GREASETECH INDIA

A Quarterly Journal of NLGI-India Chapter

Vol. XIII, No. 3, January 1-March 31, 2011

In This Issue

Page No.

On Our Cover

Published and printed by Dr. K.P. Naithani for NLGI-India Chapter, Headquarters, C/o Indian Oil Corporation Limited, Research and Development Centre, Sector-13, Faridabad-121007, India. Tel.: 91-129-2262081, Fax: 91-129-2267818, Email:naithanikp@iocl.co.in

Add IOCL

From President's Desk

13th Lubricating Grease conference on the theme "Lubricating greases – Future Prospectus" was successfully organized during February 3-5, 2011 at Ooty. Overwhelming response received from Indian and Foreign Grease industry researchers, additive suppliers and equipment manufacturers made the conference atmosphere live and interactive.

This issue includes research articles on use of lubricating grease for yaw gears of wind turbine and lubrication of hub units or cars. Research paper "Evaluation of frictional properties of lubricating greases" is a study on the selection of proper additive for lowering of friction. A research article covering use of spectroscopic techniques for the evaluation of synthetic base oils also appears in this issue.

Once again convey thanks to sponsors for their liberal support for organizing 13th Lubricating Grease Conference and look for your continued support in future too.

Dr. K. P. Naithani
President,
NLGI- India Chapter

Lubrication Requirement of Yaw Gears in Wind Turbine Gearbox

B S Nagarkoti
Hindustan Petroleum Corporation Limited,
R&D Centre, Plot D-500, TTC Industrial Area, Turbhe,
Navi Mumbai-400 075, India

Abstract

Windmills are the most popular alternative system of power generation in current energy crisis scenario, due to very low energy cost. Though the initial cost is higher but in long run these are very cheap systems. The windmill gearbox can generate upto 600 KW of wind power. The gearboxes are speed increaser type. The gearbox is used to increase the speed from 20-50 rpm to 1000-2000 rpm. Since gearbox is located at height, frequent lubrication is very difficult and expensive. Therefore lubrication of gearbox is very important that contributes to reliability of functioning and long service intervals. Due to unreliability of wind the gearbox encounters shock loading in addition to regular load. Additionally, the gearbox needs to support the power generator and disc brake and wind turbine blades through hexagonal flanged low speed shaft. Therefore lubrication requirement of gearbox is very crucial to run the windmill. Considering the severity of operating conditions of gearbox in windmill, we have attempted to develop an open gear lubricant for lubrication of yaw gears of wind mill. To achieve the high load carrying property we have studied nano particle Tungsten Disulfide in open gear lubricant. The developed open gear lubricant was tested for various parameters in laboratory including performance tests. The product has shown high load carrying properties as evidenced by higher weld load and Timken OK load.

Introduction

The key mechanical and power-generating elements in a wind turbine are a gearbox and the generator to which it is attached. The wind turbine propeller captures the wind's energy, which spins a shaft, which drives a generator and produces electricity. The blades, which spin in the wind to drive the turbine generator, along with the hub are called the rotor. The rotor attaches to the nacelle, which sits atop the tower and includes the gearbox, generator, controller and brake. A cover protects the components inside the nacelle. The entire nacelle pivots to maintain point contact with the shifting wind. The yaw drive, with the help of computer controls, keeps the nacelle pointed into the wind. The generator is usually an off-the-shelf induction generator that produces 50 or 60-cycle AC electricity. Gears connect the low-speed shaft to the high-speed shaft and increase the rotational speeds from about 20 to 25 rotations per minute (rpm) to about 1,000 to 2,000 rpm [1]. As the wind mill encounters the extreme environmental and mechanical pressure, the lubricant plays a vital role in successful running of wind turbine. The lubrication specifications for wind turbine gearbox are more stringent than those for industrial gear applications. As the lubricant is used in offshore, there is a need for extended life of lubricant and gearbox. The unreliable wind speed i.e. high-load/low-speed conditions that arise when winds are light can possibly lead to the breakdown of the lubricating film on gears and bearings, the gear lubricant should have good adhesive properties in addition to high load carrying and antiwear properties for a longer gear and bearing life. Considering these severe operating conditions of wind turbine gear box in wind mill we have attempted to develop an open gear lubricant for lubrication of yaw system.

Experimental Details

A) Preparation of Lithium Calcium Mixed Soap Grease

For development of open gear lubricant for yaw system Lithium Calcium mixed soap grease was selected as base grease. Lithium Calcium mixed soap grease has better water washout resistant property. This mixed soap grease was prepared by conventional method. The base oil viscosity was selected ISO VG 460 grade. The grease was prepared in NLGI 3 consistency range.

The grease was tested for following characteristics in addition to other regular grease tests.

1. Consistency test (ASTM D 217)
2. Drop point (ASTM D 566)
3. Copper corrosion (ASTM D 4048)
4. Oxidation stability test (ASTM D 942)
5. Roll stability (ASTM D 1831)
6. Emcor Rust test (ASTM D 6138)

(B) Preparation of Open Gear Lubricant

The open gear lubricant was prepared by using this base grease. This base grease was further fortified with high viscosity base oil to get better lubricity & high adhesiveness of gear lubricant on gear teeth. Antioxidants rust & corrosion inhibitor were incorporated to meet the requirements of humid conditions. Selection of EP additives was done very carefully to get desired EP characteristics. The load carrying capacity is very crucial for open gear lubricant in wind turbine gear box as there is no control in wind speed and wind direction. The gear box faces variable wind speed. Considering the high shock load & torque requirements of gear, nano Tungsten Disulfide having load carrying and antiwear capabilities was used. The consistency of open gear lubricant was maintained at NLGI 1.5 range for better mobility. High viscosity oil was used for better lubricity and adhesiveness on gear teeth. The developed open gear lubricant was tested for following parameters.

1. Consistency test (ASTM D 217)
2. Drop point (ASTM D 566)
3. Series of Four Ball Extreme Pressure Test conducted i.e. load wear index and wear scar diameter and weld load (ASTM D 2596)
4. Timken OK load test (ASTM D 2509)
5. Emcor rust test (ASTM D 6138)

The open gear lubricant was also tested for coefficient of friction by Universal Tribometer.

