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# DEVELOPMENT OF A BENCH TEST METHODOLOGY FOR PERFORMANCE EVALUATION OF ENERGY EFFICIENT INDUSTRIAL GEAR OILS

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**1.0 ABSTRACT:** Trends in performance evaluation indicate a shift to short duration simulated bench tests rather than running long short duration accelerated trials for assessing the performance of the lubricants. Following this trend, a laboratory test methodology using a set of bench test rigs for evaluation of various properties required for an energy efficient gear oils has been developed. This test methodology using simulated gear contacts working under various regimes of lubrication requires us to run short duration inexpensive tests and can be carried out under controlled conditions for a high degree of accuracy. This paper gives details of the test method and test results obtained with some industrial gear oils with proven field performance using laboratory bench tests like Optical Interferometry for film thickness and traction coefficient, SRV for boundary friction coefficient and Block on Ring test machine for simulated gear contact performance evaluation. The test results were validated using a FZG Gear Test modified for Efficiency studies.

**2.0 INTRODUCTION:** There is an enormous amount of interest in saving energy in the current age looking to the depletion of fossil fuels and the time to develop potential of alternative energy sources. The maxim behind this is "**Energy Saved is Energy Generated**". This is true for almost all the energy intensive equipments (Automotive as well as industrial), and efforts are on to redesign the lubricant using the viscosity modification as well as additive approach. Generally for industrial gear applications, use of gear oils formulated with friction modifiers has been generally the main approach followed by most of the lubricant majors. Although a number of laboratory bench scale test methods are available for evaluating the various load carrying parameters of lubricants, reliable methods for prediction the energy efficiency characteristics are rather limited with respect to the laboratory and field data correlation. Attempts have been made by many researchers to establish test methods for the evaluation of energy efficiency characteristics of gear oils **[1-3].** Among these, ASTM axle efficiency rest **[2]** for energy efficient automotive gear oils and CEC ECOTRONS test method **[4]** are in the process of adoption for the evaluation of EE characteristics. The ASTM test however is very cumbersome and expensive and not many laboratories can acquire it. Besides, it is not possible to get a complete assessment of the performance using a single test method, so a combination of test methods in form of a test methodology is being used for the development of an energy efficient industrial and automotive gear oils. The basic requirements of the methodology are to use reliable, simple and accurate laboratory methods which could assess the various aspects of the energy efficiency characteristics quickly. The present work describes the various evaluations carried out in the development of this laboratory test methodology.

**3.0 BASIS OF TEST METHODOLOGY:** In general, gear contacts work under the boundary and EHD lubrication regimes. It is therefore, important to assess the gear lubricants to predict the overall effect under these regimes on the gear efficiency. So it was decided to follow a step wise approach to first assess the lubricants under different regimes of lubrication using different gear oils formulated and with known performance. Various laboratory bench tests viz. The SRV friction and wear test **[6]** to assess the frictional characteristics, EHL Ultra thin Film measurement system for the mapping of the oil film thickness over a wide speed range from 20 mm/sec to 4 metres/sec by optical interferometry **[7]** and the traction performance under simulated slide roll ratio as experienced in a gear contact, and the Block on Ring test **[8]** machine for measurement of boundary friction and the temperature rise in a simulated gear contact were used for assessing the factors responsible for the Energy efficiency. Finally a gear box properly instrumented to precisely control the test parameters using the popular FZG gear test machine was selected to validate the results since it was best suited for this purpose.

**4.0 DESCRIPTION OF TEST EQUIPMENTS :**

1. **EHL Ultra Thin Film Measurement System** is a computer-controlled instrument for measuring the film thickness and traction coefficient (friction coefficient) of lubricants in the elastohydrodynamic (EHL) lubricating regime. It is as shown in **Figure 1(General schematic)**, **Figure 2(Film thickness)** and **Figure 3(Traction).** In the Film thickness mode,the instrument can measure lubricant film thickness down to 1 nm (1 millionth of a millimeter) with a precision of +/- 1 nm. In the traction mode, the Traction coefficient can be measured at any slide/roll ratio from pure rolling up to 100% sliding. The instrument measures these lubricant properties in the contact formed between a steel ball and a rotating glass or steel disk. The contact pressures and shear rates in this contact can be maintained close to those experienced by the oil in gear boxes. The EHL system measures film thickness and traction coefficient in the EHL contact formed between a 3/4 inch steel ball and a rotating 100 mm diameter disc. For film thickness measurements, the disc is made from glass and has a chromium and silica coating on the working face. For traction measurements, the disc is made from polished bearing steel. The ball is mechanically loaded against the underside of the disc and can be allowed to rotate freely or can be driven to induce sliding between the ball and disc. The load is controlled automatically and is variable between 0 and 30 N. This gives maximum contact pressures between the ball and disc of up to approximately 1.1 GPa with a steel disc and 0.7 GPa with a glass disc.

   The ball and disc are independently driven by DC servomotors. With standard gearing, the maximum rolling speed is 4 m/s and the minimum rolling speed is 25 mm/s. The ball can be allowed to idle freely in nominal pure rolling, or a drilled ball and drive shaft can be fitted. The ball can then be driven at any desired slide/roll ratio, the required ball and disc speeds being determined automatically by the control software. The traction force is measured by a high sensitivity torque transducer between the ball motor and the ball. The oil sample to be tested is contained in a reservoir constructed from a single stainless steel block. Heaters are fitted to allow measurements at temperatures from ambient up to 150°C; however our tests were carried out at test temperatures of $60^{0}$C representative of the temperatures experienced in an industrial gear box.

   The lubricant film thickness is measured by optical interferometry. The contact is illuminated by a white light source directed down a microscope through the glass disc onto the contact. Part of the light is reflected from the chrome layer on the disc and part travels through the silica layer and any fluid film and is reflected back from the steel ball. The recombining light paths form an interference image which is passed into a spectrometer and then into a high resolution CCD camera. The camera image is captured by a video frame grabber and analyzed by the control software to determine film thickness. The thin film software takes data from the spectrometer, determines the wavelength of maximum constructive interference and hence the lubricant film thickness.

   The traction software allows the user to select rolling speeds and slide/ roll ratios and logs data from the ball torque and load transducers and calculates the resulting traction coefficient. These values are measured and stored in the PC using a data acquisition system.

2. **Falex Block on Ring test rig** is used to simulate the gear contact (line) under boundary regimes. It is mainly used for the friction reduction capabilities of the gear oils chosen for the study. The machine consists of a variable speed motor which drives a shaft on which a ring is rotated, against which a stationary rectangular test block is loaded. The schematic is shown in **Fig. 4**. The Ring and block are made up of Standard Hardened Gear Material. The test block, which is held stationary against the revolving ring, is restrained from horizontal movement. The load is accurately maintained throughout the test, using a loading lever on which a load cell is mounted to measure the resulting friction between the block and ring. The oil is kept in a standard enclosed test chamber and is carried by the rotating ring to the zone of contact. As a result of the frictional heating the temperature rises,

and is measured during the test. Higher is the temperature, higher is the friction coefficient, and lower is the expected energy efficiency.

3. **SRV friction and wear test** is used to measure the boundary frictional characteristics of the oils in a point contact configuration as shown in **Figs. 5 & 6**. A steel ball of 10 mm diameter made of bearing steel (100MnCr5) is oscillated against a flat steel disc under 200 N load, 1 mm amplitude of oscillation at 50 Hz frequency, and the temperature of the oil is kept at $50^0$C. The friction is being measured over a test duration of 1 hour, and recorded on the computer..

4. **FZG Test Rig:** The principle of power circulation of FZG test rig is favourable for the measurement of friction losses, since by construction, the electric motor overcomes the losses. The power consumed by the motor is the sum of: (a) The internal losses of the motor and the friction losses in the coupling etc.(which can be reasonably taken as constant) (b) The frictional losses between gear teeth and the bearings of the machine(which is affected by oil formulation). Thus the effect of the oil on friction losses can be evaluated by the measurement of electric power **[4]**. It avoids the more delicate and cumbersome task of measuring torques of rotating shafts. This can precisely distinguish the narrow differences in energy consumed with two oils.
   The principle of the test is to measure the electric power consumption using a precise microprocessor controlled energy meter at three standard FZG test load stages (4, 6 and 8) at speeds of 1500 rpm maintaining the oil at a constant oil temperature of $80^0$C (using heating coils and cooling water) for a running period of 1 hour at each load stage. The test condition enabled us to assess the effect of both friction modifier (boundary) and viscosity (hydrodynamic) effect for the automotive gear oils. A schematic of the test setup is given at **Fig.7.**

   Studies were conducted on five different oils **(Table 1)** taking a VG320 Mineral oil (**Oil A**) as the baseline and comparing two fully synthetic VG 220 oils **Oil B and Oil C**, as well as two VG320 semi synthetic and Friction modified oils (**Oils D, E,**) with it. The film thickness mapping at 20Nload (0.48 GPa contact pressure), $60^0$C, and speed ranging from 20 mm/sec to 4 metres per sec was done for assessment of film thickness as shown in **Fig. 8**. The SRV friction studies in an oscillating sliding contact at 200N load, 50 deg C, 50 Hz, 1 mm for 1 hour are shown at **Fig. 9**. The Traction data at 30N load, speeds ranging from 20 mm/sec to 4 metres per second at 30% Slide Roll ratio corresponding to a spur gear meshing is shown in **Fig. 12**. The Block on Ring Frictional performance in terms of oil temperature rise and the frictional coefficient is shown in **Figs 10 & 11**, and the reduction in Energy consumed in FZG gear test (in %) shown at **Fig 13**.

## 5.0 TEST OBSERVATIONS & DISCUSSIONS:

From the bench tests as shown in the results and figures, we have the following observations that can be made regarding the oil performance.

(1) The Film thickness and Traction coefficient trends match with each other, this is due to lower pressure viscosity coefficient for the synthetic oils, and intermediate values for the semi-synthetic oils as compared to the mineral oils. This is indicative that the Synthetic oils will experience lower viscous drag and be energy efficient as compared to the other oils in the EHD regime prevalent in the PCD Zone.

(2) The Boundary Friction studies using the SRV and the simulated gear contact using the block on ring test machine following the same trends. Here the two friction modified oils D & E have the lowest temperature rise as well as the friction coefficient. The synthetic oils B and C do not have a friction modification so the friction coefficient with these oils are the highest. The friction coefficient for the Mineral Oil VG 320 based Oil A is intermediate to the Oils D& E and Oil B&C.

(3) From **1 & 2** above, it is expected that a combined effect of the viscous friction and boundary friction will determine the end performance of the oil in a gear contact

(4) Oils D & E being both semi-synthetic and friction modified when subjected to the FZG gear efficiency

test where the combined effect of Viscous friction and the Boundary friction is taken into account show the lowest energy consumption as compared to VG 320 oils. In case of the gear contacts, which works under Boundary, mixed and EHD regimes of lubrication (where the films are thin and nearing the surface roughness of the contact surfaces), the friction modification thus determines the overall efficiency of the equipment. Due to this the Oils D& E despite being inferior to Synthetic oils B&C in terms of viscous friction, exhibit higher energy efficiency, due to the predominant boundary effect in the gear contacts.

## 6.0 CONCLUSIONS:

(1) Gear Lubricants work under different regimes of lubrication, and using a Tribotesting methodology for the study of these can enable us to understand and work towards the energy efficiency using lubricants.

(2) Simulated testing using the SRV Test rig and the Block on Ring test rig for the Boundary regime efficiency and the EHD film thickness and Traction studies for the contribution of the viscous friction towards the fluid film energy efficiency can offer good insight and enable development of lubricants.

(3) The above combination of the Tribotesting techniques can enable development of gear lubricants with high energy efficiency without the need for expensive field trials.

(4) Maximization of energy efficiency is possible by using combined approach of viscosity optimization (to reduce the losses due to viscous drag) and Friction modifiers (boundary friction effects).

