costs little, and can be optimised by the user to obtain more accurate results by updating the database. In its current version, the software can give a fair (though not conclusive) idea of biodegradation.

Conclusion:

While cheminformatics is a promising tool for screening initial formulations, it needs to be followed up by validation and confirmation and is not a substitute for experiment. That said, computational modelling alongside informatics strategies can produce promisingly accurate results that can be used to predict desired properties (here biodegradation) at virtually no cost.

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