The test conditions were as under.

1. Load - 300 N
2. Temperature - 600°C
3. Frequency - 50 HZ
4. Time - 120 minutes
5. Contact - Pin-on-disk mode

Results and Discussion

The test results of base grease are provided in table 1. The results of base grease shows good structure stability as evidenced by 100,000 stroke worked penetration and roll stability test. There was a minimum oil separation in the product, as evidenced by oil separation test. This shows that the product has good structural and mechanical stability for longer life of gear lubricant. The product is required to pass the Emcor rust test, as there is humid climate in sea and sea shore and salty atmosphere prevails in sea. The test results of open gear lubricant are provided in Table 2. The grease was adjusted in NLGI 1.5 consistency for better mobility. Having very high viscosity base oil in open gear lubricant it has very good adhesiveness on the gear surfaces and resulting lubricity. The open gear lubricant passes the Emcor rust test. The series of Four ball EP test results i.e. higher load wear index, higher four ball OK load and higher weld load and low wear scar diameter reveal that the developed product can withstand a high shock load and torque on gear. This is also supported by high Timken OK load test. The developed open gear lubricant has shown very low coefficient of friction. This will help in minimal heat generation and enhanced energy efficiency.

Conclusions

The base grease has very good structural and mechanical stability. The gear lubricant has good mobility and adhesiveness on gear surfaces. The product passes in rust test as evidenced by Emcor rust test. The developed open gear lubricant has good load carrying capacity, as evidenced by higher load wear index, higher four ball OK load and higher weld load and low wear scar diameter. The product has shown higher Timken OK Load. Thus the developed product can withstand a high shock load on gear. The developed open gear lubricant has shown very low coefficient of friction.

Table 1. Test results of Base Grease (Lithium Calcium Mixed soap)

Characteristics	Test Results	Target	Test Method
1. Appearance	Smooth & homogenous	Smooth & homogenous	Visual
2. Colour	Amber	Amber	Visual
3. Consistency, NLGI	NLGI 3	NLGI 3	NLGI
4. Consistency,@ 25°C Worked, 60 X Worked, 1,00,000 X	235 236 262	+ 10 of 60 220-250 +30 of 60	ASTM D 217
5. Copper corrosion, @ 100°C, 24 hrs.	Passes	Passes	ASTM D 4048
6. Drop Point, °C	194	180	ASTM D 566
7. Wheel bearing test Leakage by mass, g	1.65	5 max	ASTM D1263
8. Roll Stability, %change	4.6	10 max	ASTM D1831
9. Water wash out test @ 80 °C % wt. loss	4.8	10 max.	ASTM D1264
10. Oxidation Stability, drop in pressure, psi, max	6	10	ASTM D 942
11. Emcor Rust Test	0,0	0,0	ASTM D 6138

Table 2. Test Results of Open Gear Lubricant

Characteristics	Test Results	Target	Test Method
1. Colour	Dark brown	Dark brown	Visual
2. Consistency, NLGI	NLGI 1.5	NLGI 1.5	NLGI
3. Consistency, @ 25°C Worked, 60 X	306	290 - 320	ASTM D 217
4. Copper corrosion, @ 100°C, 24 hrs.	Pass	Pass	ASTM D 4048
5. Drop Point, °C	176	170	ASTM D 566
6. Emcor Rust Test	0,0	0,0	ASTM D 6138
7. EP properties Load wear Index, kg Four ball OK Load, kg Four ball weld Point, kg Four ball wear scar dia, mm	 132 800 820 0.35	 120 750 800 0.40	 ASTM D 2596 ASTM D 2596 ASTM D 2596 ASTM D 2266
8. Timken OK Load, lb	65	60	ASTM D 2509
9. Coefficient of friction	0.075	0.10	DIN 51834

References

1. Deirdra Barr, Ethyl Petroleum Additives Ltd., Modern Wind Turbines: A Lubrication Challenge, Machinery Lubrication
2. Thomas J. Risdon, Molybdenum Disulfide in Greases A Review, NLGi spokesman, VOL 69, 12, 2006

Lubrication of Hub Bearing Units in Cars

Dr. Martin Schweigkofler
Klüber Lubrication München KG, Munich,Germany
Martin.schweigkofler@klueber.com

Heiko Stache
Klüber Lubrication München KG, Munich, Germany

Dr. Martin Schmidt-Amelunxen
Klüber Lubrication München KG, Munich, Germany

Dr. Marius Kuhn
Klüber Lubrication München KG, Munich, Germany

Abstract

The lubrication of hub bearings in passenger cars is becoming increasingly challenging: cars are becoming heavier while hub bearings are becoming smaller. As a consequence, bearing loads are increasing. Additionally, bearing lifetime requirements are rising. High driving speed and corresponding braking operations cause higher temperatures in the hub bearing. The lubricant used must therefore protect the hub bearing reliably against corrosion and wear during the entire lifetime of the car of several thousand hours, also under unfavourable conditions like (salt) water ingress, high mechanic shear stress, temperatures up to 140 °C and under micro oscillation. A Klüber hub bearing grease is taken as an example to show the correlation between lubricant concept and functionality in the hub unit. Relevant physical and chemical lubricant data and some mechano-dynamic rolling bearing test results are presented and discussed for this purpose.

1. Introduction

In this paper a proven wheel bearing grease of Klüber is to be compared, based on its recipe, with two other wheel bearing greases in relation to its water resistance, its high temperature properties and service life characteristics, as well as its suitability for low temperatures and for protection against wear caused by microoscillations. The composition of the three lubricants is given in table 1. For car wheel bearing greases, as a matter of preference greases with a base oil viscosity of between 50 and 150 cst at 40°C are used, in warmer regions with a tendency to higher viscosity [1]. At base oil viscosities < 40 cst, a continuous lubricating film is no longer ensured at elevated temperatures, conversely viscosities > 250 cst result in increased frictional drag in the wheel bearing. The Klüber grease as well as grease A and B are in the proposed range with viscosities of 130 cst, 105 cst and 65 cst respectively. All three greases compared are on a mineral oil base, the Klüber product also contains a portion of PAO (polyalphaolephine). All greases are available with a very similar consistency (NLGI 2 or slightly softer) and are thickened with urea, the Klüber hub bearing grease also contains a portion of calcium-complex soap.