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7. http://www.pcs-instruments.com/ehl/ehl.shtml, EHL Ultra Thin film measurement system.
8. http://www.falex.com/pdf/FalexBlockRing.pdf Falex Block on Ring test system



**KEYWORDS:** Friction:Energy Conservation, Additives:Friction Modifiers, Lubricants:Gear Lubricants.


## 8.0 TABLES AND FIGURES:

**TABLE 1:**

| Sr No | Oil | Type | Viscosity Grade |
|---|---|---|---|
| 1 | A | Mineral | VG 320 |
| 2 | B | Synthetic | VG 220 |
| 3 | C | Synthetic | VG220 |
| 4 | D | Part Synthetic | VG320 |
| 5 | E | Part Synthetic | VG320 |

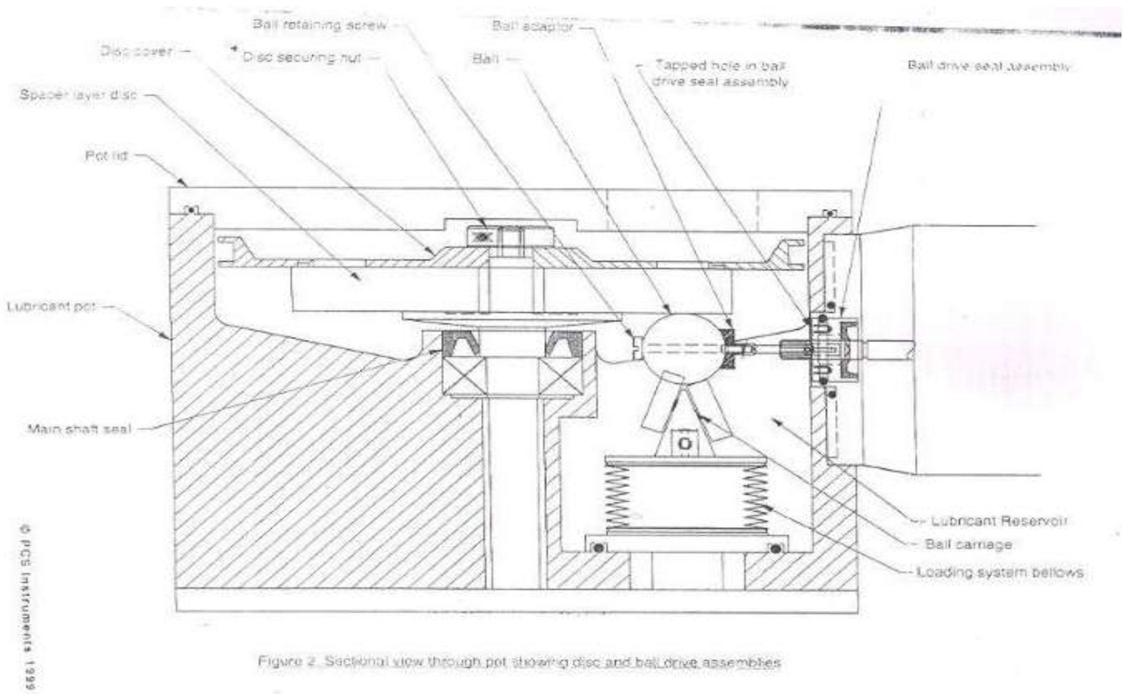


**Fig 1: Film Thickness and Traction Rig Assembly**

**Fig 2: Optical Film Thickness apparatus**

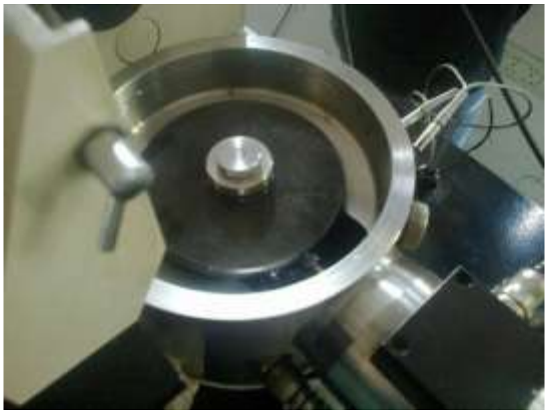

**Fig 3: Traction Test apparatus (Steel on Steel)**

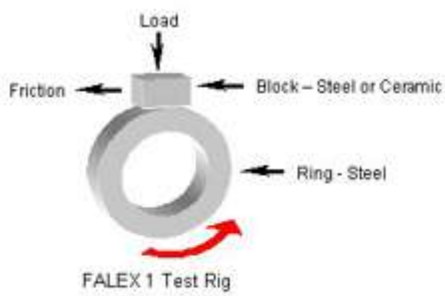


**Fig 4: Falex Block on Ring test rig**

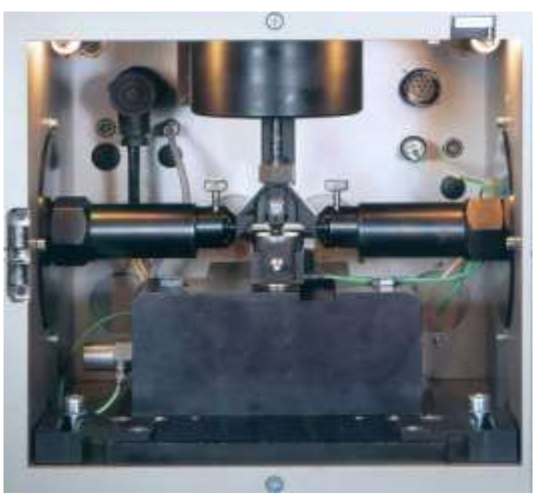

**Fig 5: SRV Test machine (Ball on Flat Disc)**

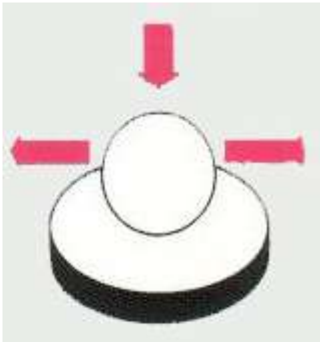

**Fig 6: SRV Test configuration**

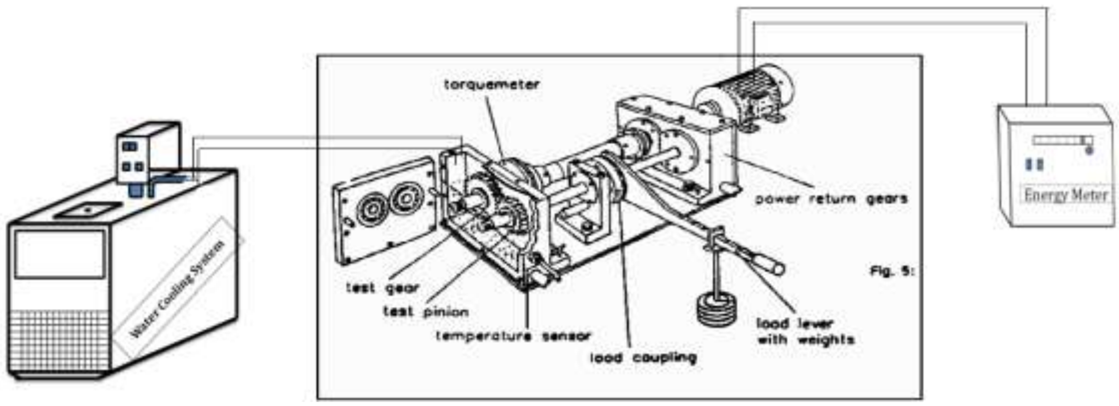


**Fig 7: Modified FZG Test schematic**

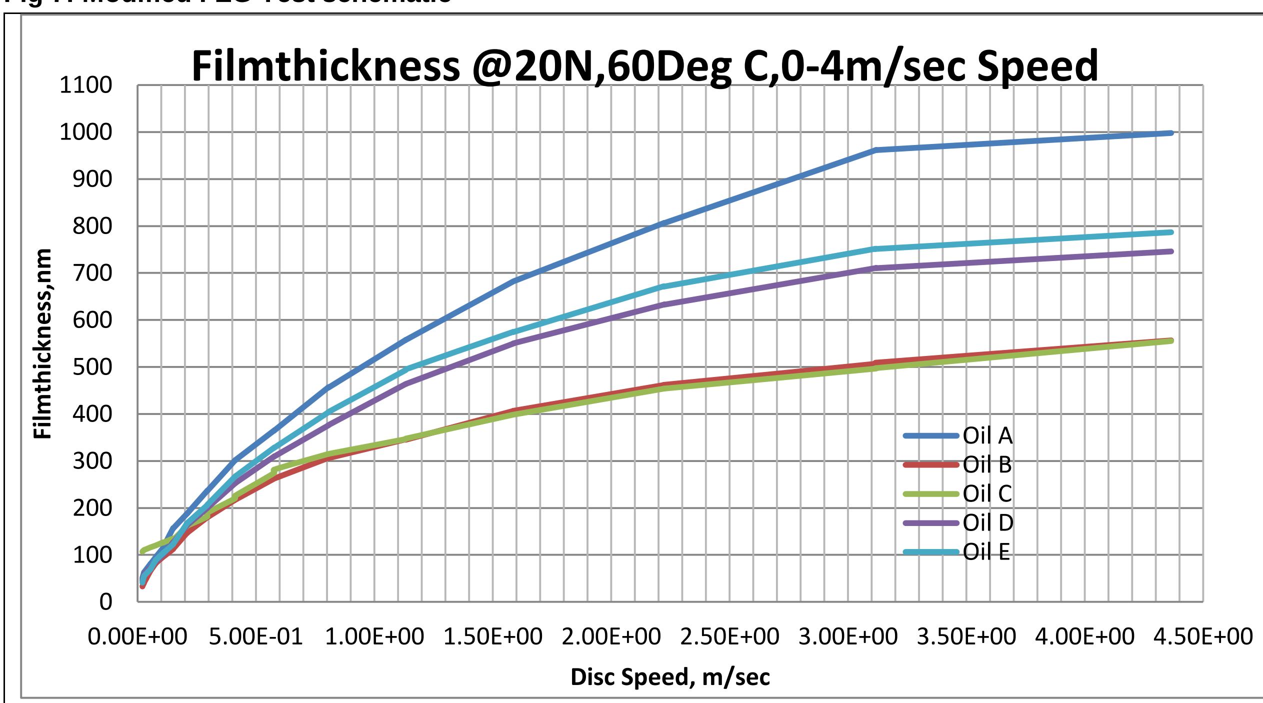


**Fig 8: Film thickness data by Optical Interferometry**

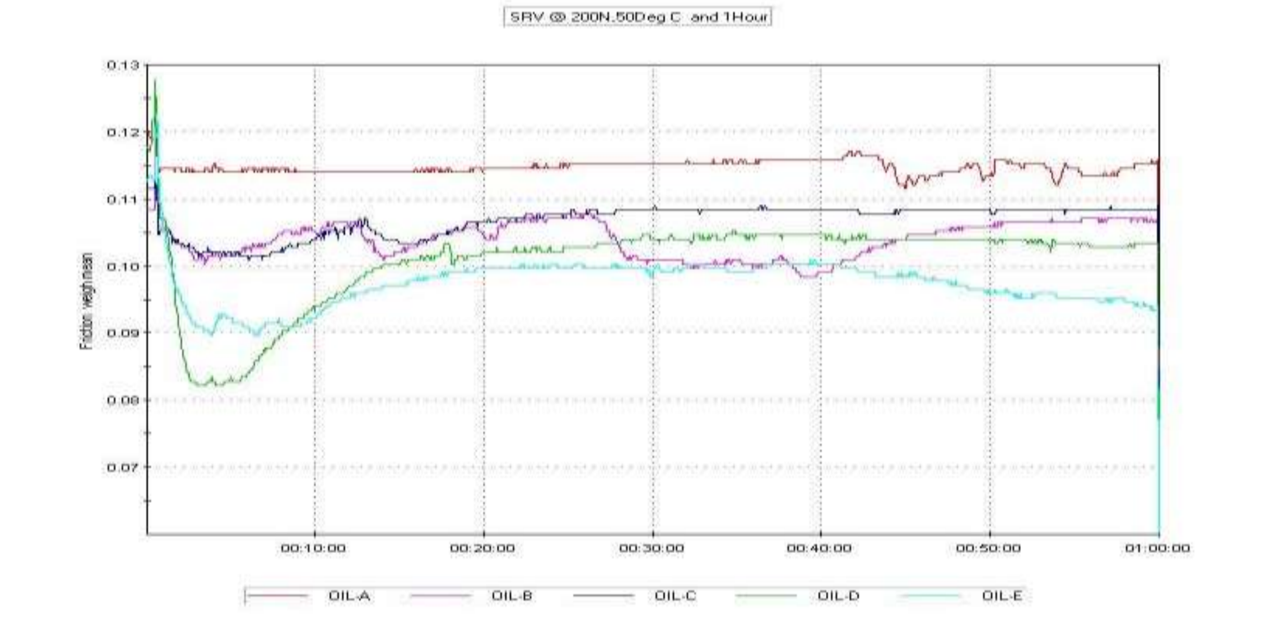


Fig 9: SRV Frictional studies

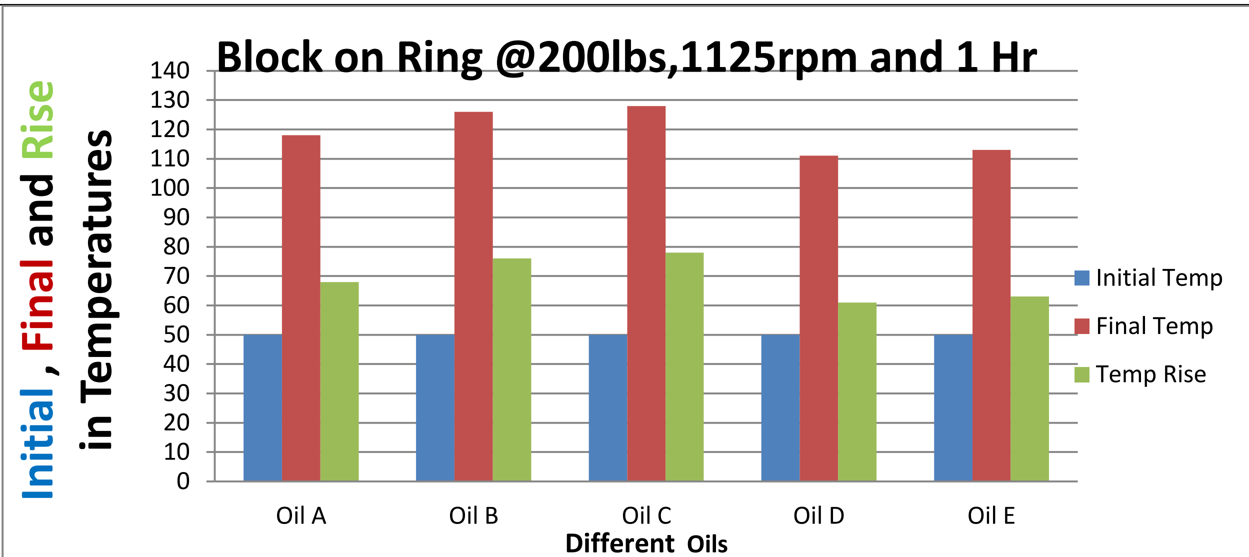


Fig 10: Block on Ring Test Gear Simulation

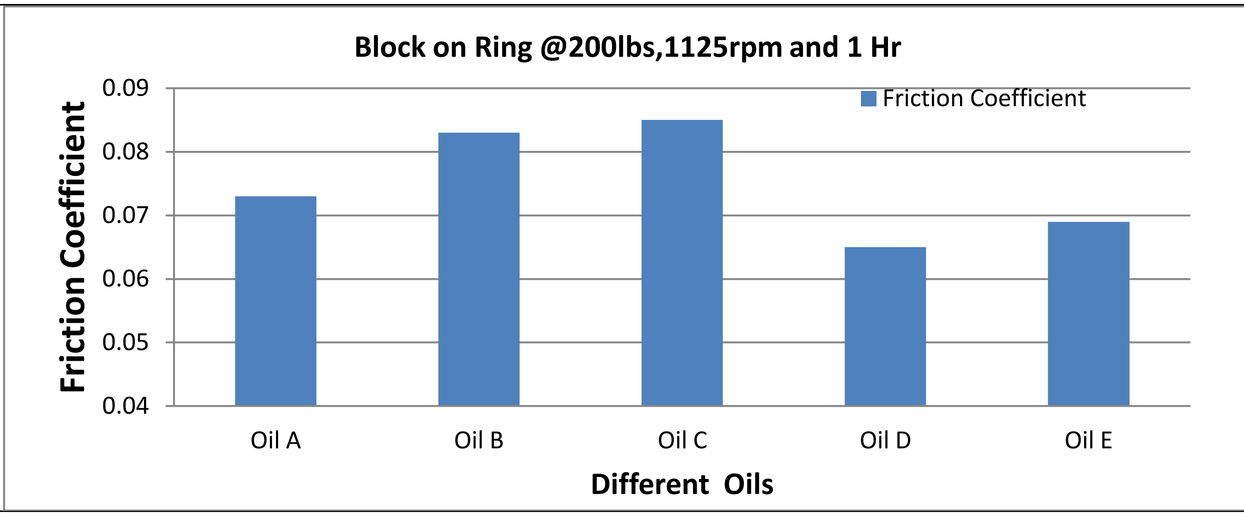


**Fig 11: Block on Ring Friction coefficient comparison**

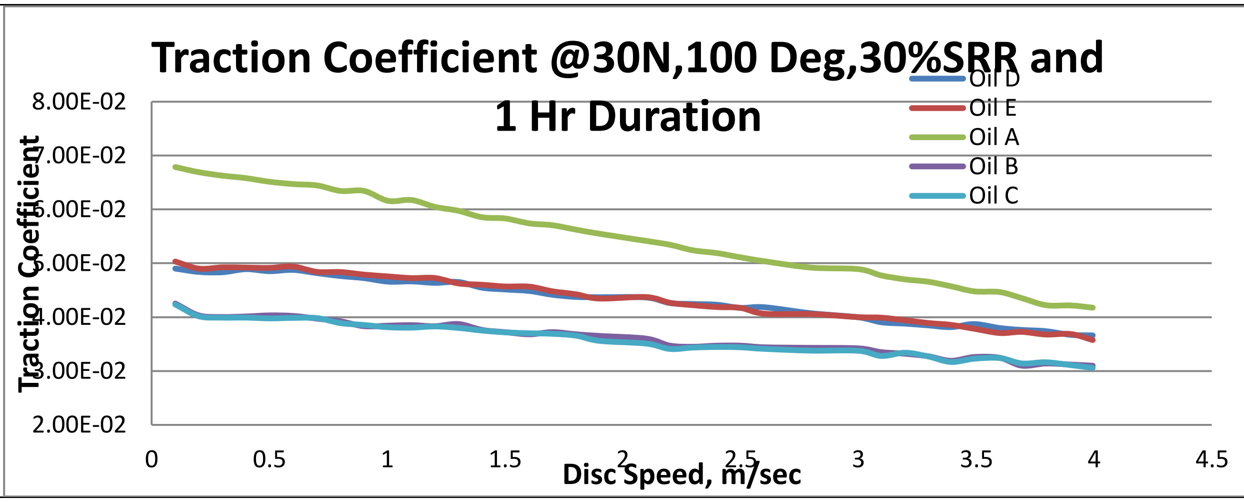


**Figure 12: Traction coefficient studies**

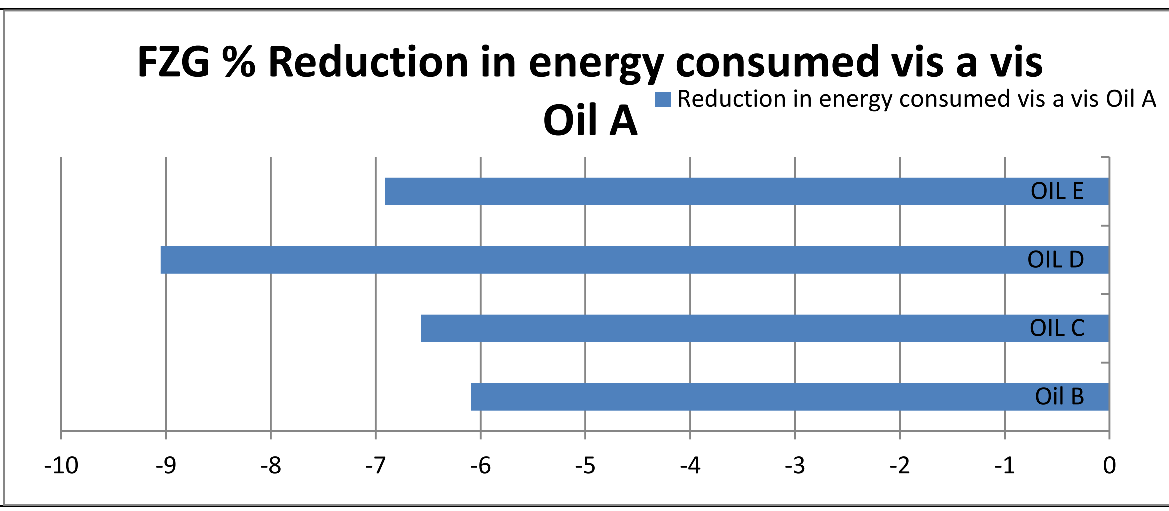


**Figure 13: Reduction in Energy Consumed in FZG Test vis a vis Oil A**

**Technical Manuscript for 15th NLGI–IC Conference Trivandrum, Kerala**

# A Study of correlation of Composition & Performance of Lubricating Greases with Appearance - an Analytical Approach

**S. Murali, and Dr. B. Ghosh**

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**ABSTRACT**

In recent years, there is a ever growing demand on Lithium based lubricating greases in both industrial and automotive applications which resulted in large increase in number of manufacturers with numerous products available to users .Among the lithium greases available in the market to customers / users , visual. Appearance of lithium greases are varying from colorless transparent to dark,opaque for a given application. Visual appearance of the lubricating greases is important and gives a aesthetic value for preferential choice of selecting a lubricating grease which may / may not be inline with actual performances. In the present work ,an attempt has been made to study the differences in the appearance in terms of composition and performances of Lubricating greases through analytical approach. These samples were subjected to analysis using various analytical techniques based on Atomic absorption Spectrometry ,Chromatography(GLC & GPC), Infrared spectrometry in addition to wet analytical methodology and physico-chemical test. The information obtained from the above study will be useful in understanding the relationship of visual appearance of lubricating greases with composition thereby on the performances for a given applications.