Table 1: Composition and basic properties of test greases

	Klüber product	Grease A	Grease B
Base oil	PAO + mineral oil	Mineral oil	Mineral oil
Base oil viscosity at 40°C [cst]	130	105	65
Thickener	Urea + Ca-complex	Urea	Urea
Consistency [1/10 mm]	291	301	297

2. Water resistance

A major challenge for the lubrication of hub units is a high water resistance and compliance with the requirement on the lubricant to retain essential properties even with increased water content. Despite capping the hub bearings, the infiltration of the lubricant by water due to splash water or increased atmospheric humidity cannot be completely avoided. In Europe the situation is even more severe due to the addition of road salt in winter to prevent from black ice.

The water resistance of a lubricating grease depends to a large extent on the thickening agent used. Sodium and potassium-soap greases have particularly poor water resistance. On the other hand, urea-thickened greases and calcium-complex soap greases are highly water resistant [2, 3]. Calcium-complex soap greases in particular have a high tolerance to increased water content. In this case the water is stably incorporated into the grease structure without degradation of the essential lubricant properties. This effect can be explained as follows: calcium has a very high hydration enthalpy, which is due to the low ionic radius of the Ca^{2+}. Here in the most stable form, octahedral hexahydrate is formed. Tests in India on the thermal behaviour of calcium malonate hydrate using differential thermal analysis (DTA/TG) show that at 158°C the dihydrate changes to the monohydrate form. In turn this form loses the last water of crystallisation only at 192°C as per [4]

$CaC_3H_2O_4$ x 2 H_2O (158°C) → $CaC_3H_2O_4$ x H_2O +

H_2O $CaC_3H_2O_4$ x H_2O (192°C) → $CaC_3H_2O_4$ + H_2O

Very similar behaviour occurs in a calcium-complex soap grease: Ca^{2+} is also coordinated here by dicarboxylic acids. Figure 1 shows the DTA curve for a hydrous PAO/calcium-complex soap grease under the following test conditions: nitrogen as carrier gas, temperature increase 1 K/min. The three endothermic signals in the temperature range 100°C – 200°C are due to evaporation processes. At 100°C water lying freely in the lubricant evaporates. The evaporation at approx. 120°C is due to water that stems from the dihydrate in the soap structure. Finally, the water evaporating at approx. 175°C stems from the monohydrate in the calcium-complex soap.

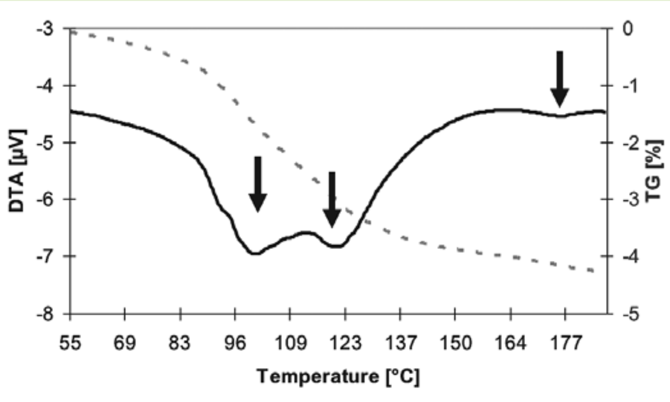


Fig. 1: Dynamic thermal analysis and thermo-gravimetry of a PAO/Ca-Complex grease

To determine the amount of water absorption and water delivery of a grease, the following static test can be done: approx. 0, 5 g of grease is applied on a metal wire net (JIS Z8801, 30 x 10 x1 mm) and immersed in water for 70 h at 90°C. Take it out and keep it at 60°C for 15 minutes. Measure the weight and calculate the water content. After that, keep it for 16 h at 80°C to evaporate the water in the grease, then measure the weight and calculate weight loss. In Table 2 the water absorption and water delivery properties according to this test can bee seen. Obviously the Klüber product has a high water absorption capacity and keeps the water strongly in the grease structure. Only 0,5 % of the 3,5 % water could be removed by evaporation under the given conditions.

Table 2: Water absorption and water release properties for different greases.

	Klüber product	Grease A	Grease B
Water content of grease after immersion in water for 70 h at 90 °C	3.5 %	3.3 %	1.7 %
Weight loss after water evaporation (16 h at 80 °C)	0.5 %	1.1 %	1.4 %

If water penetrates the lubricant, according to Matsumoto the service life of the greased bearing can be reduced dramatically by more than 90 % [5]. According to tests by Yasui et al. [6] the infiltration of lubricating greases by water is often linked with a decrease in consistency, at the same time other grease parameters such as oil separation may also change. The effect of water on the shear stability of the Klüber product as well as grease A and B is shown in table 3. For this purpose the lubricant is exposed to a roll stability test according to ASTM D 1831. At a temperature of 90°C the lubricant is subjected to reciprocations in a hollow cylinder by a roller weighing 5kg for a period of 20 h. The change in worked penetration is determined and taken as a measure of the shear stability. In a second similar test, 10 % water was added to the lubricant.

Table 3: Change of consistency after Shell roller test with and without water. Conditions: 90 °C, 20 h

	Klüber product	Grease A	Grease B
Consistency of fresh grease	291 1/10 mm	301 1/10 mm	297 1/10 mm
Consistency after Shell roll test	336 1/10 mm	338 1/10 mm	334 1/10 mm
Consistency after Shell roll test, 10 % mass water added	339 1/10 mm	350 1/10 mm	324 1/10 mm

As can be seen in the diagram, all 3 fresh greases showed some softening after the shell roller test and all of them ended in a very similar consistency of between 334 and 338 1/10 mm. If 10 % water was added to the Klüber product and the test was performed, its softening was only minimal higher to 339 1/10 mm. In case of grease A the water-induced softening was slightly higher but overall the shear stability was quite good. The softening of grease B in the presence of water was even reduced. This behaviour is excellent. A very low softening of the grease is important, as the lubricant in a hub bearing is subjected to a high shear load, especially if tapered roller bearings are used. Sometimes greases of NLGI class 3 are used for the lubrication of wheel bearings to establish a certain amount of reserve against excessive shear-related softening or loss of structure due to the infiltration of water. Based on our experience, this precaution is unnecessary with a balanced lubrication concept; the concomitant disadvantages such as unsatisfactory channeling behaviour under the effect of vibration are also significant. The results from Endom [7] also confirm this view.

According to tests by Tchemtchoua [8], the water content of lubricating grease also has a crucial effect on the wear protection properties. The wear determined on an FE8 testing machine (angular contact ball bearing, 80 kN, 7.5 rpm, continuous running) for dry grease was 12.5 mg. 0.5 % water in the lubricating grease resulted in wear of 265 mg, an increase in the water content to 10 % caused wear of 995 mg. For this paper FE8 tests were not used and the effect of water on the wear protection properties of wheel bearing greases was determined based on

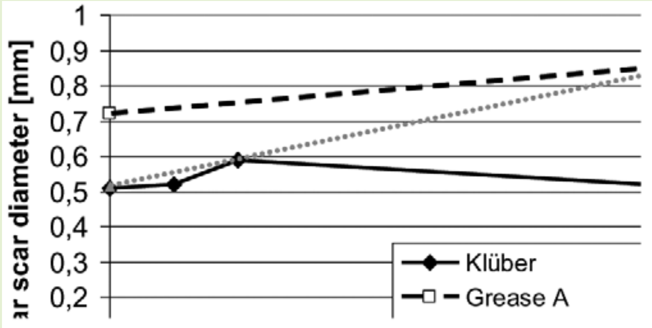


Fig. 2: Four ball wear test results dependent on water content in grease

model tests. Figure 2 shows the effect of water in the lubricating grease up to 5 % by mass on the wear protection properties of the Klüber grease in comparison to grease A and B. The four ball long-term wear (1h, 400N, RT) according to DIN 51350 for the Klüber product produced a wear scar of 0.51-0.59 mm, there is no trend to an increase in the wear with increasing water content. Conversely, with grease A and B there is a significant increase in the wear after the addition of 5 % water. For grease A the wear increases from 0.72 to 0.87 mm, in the case of grease B the wear scar increases from 0.51 to 0.90 mm.

In the case of the four ball welding load test (see figure 3), for the Klüber product there is a slight reduction in the welding load from 3200 N for the fresh grease to 2600 N for the grease with 5 % water added. However, this welding load is still significantly higher than the welding load for grease A and B, 1500 N (dry fresh grease) and 1800 N respectively and unchanged 1500 N (grease with 5 % water added).

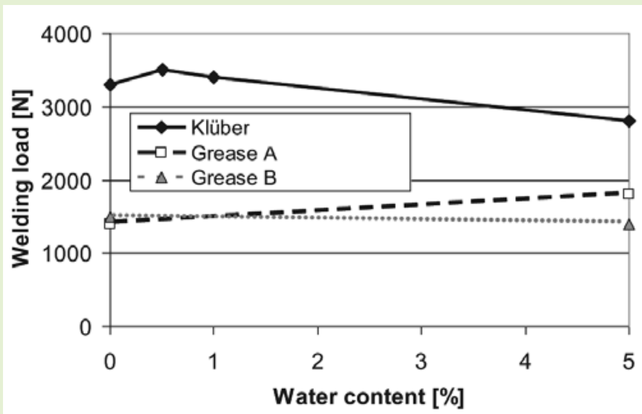


Fig. 3: Four ball welding load test results dependent on water content in grease

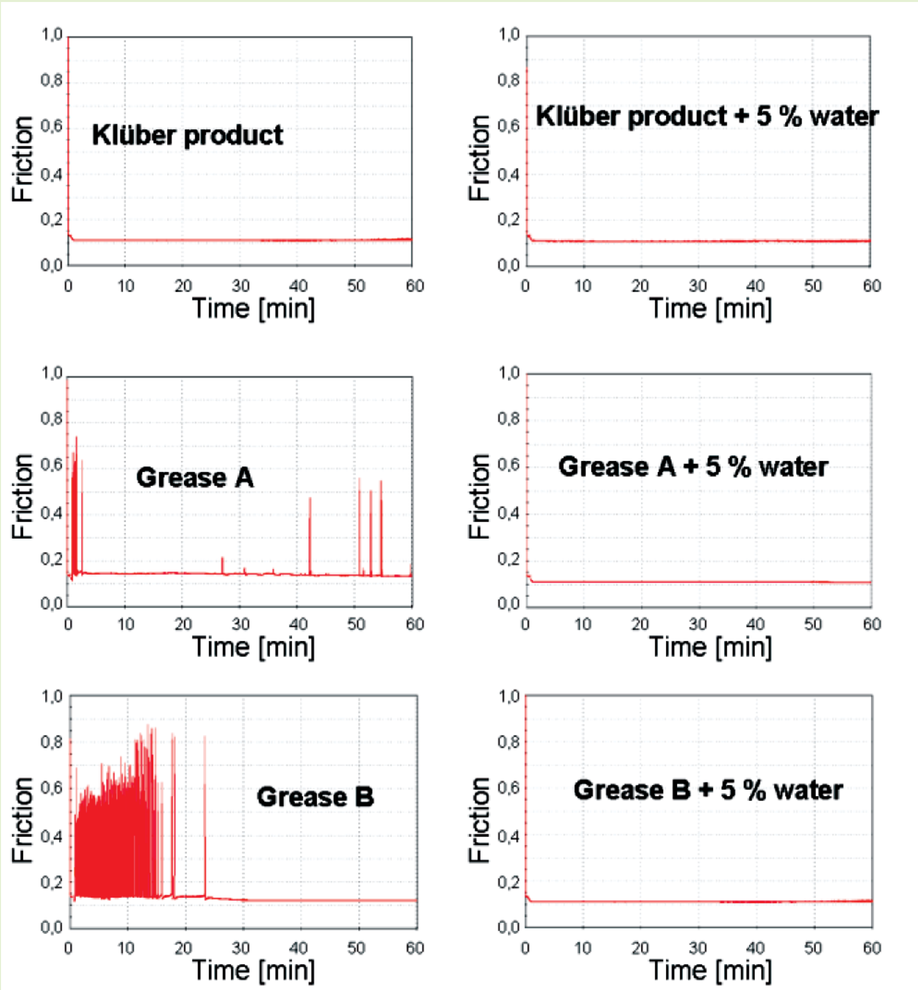


Fig. 4: SRV tests of greases with and without water. Test conditions: 400 N, RT, 50 Hz, 6 mm amplitude

Test runs on the oscillation friction wear tester showed that for the Klüber hub bearing grease, both in the fresh state and after the addition of 5 % water, the friction remained unchanged and constantly low. Conversely, in the dry state grease A and B have quite a few welding peaks, as well as generally higher friction (see figure 4).