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**A Study of correlation of Composition & Performance of Lubricating Greases with Appearance - an Analytical Approach**

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# Introduction :

There is a growing demand for the use of lithium based multipurpose lubricating greases for various end applications in both industrial and automotive sectors in recent years. Generally for lubrication of antifriction and plain bearings in automotive applications,, multipurpose grease of NLGI .2&3 consistency are recommended and used extensively. Quality of these greases depends on the quality of raw materials used, It is also observed that physical /visual appearances of greases in terms of bright /dark, transparent /opaque, with/without dye are also choice of the selection by users irrespective of their performances. For the automotive as well as other end applications , a clean and transparent lubricating greases are preferred for operational and maintenance requirements. All the lubricating greases manufacturers are attempting to produce lubricants with visual appeal such as transparency through modifying process such as deaeration as well as on composition of ingredients such as fat / fatty acid & base fluid to address this parameter.

In the present study , an attempt has been made to study and evaluate nine products of multipurpose greases used for automotive applications from known manufacturers collected from the market. The samples taken for the study were from highly transparent to bright with opque to dark greases .The market samples of lubricating greases are mostly lithium based which includes simple to complex greases. In the present study, two aspects have been attempted., The first one is to determine the composition of the greases through analytical approach and second aspect is to correlate composition with respect to performance and appearance. The samples were subjected to analysis using various analytical techniques based on Infrared spectrometry , Atomic Absorption Spectrophotometry (AAS) used for elemental composition , Gas Liquid Chromatography for fatty acid composition in addition to usual Physico – Chemical tests such as Dropping

Point, Viscosity measurement and Soap & Oil separation extraction by Soxhlet Extraction method . A laboratory performance test - Wheel Bearing leakage tendency test based on ASTM D 1263 modified) was also used to study the variations of these market samples. Correlation of the composition of market samples of greases with visual appearance and performance in a automotive application was attempted in this work..

**EXPERIMENTAL :**

**Chemicals** : All chemicals employed for the analysis were of Analytical Reagent Grade : Hexane, Anhydrous Sodium Sulphate, Concentrated Hydrochloric acid,Methanol, Xylene and Acetic Acid, Diethyl Ether, Benzene, Chloroform ,Concentrated Sulphuric acid.

**Labwares & Equipments** : Standard Glasswares of Borosil make were used for analysis. Standard Soxhlet Extraction Apparatus, Whatman 40 (12.5 cm) & Filter paper for general purpose, Heating mantle, Electric Bunsen & Furnace (upto 1100 $^0$C), Vacuum Dessicator, Platinum Crucible 30 ml capacity .

**Instruments** : Thermo Nicolet Fourier Transform Infrared Spectrometer model Magna 560 ESP (FTIR), Thermo Electron Atomic Absorption Spectrophotometer S2 AA System (AAS), Thermo Fisher make Gas Liquid Chromatograph ( GLC ) model Ceres 800 Plus,, PerkinElmer make model STA 6000 Thermo gravimetric Analyser With Differential Thermal Analysis (DTA) provision, Semi - Automatic Dropping Point Apparatus Koehler make , Petratest make KN2 model Wheel Bearing Leakage Test Rig with built in software and Temperature Programming, Viscometer baths for 40$^0$C & 100$^0$C and viscosity tubes (glass)

**PROCEDURE :**

Nine market samples of Lithium multipurpose greases for automotive application marked as ‘A to I’were collected. These samples were subjected to above study by adopting the following procedures **:**

**Elemental Composition (Metals) in Lubricating Greases** : All the samples taken for study were subjected to elemental analysis for metals by Atomic Absorption Spectrophotometer by adopting the methodology given below. The samples were checked for the presence of the following metals - Lithium ,Calcium, Sodium , Zinc and Magnesium. The procedure adopted for each sample is given below - Weighed about 5-10 grams of sample in a platinum crucible and subjected to ashing at 750 $^{0}$C for 3 hours in a electrical furnace. after removing the volatiles over electric bunsen. Removed the crucible containing ash from the furnace and placed it in a dessicator for cooling to room temperature. Dissolved the ash in the crucible by placing the platinum crucible in a 250 ml beaker and adding 50 ml concentrated hydrochloric acid and diluting with 100 ml distilled water. The solution was kept over a hot plate until complete dissolution of sample's ash occurred. Transferred the content carefully through a Whatman 40 filter paper into a 250 ml volumetric flask along with washings and the remaining volume was made up with distilled water. This sample stock solution was subjected to AAS analysis for metals.

**Soap Content by Soxhlet Extraction Procedure** : The soap content in the samples were estimated by Soxhlet Extraction method. About 25 grams of each sample was taken in previously weighed thimble made of filter paper and placed in Soxhlet Extraction Apparatus. in which 250 ml hexane was taken to extract the oil .The apparatus was kept on a heating mantle and heated until hexane started boiling. Hexane under reflux condition for five hours, re-circulated through the sample and extracted out the entire base oil with additive extracted out completely. After 5 hours, heating was stopped and the extracted oil with solvent was allowed to cool down. Transferred the hexane soluble portion into previously weighed 400 ml beaker with hexane washings and kept the beaker with content over a boiling water bath to remove the hexane completely . The separated oil obtained was kept in a vacuum dessicator to remove completely any entrapped hexane. Weighed the beaker with the separated oil until constant weight was obtained. Similarly, hexane insoluble portion - the filter paper thimble containing soap was removed and kept in a clean petridish in a oven maintained at 90-100 deg.C for drying. After complete drying to constant weight, weighed the thimble with residue. From the difference in weight of the thimble with residue and empty thimble, the percentage soap content was obtained. The separated oil and soap from the sample obtained through soxhlet extraction method were subjected to FTIR spectral analysis & GLC analysis.

**Characterisation of Soap for the fatty acid composition by Gas Liquid Chromatographic analysis :**

The fatty acid portion of the separated soap obtained from above method was converted into its methyl ester for GLC analysis through a procedure given below:
1-2 gms of separated soap was taken 250ml conical flask, added 100ml of methylating agent prepared by taking solvents with acid catalyst in the ratio in ml ( Benzene : Methanol : sulphuric acid )( 55 : 190 : 5 ) with addition of few procelin chips . The solution was refluxed for 3 hours with water condenser connected with water circulation. After 3 hours, the heating was stopped and the solution was cooled to ambient temperature. The solution was removed with detachment of condenser after washing of

condenser with water .The solution was transferred to 1 litre separating flask and extracted out the converted methyl esters of fatty acids with solvent diethyl ether. The aqueous layer was removed and ether layer was thoroughly washed with water to remove any adhering mineral acid. The ether layer was subsequently passed through a funnel containing anhydrous Sodium Sulphate taken in filter paper and collected in a 250 ml beaker. The solvent ether with benzene present were removed over a boiling water bath. The residue obtained as methyl esters of fatty acids from soap obtained was dissolved in a chloroform and suitable stock solution 50 ml was made and subjected to GLC analysis using 2m long,1/8" I.D packed SS column with inner material 10%DEGS liquid coated on solid Chromosorb-W /HP. Isothermal condition at column temperature 180deg.C was used with injector and detector FID temperature at 200 deg.C and Nitrogen flow rate 30ml/minute was used for analysis. 1-2 microliter solution from stock solution was injected into GLC using 10 microliter syringe.

**Viscosity data of Extracted oil from Lubricating Greases :** Viscosity of the extracted oil from the lubricating greases was measured by ASTM D 445. Kinematic viscosity at 40 $^0$C & 100 $^0$C ,Viscosity index were obtained for all the extracted oil from lubricating greases.

**Fourier Transform Infrared Spectral Analysis of Lubricating Greases :** Infrared spectra of each of the samples along with the separated oil through Soxhlet extraction method were recorded directly as such in Potassium Bromide cell windows in a IR Demountable cell. Separated soap ( in solid form ) from grease was subjected to Nujol mull preparation before recording IR spectrum similarly between Potassium Bromide cell windows.

**Differential Thermal Analysis of Lubricating Greases using Thermogravimetric (TGA) Analyser:**

30-50 mg of each of the sample of lubricating greases was taken in sampler holder and kept in a sample compartment of TGA instrument. Nitrogen gas purged at a flow rate of 40ml/ minute and sample was subjected to heating at a rate 20deg.C /minute with starting temperature from 50deg.C to 900 deg.C. Both thermogram and differential thermogram was recorded for each of the samples above temperature range

**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.

**Wheel Bearing Leakage Tendency Test for Lubricating greases** : This performance test was performed on each of the greases as per ASTM Standard D 1263 ( modified) using spindle temperature condition of 130 $^{0}$C for 6 hours at a 660 rpm using 90 gms of sample to study any distinct variation in leakage tendency using similar conditions for better correlation of performance.

**Results and Discussions :**

**Elemental Composition (Metals) in Lubricating Greases** :

Table 1 shows the results of elemental composition of metals in the lubricating grease samples estimated by Atomic Absorption Spectrophotometer Analysis.

**Table 1**

| **S. No** | **Sample Code** | **Appearance** | **Lithium (%)** | **Sodium (%)** | **Calcium (%)** | **Magnesium (%)** | **Zinc (%)** |
|---|---|---|---|---|---|---|---|
| 1 | **A** | Transparent | 0.1788 | 0.0034 | 0.0091 | 0.0008 | 0.0019 |
| 2 | **B** | Transparent with red dye | 0.2536 | 0.0313 | 0.3540 | 0.0092 | 0.0011 |
| 3 | **C** | Transparent | 0.2030 | 0.0931 | 0.0336 | 0.0023 | 0.1104 |
| 4 | **D** | Transparent | 0.1352 | 0.1021 | 0.0304 | 0.0044 | 0.0022 |
| 5 | **E** | Transparent | 0.1460 | 0.0036 | 0.0120 | 0.0026 | 0.1416 |
| 6 | **F** | Bright opaque | 0.1820 | 0.0742 | 0.0233 | 0.0044 | 0.0004 |
| 7 | **G** | Bright opaque | 0.1899 | 0.1555 | 0.0417 | 0.0089 | 0.1104 |
| 8 | **H** | Bright,opaque | 0.2030 | 0.0116 | 0.0390 | 0.0017 | 0.0010 |
| 9 | **I** | Dark ,opaque | -- | 1.3966 | 0.0629 | 0.2273 | 0.0012 |

It was observed from the table that among the lubricating greases under study ( **'A,B,D, E F,G &,H'** ) were mostly lithium soap based with calcium & sodium presence. Zinc presence is mainly attributed to Zinc based Antiwear additives or from fillers such as Zinc Oxide. However, there is a variation in the lithium content in the eight greases mentioned above mainly due to variation in soap thickener content . It was also observed that highly tranparent grease such as sample **'A'** purely a lithium based and Sample'**C**' has very low calcium & zinc content to influence for the transparency. Sample **'I'** has indicated sodium based thickener with high percent of sodium and absence of lithium .

**Soap Content by Soxhlet Extraction Procedure** :Table 2 shows the results of separated soap and oil content from the lubricating greases under study.

**Table 2**

| S. No | Sample Code | Appearance | Separated Soap content (Wt%) | (% )Separated Oil plus additives content (Wt%) |
|---|---|---|---|---|
| 1 | **A** | Transparent | 9. 7 | 90. 3 |
| 2 | **B** | Transparent with red dye | 21 .6 | 78. 4 |
| 3 | **C** | Transparent | 13 .8 | 86. 2 |
| 4 | **D** | Transparent | 15. 6 | 84. 4 |
| 5 | **E** | Transparent | 7. 9 | 92. 1 |
| 6 | **F** | Bright opaque | 15. 5 | 84 .5 |
| 7 | **G** | Bright opaque | 12. 8 | 67 .2 |
| 8 | **H** | Bright ,opaque | 16. 6 | 83. 4 |
| 9 | **I** | Dark ,opaque | 19. 4 | 80 .6 |

From Table 2, it was observed that different samples have indicated different soap contents. As observed that sample- **'E & A'** has the lowest soap content with transparency and sample - **B & I** the highest in soap content has among the market samples . Sample '**B'** has maintained high transparency despite high soap content. This reflects that there is a distinct variation in composition offered by different manufacturers of lubricating greases for similar end application .It was also observed low soap content can improve the transparency as observed in Samples **'A & E'** .

**Characterisation of Soap for the Fatty Acid Composition by Gas Liquid Chromatographic (GLC) analysis :**

From Table 3, the fatty acid composition of soap constituting the lubricating greases estimated by Gas Chromatographic Analysis .It was observed that sample **'A'** most tranasparant grease has shown different fatty acid composition with relatively higher palmitic acid & stearic acid content and low 12HSA content. Sample **'I'** Dark opaque grease did not 12HSA fatty acid based soap thickener but may be tallow based/ unsaturated fatty acid based. Remaining lubricating grease samples from **'B to H'** are all based on 12HSA fatty acid soap based. Good transparency of the lubricating can also achieved through taking different fatty composition ( inclusion high palmitic acid along with 12HSA ) for making soap as observed in sample **'A'**.

**Table 3**
**% Fatty Acid as Methyl Ester by GLC**

| S. No | Sample Code | MA C 14:0 | PA C18:0 | SA C18:0 | OA C18:1 | AA C20:0 | 12 Keto SA 12 Keto C18:0 | 12HSA 12Hydroxy SA C18:0 | Others |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **A Transparent** | 0.6 | 16.0 | 18.0 | --- | 0.1 | 1.9 | 63.4 | -- |
| 2 | **B Transparent with red dye** | 0.4 | 1.5 | 12.0 | -- | 0.1 | 2.2 | 83.9 | -- |
| 3 | **C Transparent** | 0.2 | 1.8 | 11.5 | -- | 0.3 | 1.5 | 83.2 | -- |
| 4 | **D Transparent** | 0.5 | 1.6 | 11.3 | -- | 0.2 | 3.3 | 83.3 | -- |
| 5 | **E Transparent** | 0.2 | 1.3 | 11.4 | -- | 0.4 | 1.6 | 84.9 | -- |
| 6 | **F Bright opaque** | 0.3 | 1.2 | 9.9 | -- | 0.3 | 2.4 | 84.2 | -- |
| 7 | **Bright opaque** | 0.4 | 1.3 | 11.2 | -- | 0.2 | 3.1 | 83.8 | -- |
| 8 | **H Bright opaque** | 0.5 | 1.3 | 11.1 | --- | 0.7 | 3.2 | 83.2 | -- |
| 9 | **I Dark ,opaque** | 2.6 | 28.6 | 13.8 | 47.4 | 0.2 | -- | ---- | 7.9 |

- MA– Myristic acid, PA - Palmitic Acid ,SA – Stearic Acid , OA- Oleic Acid, AA- Arachidic Acid, 12Keto Stearic Acid, 12Hydroxy Stearic Acid,( 12HSA),Others- Linoleic Acid, Linolenic Acid, Erucic Acid & Palmitooleic acid etc.