Furthermore the lubricant must not be dissolved by water and the thickener's adhesion to the metal surface must not be reduced in the presence of water. Otherwise lubricant starvation due to grease leakage as well as corrosion could occur.

Figure 5 shows the principle of a water wash-out test according to DIN 51807. In this test a defined water jet is directed onto a capped deep grove ball bearing (600 rpm, 80°C, 1 h) and the grease loss in weight percent is determined. A typical grease requirement for hub units is max weight loss of 2 % which is fulfilled by the Klüber product and grease B. Grease A showed an inacceptable grease leakage of 9.5 %.

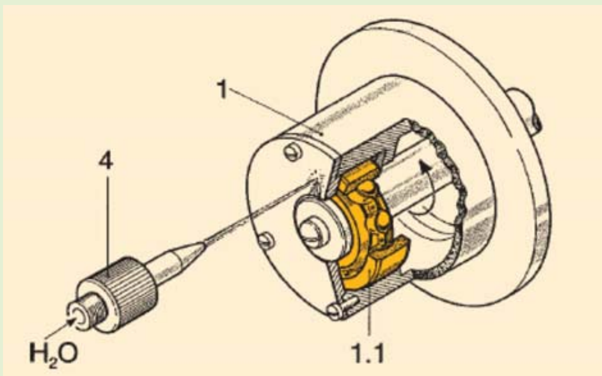


Fig. 5: Water washout test according to DIN 51807

	Klüber product	Grease A	Grease B
Water washout	2.0 %	9.5 %	1.5 %

The SKF-EMCOR test according to DIN 51802 is a commonly used mechanic-dynamic bearing test to check for corrosion protection. The self-aligning ball bearing used is subjected to defined cycles of standstill and running at a speed of 80 rpm for the duration of the test of 1 week. Normally the bearing is filled with a mixture of lubricating grease and distilled water. Wheel bearing greases must have increased corrosion protection properties. Under tightened test conditions (1 week, 3 % salt water) grease B showed excellent corrosion protection properties (grade 0, no corrosion). Also the Klüber hub bearing grease showed good performance with corrosion grade 1 (traces of corrosion), whereas the anticorrosion properties of grease A were quite poor (grade 4, heavy corrosion) under these conditions.

3. High temperature and life time properties

Hub units are these days designed for the life of the car, and accordingly the lubricant must also function for approx. 250000 km or 5000 working hours under the prevailing conditions. The temperatures that occur in the wheel bearing are up to 140°C, after extreme braking manoeuvres the lubricant may even be subjected to 150°C. Wheel bearing greases must have correspondingly good thermal stability so they do not age prematurely. This stability can be achieved both by the selection of stable base oil, thickening and additive components, as well by a corresponding lubricating grease recipe with, e.g., correspondingly low oil separation. Structural elements of mineral oils and PAOs are shown in figure 6. It can be seen in the figure that particularly naphthene base mineral oils are the target of thermo-oxidative attack due to the related formation of the energetically favoured R3C. radicals.

The comparison greases A and B are both fully mineral oil-based. In the case of the Klüber product, a base oil mixture comprising paraffinic mineral oil and a

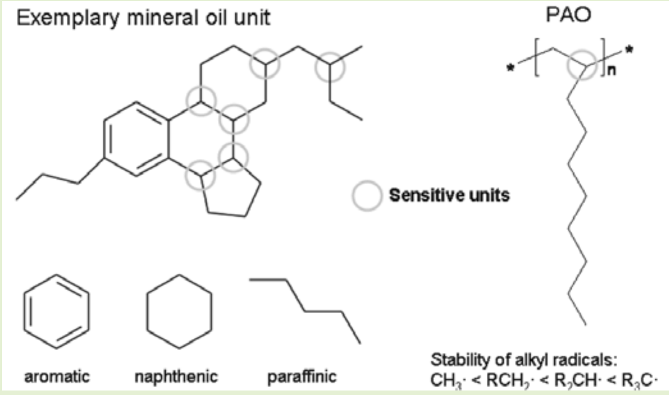


Fig. 6: Structural elements of mineral oil and PAOs

synthetic hydrocarbon (PAO) was selected, which has a generally higher thermal stability. This situation is due to its extremely close molecular weight distribution compared to mineral oil, see fig. 7.

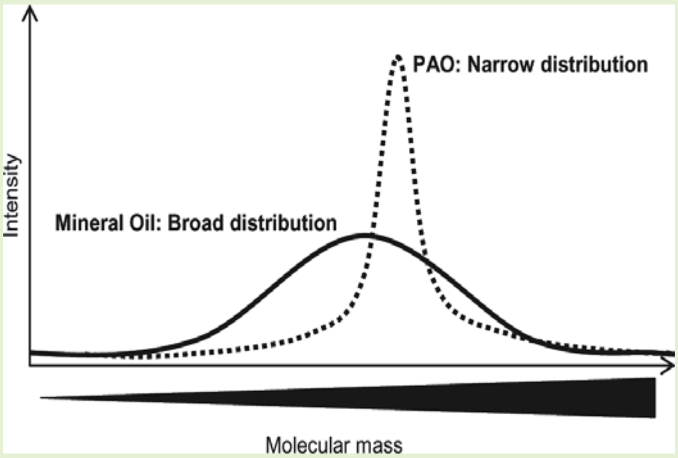


Fig. 7: Illustration of the molecular weight distribution of PAOs versus mineral oil.

Accordingly at the same viscosity the tendency of a PAO to evaporate is significantly reduced. In the case of the Klüber hub bearing grease a low-viscosity PAO was selected and mixed with a more viscous and therefore also very low evaporation mineral oil. Accordingly, this mixture has good thermal stability. In table 4 evaporation losses for the Klüber product at 100°C, 120°C and 160°C are given and compared to the values for grease A and B.

Table 4: Evaporation loss according to DIN 58397, 140°C

	Klüber product	Grease A	Grease B
Evap. loss after 24 h	1.7 %	1.7 %	5.1 %
Evap. loss after 48 h	2.4 %	2.8 %	7.1 %
Evap. loss after 72 h	3.1 %	3.7 %	8.8 %
Evap. loss after 144 h	4.6 %	6.1 %	14.8 %
Evap. loss after 168 h	4.9 %	7.0 %	15.7 %

All three wheel bearing greases tested are thickened with urea, the Klüber product also contains a portion of Ca-complex soap. The advantage of urea-thickening agents is, on the one hand, that as radical interceptors they have a certain degree of anti-oxidant action [8] and as a result they can increase the service life of the grease.

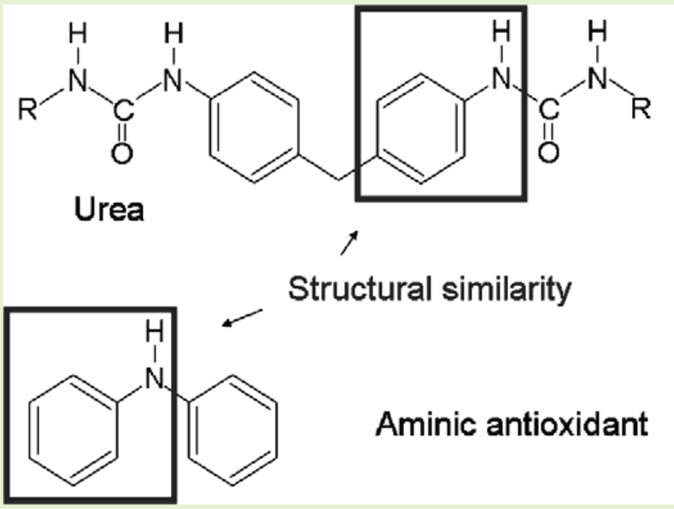


Fig. 8: Structural similarities of urea and aminic antioxidants

On the other hand, ureas with aliphatic amine components have an extremely high degree of oil retention. This effect is exploited in the Klüber bearing grease to keep the oil separation low at elevated temperatures. In figure 9 FTMS oil separation figures at 100°C to 160°C over a period of 24 h and 300 h are shown for the greases tested. The significantly reduced oil separation for the Klüber product is obvious. A low oil separation is advantageous because due to the reduced oil surface area, evaporation losses and thermo-oxidative attacks are minimised and longer grease usage is possible.

The utilisation of drum brakes in cars in older model

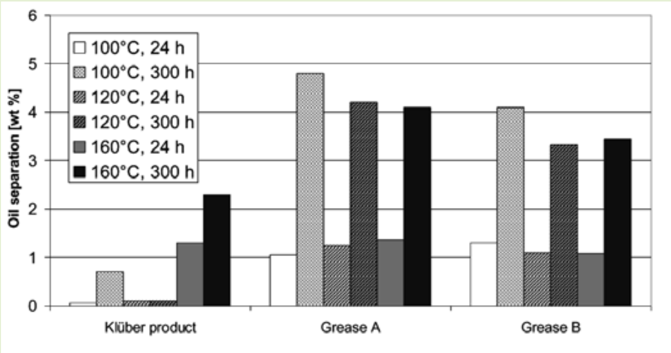


Fig. 9 : Oil separation according to FTMS 791°C 321.3

series required the usage of tapered roller bearings in hub units; in the meantime this situation has changed due to the increasingly frequent usage of disk brakes. As a consequence these days predominantly double-row angular contact ball bearings are used. In comparison to tapered roller bearings this type of bearing requires a significantly lower oil separation in accordance with DIN 51817 [10]. Lubricants for tapered roller bearings often show DIN oil separations of approx. 3 %, for ball bearings the recommended DIN oil separation is approx. 1 % [10]. The Klüber product shows a DIN oil separation of approx. 1.5 %, for grease A and B these values are not available.

To determine the service life and upper service temperature of lubricating greases the R0F rolling bearing grease tester according to SKF may be used. The radial and axial loads in this test are quite low (50 N and 100 N, respectively), so the transferability to conditions in hub bearings is limited. Nevertheless this test gives good indications about long term grease performance at elevated temperatures. Figure 10 shows the bearing failure probability of Klüberplex BEM 34-132 evaluated by means of WEIBULL statistics. Test conditions were as follows: Temperature 140°C, speed factor ndm = 330 000. The L10 value of 1501 h and the L50 value of 2124 h impressively demonstrate the performance of lubricating grease in angular contact ball bearings.

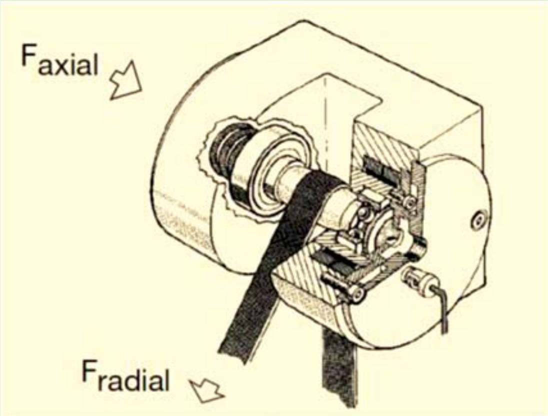


Fig. 10: Principle of R0F and performance of the Klüber hub bearing grease at 140°C

WEIBULL-evaluation, 90 % confidence belt	Klüber product
L10	879 h < 1501 h < 2563 h
L50	1617 h < 2124 h < 2791 h
β	5,4

A more stringent test to determine service life and upper service temperature of bearing lubricants is the FE 9 according to DIN 51821. This is a ball bearing test rig operated at medium load and speed. Figure 11 shows the WEIBULL statistics of the Klüber product at 140°C, 6000 rpm and axial load of 1500 N (assembly A). Again an L10 value of 46 h and L50 value of 201 h demonstrate suitability as a lubricating grease for bearings up to 140°C. Grease A and B under these conditions resulted in L50 values of 81 h and an unacceptable 11 h, respectively.