Three typical Gas Liquid Chromatogram are given in Figures 1, 2 and 3 are observed in these analysis viz.Sample **‘A’ , ‘B to H’** and **I.**

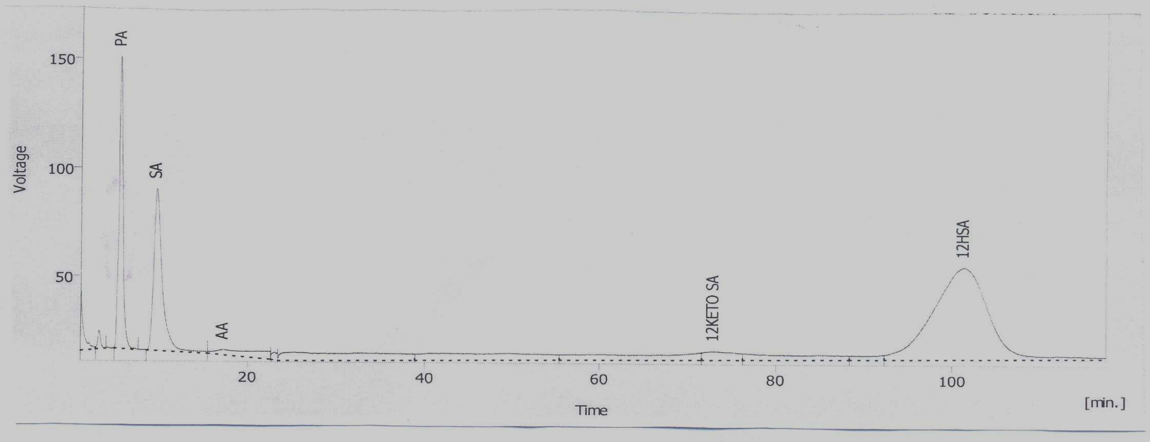



Figure 1 GLC Chromatogram of the fatty acid composition from Soap - Sample A

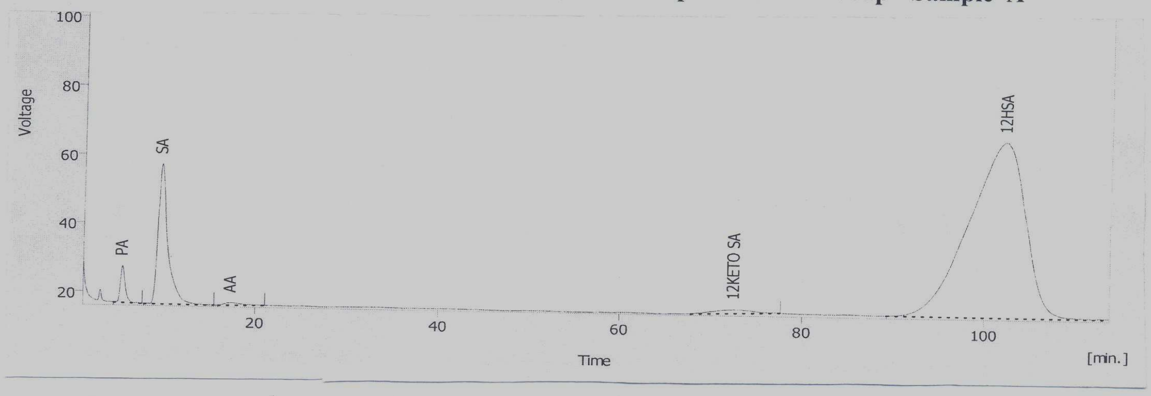



Figure 2 GLC Chromatogram of the fatty acid composition from Soap – Sample B to H'

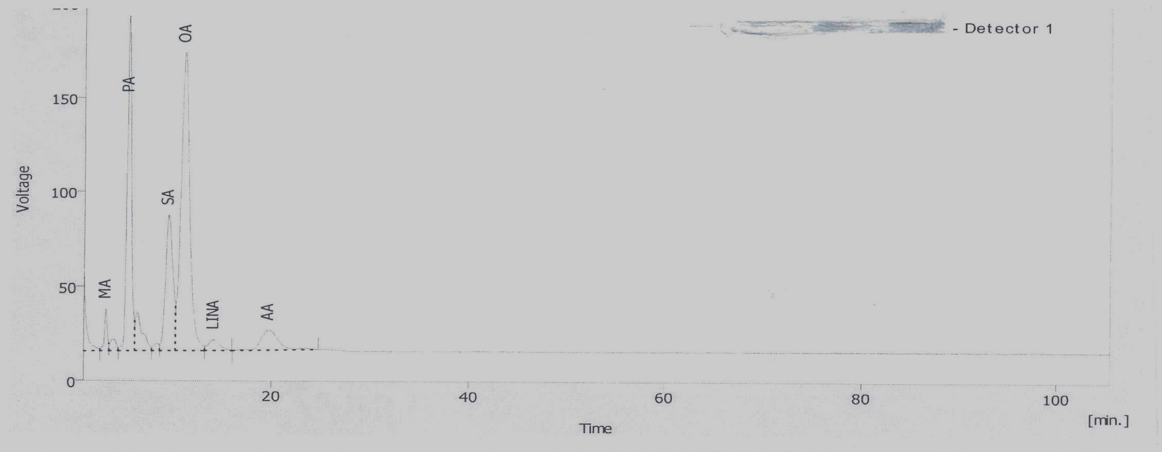



Figure 3 GLC Chromatogram of the fatty acid composition from Soap – Sample I

**Viscosity data of Extracted Oil from Lubricating Greases :**

Table 4 indicates viscosities data of the extracted oil from lubricating greases by Soxhlet Extraction Method.It was observed that the base oils used were varying in kinematic viscosities at both $40^0$C and $100^0$ C which is offered by different manufacturers of lubricating greases for similar end application .Absence of polymeric additives in most of the greases indicated by the VI ( Calculated ).The range VI( Calculated) in the range 87-96 which shows conventional base fluidsbased on paraffinic and naphthenic were being used. Sample **'I'** has indicated a mixture of Aromatic rich oil with paraffinic oil.

**Table 4**

| S. No | Sample Code | Appearance | K.V at 40deg.C , cSt | K.V at 100deg.C, cSt | VI (Calc) | Remarks |
|---|---|---|---|---|---|---|
| 1 | **A** | Transparent | 159.40 | 11.75 | 39 | Amber color oil ,Naphthenic type |
| 2 | **B** | Transparent with red dye | 339.25 | 19.34 | 51 | Red color oil<br>No polymer presence in extracted oil *but polymer is binded to Soap. |
| 3 | **C** | Transparent | 202.41 | 16.44 | 82 | Amber color oil ,Naphthenic & paraffinic oil type |
| 4 | **D** | Transparent | 114.87 | 9.87 | 47 | Amber color oil ,Naphthenic type |
| 5 | **E** | Transparent | 172.60 | 16.07 | 96 | Amber color oil ,group I paraffinic oil |
| 6 | **F** | Bright opaque | 111.15 | 12.12 | 98 | Amber color oil ,group I paraffinic oil |
| 7 | **G** | Bright opaque | 130.33 | 13.31 | 96 | Amber color oil ,group I paraffinic oil |
| 8 | **H** | Bright ,opaque | 84.46 | 10.73 | 112 | **Amber color oil<br>Polymer OCP presence |
| 9 | **I** | Dark ,opaque | 182.62 | 14.65 | 73 | Dark ,Aromatic based and Paraffinivc oil mixture. |

**Dropping Point determination of Lubricating greases** : Table 5 shows the results of dropping point of the greases under study as per standard test method ASTM D 566.

**Table 5**

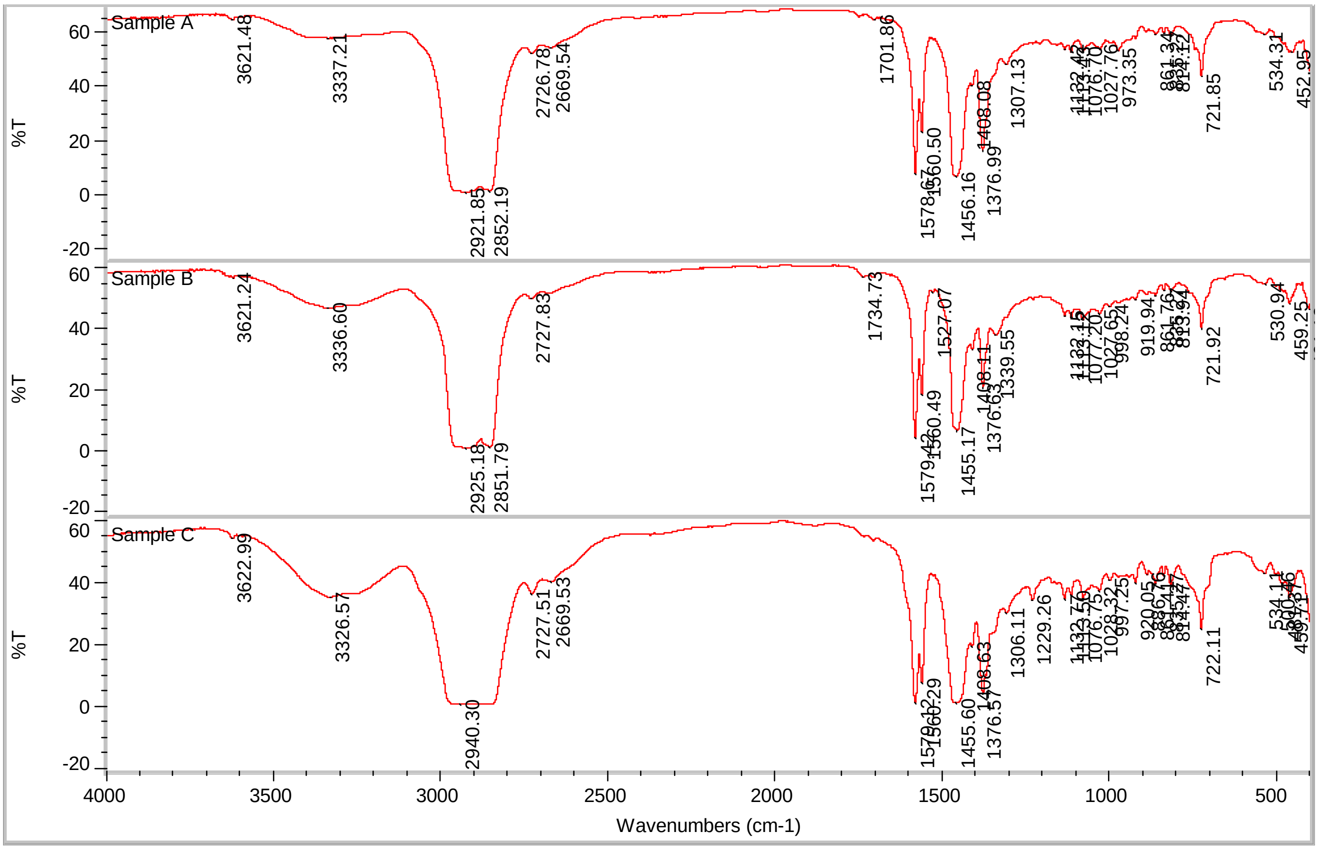
| **S No.** | **Sample code** | **Drop point $^0$C** |
|---|---|---|
| 1 | **A** | 200 |
| 2 | **B** | 240 |
| 3 | **C** | 204 |
| 4 | **D** | 276 |
| 5 | **E** | 276 |
| 6 | **F** | 199 |
| 7 | **G** | 205 |
| 8 | **H** | 200 |
| 9 | I | 177 |