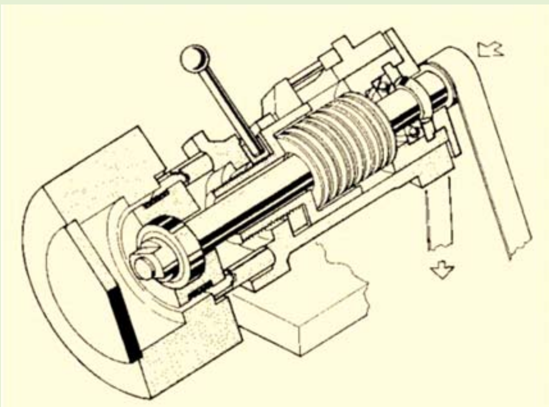


Fig. 11: Draft of FE9 test unit and performance of greases at 140°C, 6000 rpm, 1500 N, assembly A

	Klüber product	Grease A	Grease B
L10	46 h	17 h	7 h
L50	201 h	81 h	11 h
β	1,3	1,2	3,7

Rolling bearings and therefore also wheel bearings are protected with an anticorrosion oil prior to the application of grease. In the case of the Klüber hub bearing grease it was tested as to what extent the expected service life can be influenced by a balanced system of anticorrosion oil and wheel bearing grease. It is very well known in the literature that corrosion protection additives and other surface-active additives influence each others' effectiveness [8, 11]. During these tests FE9 bearings were cleaned, anticorrosion oil Klübersynth BZ 44-4000 applied prior to greasing and a further FE9 test carried out under the stated conditions. Figure 12 shows the related WEIBULL analysis for the Klüber product.

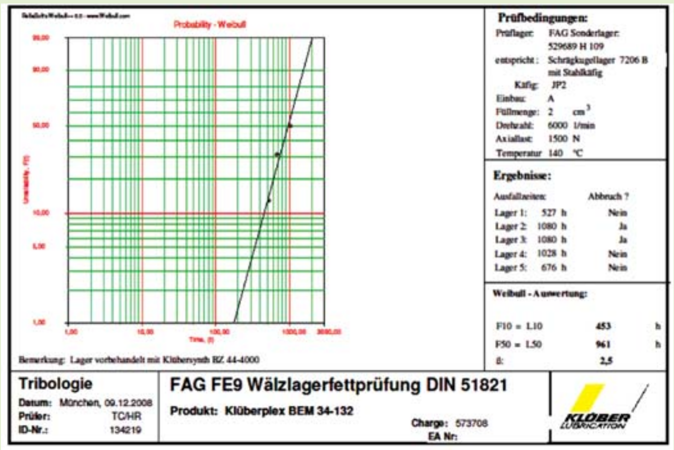


Fig. 12: FE9-performance of the Klüber product at 140°C with optimized corrosion protection on bearings

Values are results from one-time measurement and serve for information only. No assurance of values/ properties of the series-produced product. It is clearly possible to significantly further increase the service life of the grease by using an optimised bearing anticorrosion agent. If possible, this fact should be discussed with the bearing manufacturer prior to the application of the grease.

4. Suitability for low temperatures and suitability for protection against false-brinelling

A requirement on wheel bearing greases in Europe is the possibility of use at temperatures down to –35°C. At these temperatures it is to be possible to move the wheel bearings silently and with low torque. This characteristic can be achieved with low oil viscosities and by using synthetic hydrocarbons with their significantly higher viscosity index compared to mineral oil. In the case of the Klüber hub bearing grease, despite the increased base oil viscosity of 130 cst compared to grease A and B, it was possible to achieve excellent low-temperature behaviour due to the use of PAO. The low-temperature behaviour of lubricating greases is normally checked based on the flow pressure in accordance with the standard DIN 51805 or based on the low-temperature torque in accordance with IP 186. In the case of the latter test a ball bearing is used, accordingly this test better simulates the behaviour of lubricating greases in a wheel bearing. Torques according to IP 186, measured at –35°C are given in table 5. Only the Klüber hub bearing grease was able to meet the limits required by many OEMs of a start torque max 1000 mNm and a run torque max 100 mNm. In particular, grease A with a run torque of 177 mNm had significantly higher values. 7/8

Table 5 : IP 186 low temperature torques at –35°C

	Klüber product	Grease A	Grease B
Starting torque	179 mNm	661 mNm	320 mNm
Running torque	78 mNm	177 mNm	101 mNm

So-called false-brinelling damage was first observed on car wheel bearings during the transport of fully assembled cars from Europe to America by ship. Vibration due to the diesel engines as well as the inadequate damping on the transport decks caused wear scars on the functional surfaces of the new and practically unused wheel bearings. Transport of vehicles by rail is also critical in relation to false-brinelling damage and it is now known that even on vehicles driving past parked cars, the wheel bearings are subjected to micro-oscillations that shorten the service life. From practice it is known that grease-lubricated bearings are more susceptible to standstill marks than oil-lubricated bearings, which results in the conclusion that the channeling behaviour has a major effect on the production of these marks. The latter is also affected by good low temperature behaviour. Thiede [12] therefore suggests the inclusion of rippling protection tests at temperatures between –30 °C and –10 °C for the qualification of wheel bearing greases. In the literature various testers have been proposed for testing the wear protection behaviour of lubricating greases against false-brinelling damage, these include the Fafnir testing machine in accordance with ASTM-D 4170, the SNR-FEB 2 tester or the HRE-IME tester [8]. For larger rolling bearings and oscillating movements, e.g. in truck hub units, the modified FE8 rolling bearing grease tester in accordance with DIN 51819 [13] is also suitable. Due to the varying oscillation amplitude that is used during the different tests, the scopes vary widely. While during the Fafnir test the rolling elements perform a real rolling motion, during the HRE-IME test real micro-oscillation is used. The SNR-FEB 2 test is normally carried out at an oscillation amplitude of + 3° and therefore lies between the Fafnir test and the HRE-IME test in relation to the oscillation range. In table 6 wear rates of different greases are given after the SNR-FEB 2 test at + 3°.