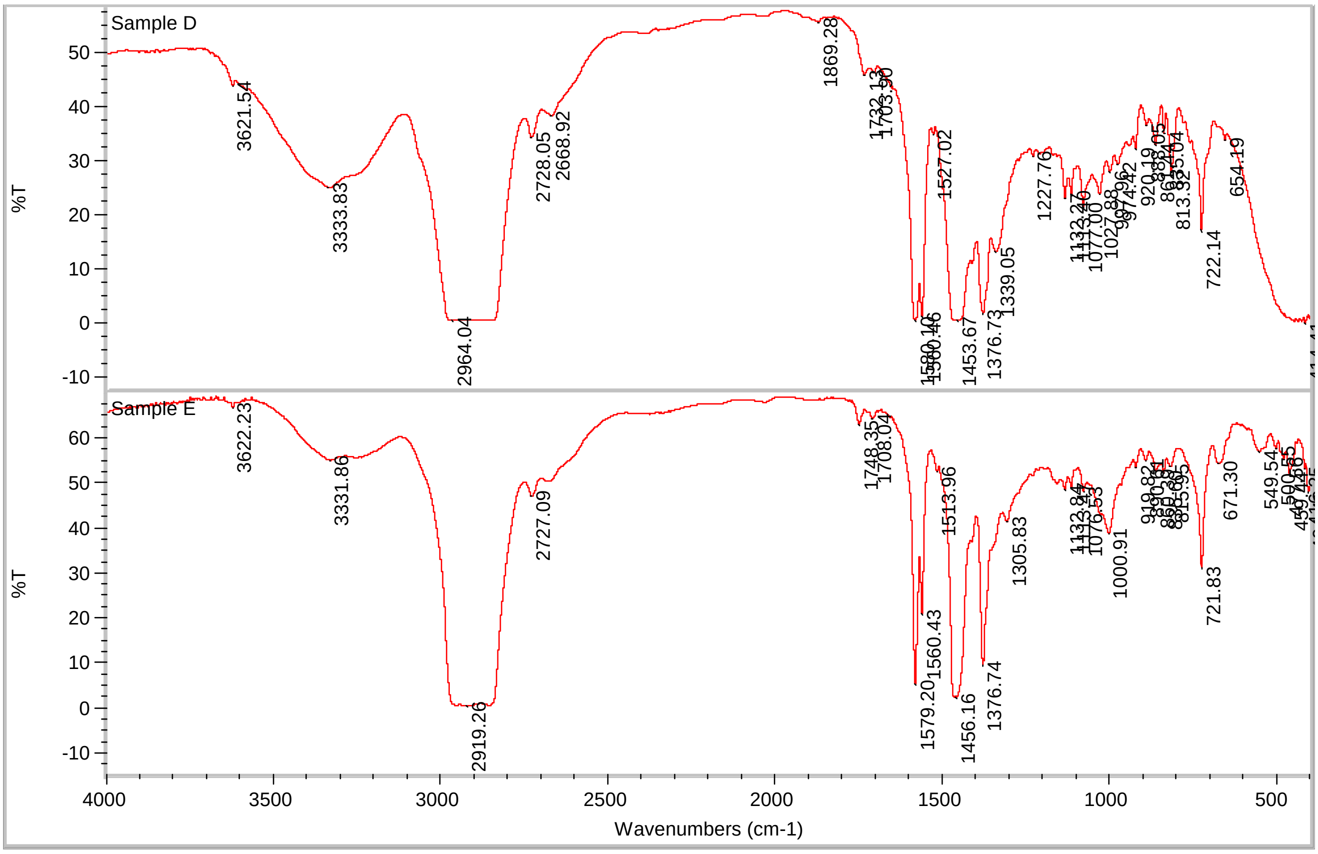
It was observed from the above table that there is no distinct variation in the dropping points of sample of greases under study with similar dropping point kept by manufacturers although samples **'A,C, F, G & H'** all together different composition. Dropping point may or may not reflect better performance of grease in a typical end application .It is also observed that transparent lithium greases ( samples- '**B,D &E"** are complex type greases are available to users besides simple transparent based greases sample **'A & C'**. Sample **'I'** Sodium based grease with different composition.

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

Separated soap and oil from the samples of greases under study were checked for recording infrared spectra. IR spectral analysis of most of the grease samples under study **('A to H'**) and its separated constituents indicated similar characteristic peaks of soap thickener based on Metal 12 -Hydroxystearate ( 3337 cm$^{-1}$,1579 cm$^{-1}$ and 1560 cm$^{-1}$,721 cm$^{-1}$). However, the intensity of soap thickener peaks varies in each sample under study due to variations in soap thickener content in the greases.
Sample**'I'** has shown different Infrared Spectrum of Lubricating greases characteristics of Sodium Soap thickener.

Figure 4 shows IR spectra of nine typical grease samples under study .All the grease samples **('A to H')** under study gave similar type of spectra except IR spectrum of sample **('I')** .


Sample A
Sample B
Sample C
%T
Wavenumbers (cm-1)
3621.48
3337.21
2921.85
2852.19
2726.78
2669.54
1701.86
1560.50
1456.16
1408.08
1376.99
1307.13
973.35
721.85
534.31
452.95
3621.24
3336.60
2925.18
2851.79
2727.83
1734.73
1527.07
1560.49
1455.17
1339.55
919.94
721.92
530.94
459.25
3622.99
3326.57
2940.30
2727.51
2669.53
1408.63
1455.60
1376.57
1306.11
1229.26
722.11


Sample D
Sample E
%T
Wavenumbers (cm-1)
3621.54
3333.83
2964.04
2728.05
2668.92
1869.28
1527.02
1453.67
1376.73
1339.05
1227.76
722.14
654.19
3622.23
3331.86
2919.26
2727.09
1513.96
1560.43
1579.20
1456.16
1376.74
1305.83
1000.91
721.83
671.30
549.54

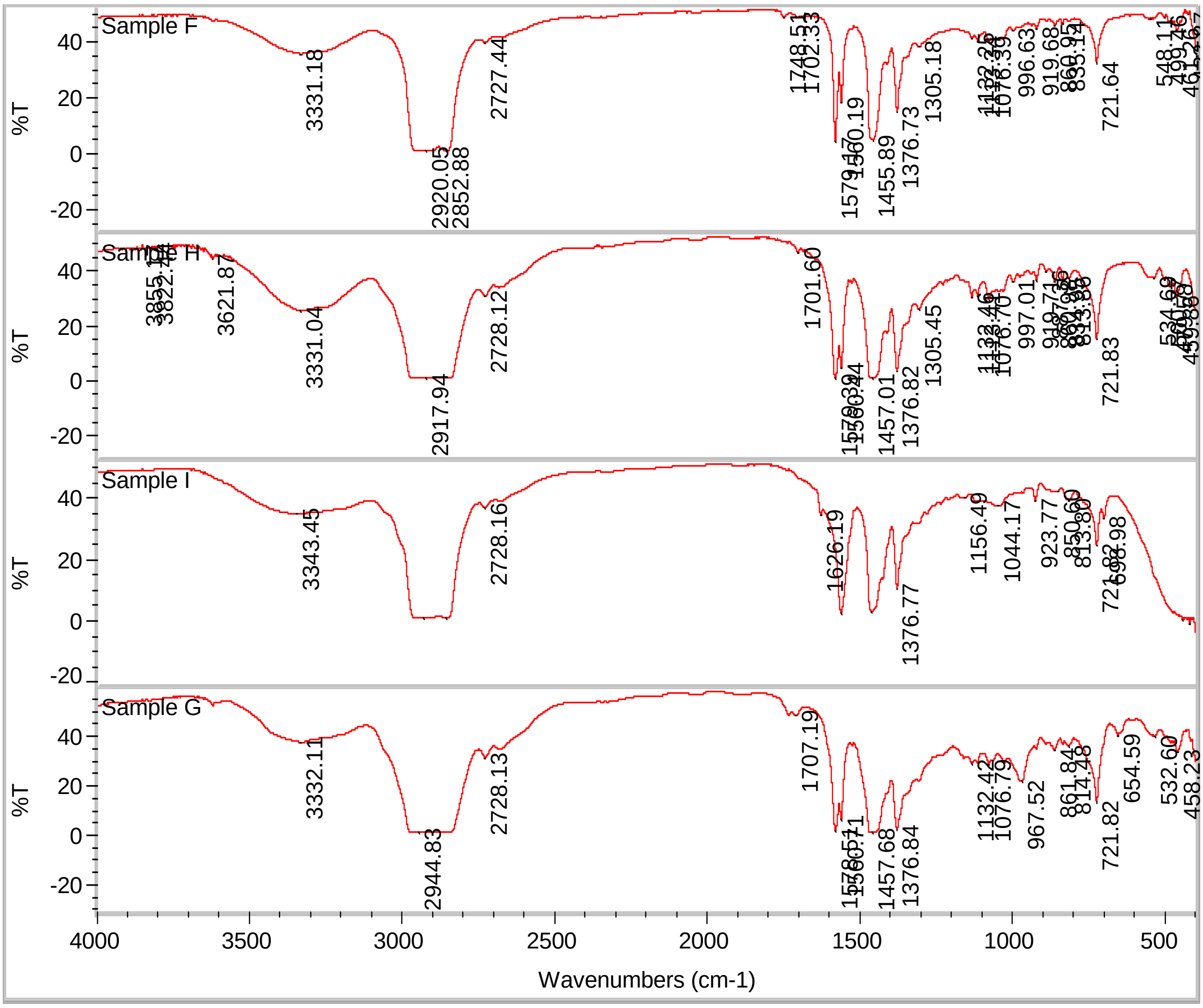


Figure 4 FTIR Spectra of all nine lubricating Greases **( 'A to I' )**

Table 6 shows the peaks characteristic of the components soap thickener and base fluids used along with additives in the lubricating greases.

# Table 6

| S.No | Sample Code | Type of Soap Thickener Used | Type of Oil & Additives Used |
|---|---|---|---|
| 1 | **A** | Lithium 12-hydroxy Stearate based Soap 3331 $cm^{-1}$, bifurcated peaks 1579&1560 $cm^{-1}$, and 721 $cm^{-1}$ | Amber transparent Hydrocarbon based Naphthenic oil less paraffinic type Absence of Additives ZDDP, PIB in the Base fluid .Presence peak at 973 $cm^{-1}$, P-S based additive. |
| 2 | **B** | Metal 12-hydroxy Stearate based Soap3333$cm^{-1}$, bifurcated peaks 1579 & 1560 $cm^{-1}$, and 721 $cm^{-1}$ Polymer is combined with soap . | Red color transparent Hydrocarbon based Naphthenic oil less paraffinic type Absence of Additives ZDDP, PIB in the Base fluid .Presence peak at 986 $cm^{-1}$P-S based additive .Presence of red color dye. |
| 3 | **C** | Lithium 12-hydroxy Stearate based Soap3334 $cm^{-1}$, bifurcated peaks 1579 & 1560 $cm^{-1}$, and 721 $cm^{-1}$ | Amber color transparent Hydrocarbon based Naphthenic oil and paraffinic oil mixed . Presence of Additives ZDDP (937 $cm^{-1}$& 667 $cm^{-1}$). Presence of Polybuene (PIB )-(1227 $cm^{-1}$ ,bifurcated-970 &986 $cm^{-1}$ ),in the Base fluid . |
| 4 | **D** | Metal 12-hydroxy Stearate based Soap 3333$cm^{-1}$, bifurcated strong peaks 1580&1560 $cm^{-1}$, and 721 $cm^{-1}$,Sodium soap/ filler may be present | Amber color transparent Hydrocarbon based Naphthenic oil with less paraffinic oil . Absence of Additives ZDDP(937 $cm^{-1}$& 667 $cm^{-1}$)but indicated the presence of Polybuene (PIB )-(1227 $cm^{-1}$ ,bifurcated-970 &986 $cm^{-1}$ )in the Base fluid . Presence peak at 989 $cm^{-1}$P-S based additive |
| 5 | **E** | Metal 12-hydroxy Stearate Soap 3331$cm^{-1}$, bifurcated peaks 1579&1560 $cm^{-1}$, and 721 $cm^{-1}$ | Bright yellow color transparent Hydrocarbon based paraffinic oil ( refined group I ) Presence of Additives ZDDP (1000$cm^{-1}$& 674 $cm^{-1}$). Absence of Polybuene (PIB ) - (1227 $cm^{-1}$ ,bifurcated-970 &986 $cm^{-1}$ )in the Base fluid . |
| 6 | **F** | Lithium 12-hydroxy Stearate Soap with filler 33301$cm^{-1}$, bifurcated peaks 1579 &1560 $cm^{-1}$, and 721 $cm^{-1}$ | Bright yellow color transparent Hydrocarbon based paraffinic oil ( refined group I ) Absence of Additives ZDDP (1000$cm^{-1}$& 674 $cm^{-1}$). Absence of Polybuene (PIB ) - (1227 $cm^{-1}$ ,bifurcated-970 &986 $cm^{-1}$ ),in the Base fluid . Presence peak at 996 $cm^{-1}$P-S based additive |
| 7 | **G** | Lithium 12-hydroxy Stearate Soap 3331 $cm^{-1}$, bifurcated peaks 1579&1560 $cm^{-1}$, and 721 $cm^{-1}$ | Bright yellow color transparent Hydrocarbon based paraffinic oil ( refined group I ) Presence of Additives ZDDP (967 $cm^{-1}$& 654 $cm^{-1}$). Absence of Polybuene (PIB ) - (1227 $cm^{-1}$ ,bifurcated-970 &986 $cm^{-1}$ ),in the Base fluid . |
| 8 | **H** | Lithium 12-hydroxy Stearate Soap 3331 $cm^{-1}$, bifurcated peaks 1579&1560 $cm^{-1}$, and 721 $cm^{-1}$ | Bright yellow color transparent Hydrocarbon based paraffinic oil ( refined group I ) absence of Additives ZDDP (1000$cm^{-1}$& 674 $cm^{-1}$).& Absence of Polybuene (PIB ) - (1227 $cm^{-1}$ ,bifurcated-970 &986 $cm^{-1}$ ),in the Base fluid |
| 9 | **I** | Metal Stearate / oleate based Soap 1560 $cm^{-1}$, and 721 $cm^{-1}$. Presence of OH at 3343 cm-1 indicated moisture/water in the sample | Dark brown color oil consist of mix of aromatics rich with paraffinic oil .Presence of Additives ZDDP (1044$cm^{-1}$& 694 $cm^{-1}$).& Absence of Polybuene (PIB ) - (1227 $cm^{-1}$ ,bifurcated-970 &986 $cm^{-1}$ ),in the Base fluid |

It is also observed that although some of the lithium greases are complex types as observed from their respective dropping point temperature , the IR spectra of greases cannot distinquish the complex greases ( Sample **'B D, E'** ) from simple greases (Sample **'A C, F,G, and H'**) and are similar. Sample **'I'** has shown different IR Spectrum from remaining above greases .

**Differential Thermal Analysis of Lubricating Greases using Thermogravimetric (TGA)Analyser :**

Thermogram and its differential thermogram of each of the lubricating greases were recorded and were analysed for their thermal behavior pattern.

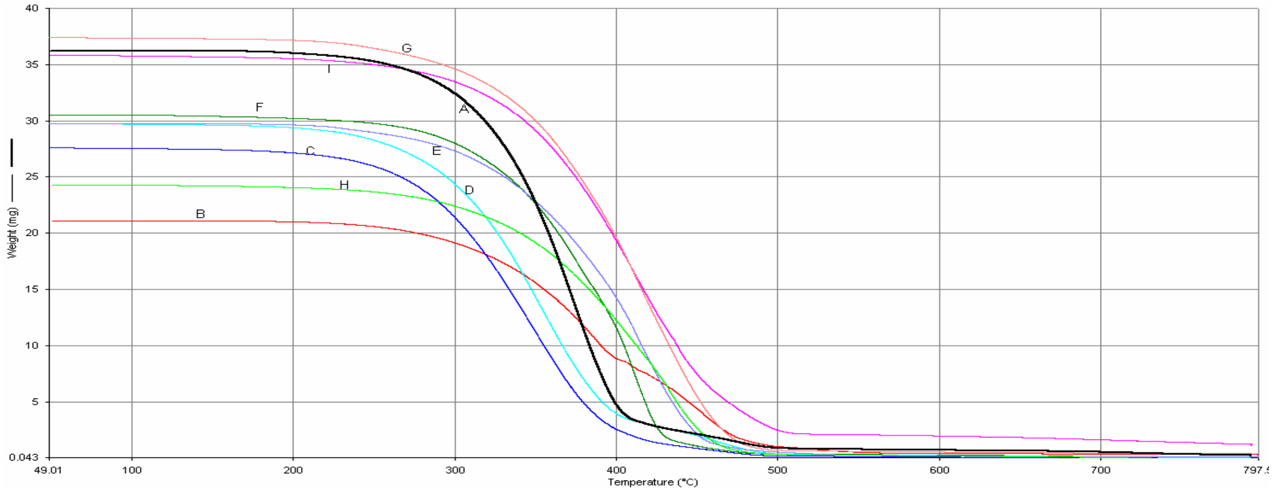



**Figure 5 typical TGA curves of lubricating greases (A to I )**

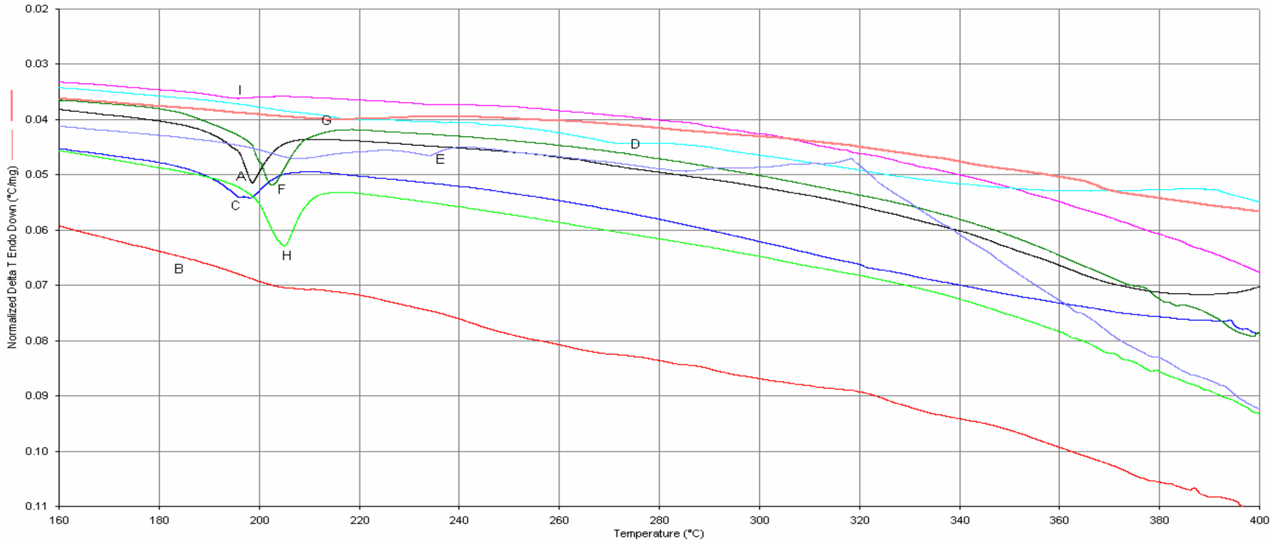



**Figure 6 typical Differential Thermogra curves of lubricating greases ( A to I )**

From the above Differential Thermogram of lubricating greases ,it was observed that highly transparent grease with low soap content as well as different fatty acid composition of such as Sample **'A'** has shown very sharp peak of soap melting around respective dropping point temperature and high soap content grease such as sample **'H'** has shown relatively broader peak of soap melting around respective dropping point temperature .Sample **'C','F' & 'G'** has shown with intermediate soap content have shown relatively broader peak of soap melting due to similar fatty acid composition of soap.

The samples of lithium complex soap based lubricating greases including transparent types such as **'B', 'D' and 'E'** observed no distinct characteristics peaks of soap melting but seen 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 soap melting .
Sample 'I' which is sodium soap based has shown hump around respective dropping point due to soap melting This difference could be due to fatty acid composition of the soap.

**Wheel Bearing Leakage Tendency Test for Lubricating greases** :
Wheel Bearing leakage tendency test was carried out as per standard test conditions but at 130 $^{0}$C (ASTM D 1263 modified) in all samples. It was observed that all the samples of greases under study, do not show the same degree of leakage tendency in this performance test . In order to observe the distinct differences between the samples, the performance test was performed at slightly higher temperature at 130 $^{0}$C.

Table 8 shows the results of the Wheel Bearing leakage tendency test performed at130 $^{0}$C.

**Table 7**

| **S. No.** | **Sample Description** | **Leakage from bearings (in Grams )** | **Remarks , if any** |
|---|---|---|---|
| 1 | A | 8.1 | Less grease and more oil leakage |
| 2 | B | 5.4 | Less grease and less oil leakage |
| 3 | C | 7.3 | Less grease and more oil leakage |
| 4 | D | **5.1** | Less grease and less oil leakage |
| 5 | E | 5.9 | Less grease and less oil leakage |
| 6 | F | 9.1 | Less grease and more oil leakage |
| 7 | G | 8.4 | Less grease and more oil leakage |
| 8 | H | 8.9 | Less grease and more oil leakage |
| 9 | I | 12.3 | Less grease and more oil leakage |

It was observed from the table that sample **'B'** , **'D' & 'E** 'has shown minimum leakage tendencies even at higher temperature indicating this grease may perform better in actual application condition due to its better thermal stability. The leakage tendency is maximum in Samples **'A, C, F ,G & H** 'indicates that these greases relatively may not perform equally well in actual application as compared to **'B , D& E'** . Sample **I** has shown highest leakage tendency which may not perform relatively to other greases .Despite highly transparent Sample **'A'** did not show very high performance in this test and are in close in line with sample **'F,G & H** samples which bright opaque greases.

## Conclusions :

The above study is attempted to analyse the market samples of lubricating greases to observe the distinct variations in composition in terms of soap content , base oil content and type of soap thickener, base oil used, with visual appearances in terms transparency / opaque , color as well as observed in variation in performance test such as Wheel Bearing Leakage Test for a given end application .

Among the samples under study, sample **A** a highly transparent lithium soap based grease has shown low performance as against transparant **( B ,D & E )** lithium complex soap greases actually observed in performance test-Wheel Bearing leakage test for the greases. Among the lithium soap greases , sample **A** & Sample **C,** transparant greases have shown very similar performance test when compared with sample **- F, G** & **H** which are bright and opaque type. There is no distinct advantage over transparency.over bright /opaque greases. Sample **I** having different composition and visual appearance, has shown highest leakage tendency which may not perform well relatively to other greases as observed in the study .

Soap content & composition of highly transparant grease Sample **A** is different as observed in GLC analysis in terms of fatty acid composition . Transparancy could be achieved by varying the fat composition as observed in highly transparant Sample **'A'.**

In the elemental composition study incorporation of element such as calcium , zinc and magnesium may not improve the transparency of the greases as observed in samples **A & C** under this study.

Dropping point of greases, though an important parameter for the end user as well as the manufacturer, as such alone will not reflect on the quality and performance of observed in this parameter. It is also observed that lithium greases ( samples- '**B,D &E"** are transparent complex type greases are available to users besides simple transparent based greases sample **'A & C'**. Sample **'I'** sodium based grease with different composition.

Differential thermogram study have indicated a very sharp soap melting peak in the case of transparant greases sample **A & C** and relatively broader soap melting peak around the dropping point temperature of respective greases in the case of sample **F, G & H** in the case of lithium soap based greases . The intensity of the peak is also depend on soap content of the greases. However , Samples lithium complex soap based greases ( transparant complex greases), soap melting peaks are spread as a humps not intense and clearly defined as observed in the samples **– B, D, E.** Sample **I** has shown very similar thermal behavior pattern as lithium complex greases with a hump. Differntial Thermal study can be used as a tool to differentiate quickly simple soap based greases from complex greases .

From the above study , transparency could be achieved through normal composition of fat , good grade bright base fluid and processing manufacturing procedures as observed in Samples – '**B , D,** & **E'** where unusal soap composition was not observed and also could be achieved with varaiation in soap content as well as its fatty acid composition.

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# The long story of a high performance anticorrosion grease: a new relevant centenary application

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## ABSTRACT

The origin and the development over the latest years of high protective and anticorrosion grease, with both its classical and new long term applications, is described.
The special grease was originally formulated in the early 60's when **eni** (at the time Agip Petroli) started to produce greases in its plant of Porto Marghera.
Time by time the product has been continuously updated increasing high performance in protective and lubricating properties, thus becoming a multifunctional product with high EP characteristic, capable of lubricating up to 120°C and guaranteeing a top salty water protective performance. Recently it has been evaluated a 40 year old sample of the grease, completing in this way the assessment of its performance and the inherent results are presented.
The product was originally developed for automotive applications, in order to provide a white coloured grease for protection of cables and hinges. Nevertheless the grease showed a very good behaviour in applications working under corrosive condition or saline marine environments.
For its very high performance achieved in anti corrosion properties, the product has been selected for an application where a hundred year duration is requested: the filling of hinges of the **MOSE** (**MO**dulo

**S**perimentale **E**lettromeccanico - *Experimental Electromechanical Module*). The MOSE system is a very costly project, designed to protect Venice from floods of high tide, consisting of a system of mobile barriers at the three inlets which will separate the Venetian Lagoon from the Adriatic Sea, when the height of tide reaches an established level.

**The origin of the product**

The special grease was originally formulated in the early 60's when **eni** (at the time Agip Petroli) started to produce greases in its plant of Porto Marghera, when the company, who was manufacturing lubricants under license, decided to develop own original proprietary formulas and produce them.

In that period it was a common practice to label all products with «AGIP F. 1 » (that stands for formula one) followed by a specific code. This way to name AGIP products was linked to the fact that Agip Petroli had been a Ferrari's sponsor and supplier for lubricants and fuel for 22 years, between 1974 and 1995.

In order to guarantee a high water washout resistance, the choice fell on an anidrous calcium soap. The automotive application required the clearest colour and that was obtained by adopting a high percentage of zinc oxide, which guaranteed a high anticorrosion level.

**The first formula**

The product reflected the know-how and technologies available at that time, so that it was utilising 100% of naphtenic oil.

**First Formula - 1964**

| **Components** | **% wt** |
|---|---|
| Mix base oils | 81.00 |

| | |
|---|---|
| Calcium soap | 11.00 |
| Tackiness agent | 0.50 |
| Zinc dioxide | 5.00 |
| Antirust A | 2.50 |

**Table 1**

The antirust function was imparted by Zinc dioxide and by an antirust based on sodium and barium sulphonates. The antirust performance was evaluated by SKF Emcor 164 h – distilled water, and the result was 0/0.

From the point of view of the consistency it is noticeable that since from the beginning the product was indicated like an NLGI grade 2, but in real, to be more stable, its consistency, reported in typical data of official sheets, was of about 250 dmm.

**Reformulation in 1975 -76**

In 1975-76 the product was reformulated to introduce some paraffinic oil in formula keeping the naphtenic part: 2 different versions of the product were made, the cheaper for marine and industry with about 20% of paraffinic oil and a version for automotive with 25% of paraffinic base for a more resistant product to oxidation. The 2 paraffinic oils differ in composition but they had similar viscosity, this also caused a slight increase in viscosity.

In any case the substitution of a part of very solvent naphtenic oil was compensated with a slight increase of the percentage of soap.

**Second Formula - 1976**

| **Components** | **% wt** |
|---|---|
| Mix base oils | 79.50 |
| Calcium soap | 2.50 |
| Polymer | 10.00 |
| Thachiness agent | 0.50 |
| Antirust | 2.50 |
| Zinc dioxide | 5.00 |

**Table 2**

**Reformulation in 1982 – a real upgrading!**

The new formulation was a real upgrading, because the antirust properties of the product were increased, the aim was to meet the official German army specification BWB TL 9150-066 (NATO Code G-460).
To gain this result the product was modified upgrading the anticorrosive properties by inserting a new antirust, based on a different technology, in addition to the previous component.

**Third formula - 1982**

| Components | % wt |
|---|---|
| Mix base oils | 77.50 |
| Calcium soap | 12.50 |
| Thackiness agent | 0.50 |
| Zinc dioxide | 5.00 |
| Antirust A | 2.50 |
| Antirust B | 2.00 |

**Table 3**

The modification was very successful, because the product was homologated and bought by the German army. In the following Table 4 some technical details are reported.

**Typical data of reformulation of 1982**

| Characteristic | Unit | Values |
|---|---|---|
| Worked penetration | dmm | 250 |
| ASTM dropping point | °C | 130 |
| Base oil viscosity at 40°C | $mm^2/s$ | 86 |
| SKF Emcor 164h – 3% NaCl | ... | 1/1 |
| CRC bearing corrosion 48h -52°C ASTM D 1743 | ... | 0 |
| Steel corrosion DEF STAN 94-31/1 | ... | No corrosion |
| Friction wear SRV (cylinder/area) | ... | No tribocorrosion |

**Table 4**

**Reformulation in 1993 – alignment with NLGI**

This was a minor, but necessary modification, the penetration was reported in the official grade 2 reached by a proper level of soap content.

**Reformulation in 2000 – a top universal product**

For 21st century the product was completely reformulated to upgrade the global performances and giving also some outstanding properties, both in protection and lubrication. The occasion was given by the need to eliminate the barium as new safety rules required.

To obtain the improvement in lubrication the product was reinforced in antioxidant and antiwear/EP properties, basically utilising a suitable zinc dithiophosphate, and the result was really very good for an anidrous calcium grease. In fact the product reached 250kg in four ball weld, so that it is classifiable like EP product.

**Reformulation of 2000**

| **Components** | **% wt** |
|---|---|
| Mix base oils | 72.60 |
| Calcium soap | 8.90 |
| Tackiness agent | 0.50 |
| Zinc dioxide | 10.00 |
| Antirust mix (4 different types) | 7.00 |
| Antiwear/EP | 1.00 |

**Table 5**

Also for lubricating properties it obtained very good results in rig tests. The first test was run internally in **eni** laboratories and the product passed the SKF R2F test at 120°C. But the really top results were obtained at FAG laboratories where the product was tested at the limit temperature of 120°C with excellent long life behaviour of about 250 hours.

Furthermore the anticorrosive properties were reinforced. The amount of zinc oxide was increased and anticorrosion properties were obtained with a balanced mix of 4 antirust additives: introducing into the formulation two proprietary calcium sulphounates, and an internal produced zinc based antirust. All these additives have given also synergistic effects in EP performance. In terms of anticorrosion properties the product obtained very good results in tests like Humidity cabinet and Humidity cabinet typical of preservative products (see Table).

**Performance tests of the formula of year 2000**

| Tests | Method | Unit | GREASE |
|---|---|---|---|
| Copper corrosion | ASTM D 4048 | - | 1b |
| Emcor test, distilled water | IP 220 | - | 0/0 |
| Emcor test, salt water | IP 220 | - | 0/0 |
| Water washout | ASTM D 1264 | %wt | 1 |
| Humidity cabinet | ASTM D 1748 | h | > 1500 |
| Humidity cabinet testing | ASTM B 117 | h | > 1000 |

**Table 6**

**Tribological Tests of the formula of year 2000**

| Tests | Method | Unit | GREASE |
|---|---|---|---|
| 4-ball EP test | DIN 51350 | | |
| • max. load prior to seizure | | daN | 80 |
| welding load | | daN | 260 |
| Timken | ASTM D 2509 | | |
| • OK load | | lbs | 45 |
| • specific pressure at OK load | | | 158 |
| 4-ball wear test | ASTM D 2266 | | |
| • wear diameter | | mm | 0.65 |
| • specific pressure | | $MN/m^2$ | 495 |
| SKF at 120°C | R2F | | Pass Rating 1 |
| FE 9 F 50, 120 hours | DIN 51821 | hours | 250 |

**Table 7**

The last reformulation, still in progress, has become necessary for new limits on zinc oxide in case of pollution of the environment, so that it will be reduced and partially replaced with titanium dioxide to maintain the white colour. This will require a readjustment in the blend of antirust, by eliminating also the fourth antirust that could give some concerns of potential toxicity.

**Long life protection**

In the 2011 the product has been selected for extra long life application, that will be successively illustrated.

For greases there are no specific tests to valuate the performance for long time duration.

We had the lack opportunity to find out a tube of grease of more than 40 years old, left in the laboratory; so that it was possible retrieve some information on the behaviour in static conditions,


**Picture N° 1 – The old tube of grease founded in a workshop**

Despite the aspect of the tube, the product is resulted in very good conditions: it is still now of light amber colour.

**Picture N° 2 – The grease squeezed from the tube**

The results of the analysis carried out the sample of unused grease are reported as follows in the Table 8.

**Typical values of a 40 years old grease**

| **Characteristic** | **Values** |
|---|---|
| Aspect | Smooth |
| Colour | Light amber |
| Worked penetration, dmm | 259 |
| NLGI consistency | 2 / 3 |
| Dropping Point, °C | 155 |
| Water Washout , % wt | 3.875 |
| Oil separation, % wt (FTM 321,3) | 5 |
| Acidity, mg KOH/g | 3.28 |

**Table 8**

The analysis confirm the good condition of the products and do not reflect the age of grease. The value of penetration reflects the typical of that time for this grease. It looks quite a new product, only water washout and oil separation look higher of the expected.

The good general condition of the product can be justified by the long storage in a limited and not extreme range of temperatures (+5 / +30°C), in static condition, without contact with air.
Based on the performance of the grease and on these results, we decided to propose this product where an extra long term application is required: the MOSE system having very similar conditions for: temperatures, absence of air and static situation of the grease has been the tremendous opportunity.

**The centenary application in MOSE project - Venice**

The beautiful, famous and unique city of Venice is under serious threat due to the rise in sea level and sinking of land. The consequence is the flooding by high tides that periodically submerges parts of the city. This phenomenon is called by Venetians as the "*acqua alta",* ("high water" level).

**Picture N° 3 – San Marco Square with "high water" (Photo Wikipedia)**

To solve the problem many actions are planned, as building a dozen of wells surrounding Venice in a ten kilometre circle and pumping water into the ground over a ten-year period, nearly 150 billion litres, for competing the sinking. But this action can not eliminate completely the problem, because due to the concomitant fact that the Adriatic Sea is swelling with the average local sea the water level is predicted to rise about 25 cm by the end of this century.

The first massive action undertaken is MOSE project system, a very costly structure, designed to protect Venice from floods of high tide. The MOSE should prevent the Venetian Lagoon from being submerged by the Adriatic Sea and protect the city and the neighbouring areas from flooding, and it is expected to be operative by 2014.

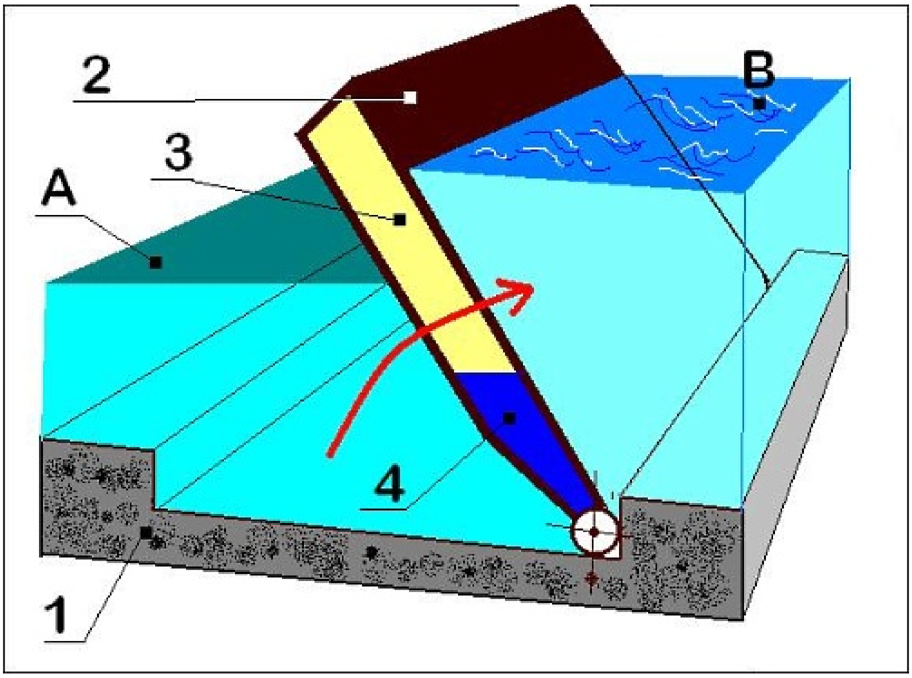
The evocative name **MOSE** is the acronym of **MO**dulo **S**perimentale **E**lettromeccanico (*Experimental Electromechanical Module*) and alludes to the story of Moses parting the Red Sea.

The project will prevent flooding through the installation of four mobile gates at three inlets, namely Lido, Malamocco and Chioggia, which will separate the Venetian Lagoon from the Adriatic Sea.


**Picture N° 4 – Venice and the three entrance at the lagoon**

The project includes the realisation of four mobile gates capable of creating mobile barriers rescuing Venetian lagoon from the Adriatic Sea, when the height of tide reaches an established level (110 cm) and up to a maximum of 3 m.

MOSE consists of a system of retracting oscillating buoyancy flap gates that must not modify water exchange between the sea and the lagoon to avoid damaging lagoon morphology and water quality, must not obstruct navigation, thus interfering with port activities and fishing, and must not alter the extraordinary beautiful landscape. The gates are realized with a system of 78 mobile barriers designed to protect the three entrances to the Venetian Lagoon. At rest each gate fills with water and lies flat on the seafloor until high tides and storms are forecast. In the event of unusually high seas, compressed air forces water out of the gates, making them rise. They will then be floated, blocking the sea from the lagoon and effectively reducing high water levels.




**Picture N° 5 – Schematic that shows how MOSE is working:**
**A: lagoon; B: open sea**
**1: concrete basement; 2: mobile barrier; 3: compressed air; 4: expelled water**

The so called hinge assembly connectors are filled with grease. The maintenance of the gates is scheduled every 5 years; however it has been stated that the female element is never removed, therefore the grease is working in an inert environment, without water or oxygen and at a fixed temperature of approximately 25°C, and the system hinge group has been designed to ensure a durability of 100 years.

The characteristics of the grease structures evaluated on the 40 year old sample show a high mechanical and chemical stability of the product which can be extrapolated to a good performance over 100 years, in static and no oxygen conditions.

## Conclusions

In this paper we have described the successful story of a grease, specifically tailored for automotive application, with a very high performance (water washout, tribology), which over time revealed an excellent aging resistance, as showed by the analysis of a 40 year sample carried out in our labs. The original anti-corrosion performance has been increased time by time (during the routine formulation upgrading) as well as anti-wear and lubricating properties, making this product an excellent universal product.

The product results effective for long periods since its high oxidation resistance makes it useful for application working at temperature up to 120°C.

This evolution has been driven using the most advanced technology currently available and compatible with human health and environment protection.

This product has been chosen by MOSE engineers for its properties as a long life product capable to resist for 100 years in a marine contest.