Table 6: KLM FAB test, –20°C, + 3°, test duration 5 h

	Klüber product	Grease A	Grease B
wear [mg]	66	83	82

During the tests carried out here additionally a modified SNR-FEB 2 test with reduced oscillation amplitude of 0.06° was undertaken to better represent the problems of micro-oscillations. As a consequence significantly higher requirements are placed on the lubricating grease in relation to protection against rippling [10]. The tests were carried out at a temperature of –20°C over a period of 50 hours. After this time period it is possible to differentiate between different lubricants.

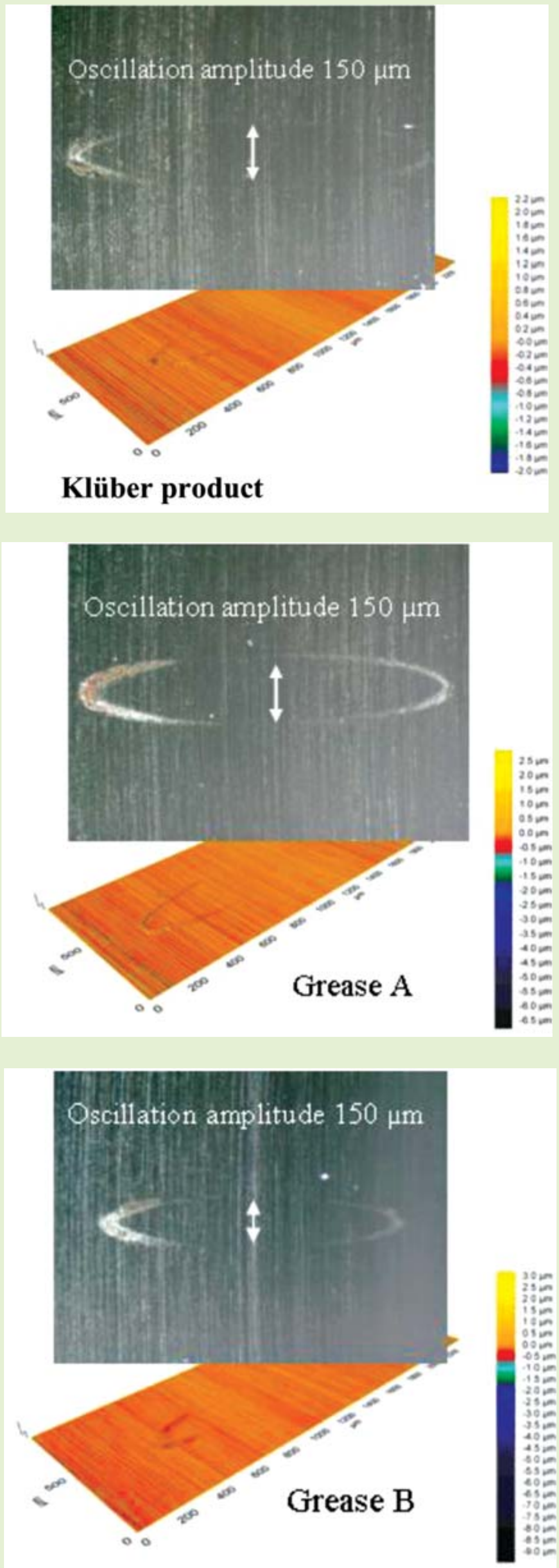


Fig. 13: Wear marks of greases tested by modified SNR-FEB 2 with reduced amplitude of 0,06° at –20°C

The wear scars produced after this test were checked and analysed using white-light interferometry. In figure 13 such wear scars are shown for the greases studied.

The wear volumes for the three greases compared after the SNR-FEB 2 test can be seen in table 7. Again the excellent low-temperature behaviour of the Klüber hub bearing grease was demonstrated with a correspondingly low wear depth.

Table 7: Wear volumes by modified SNR-FEB 2 with amplitude of 0.06° at –20°C

	Klüber product	Grease A	Grease B
wear volume	660 μm^3	1400 μm^3	700 μm^3

5. Summary

Important requirements on wheel bearing greases have been identified as well as a method for demonstrating the suitability of lubricating grease based on mechanic-dynamic tests and laboratory tests. Based on the recipe of the Klüber hub bearing grease it has been explained how physicochemical properties of a grease are related to the performance of the lubricant in the wheel bearing. The stated lubricating grease is able to meet also the increased requirements to be expected in the future in relation to bearing load and service life.

References

1. Patent application US 20090003742: Grease Composition for hub unit bearing, and hub unit bearing for vehicle, 2009.
2. Möller, U. J.; Nassar, J.: Schmierstoffe im Betrieb. 2. Auflage. Springer-Verlag, 2002.
3. Bartz, W.J.: Schmierfette- Zusammensetzung, Eigenschaften, Prüfung und Anwendung. Expert Verlag, Band 500, 2000
4. Varughese, P.A.; Saban, K.V.; George, J.; Paul, I.; Varghese, G.: Crystallization and structural properties of calcium malonate hydrate, Journal of materials science, 39, 2004, pp 6325-6331.
5. Matsumoto, Y.; Murakami, Y.; Oohiri, M.: Rolling contact fatique under water-infiltrated lubrication, Bearing steel Technology, ASTM STP 1419 2002, pp 226-243.

6. Yasui, H.; Yoshida, T.; Komiya, H.; Muzychenki, W.: Effect of water on the performance of railroad roller bearing grease, Journal of the american society of lubrication engineers (ASLE), 36 (6), 1980, pp 353-360.
7. Endom L.; Gruber, S.: Schmierfette zur Verhinderung von Schwingungs-verschleiß in Radlagern, Tribologie und Schmierungstechnik, 36 (3), 1989, pp 130-133.
8. Tchemtchoua, B.: Untersuchung des Wassereinflusses auf die Schädigungen gefetteter Wälzlager, Dissertation RWTH 2008.
9. Patent DE10201937B4: Verfahren zur Herstellung von mit Additiven versetztem Ammoniumdinitramid (ADN), 2005.
10. Kühl, R.: Ölabgabeverhalten bei tiefen und hohen Temperaturen: Einfluss auf den Temperature in satzbereich eines Schmierfettes in Wälzlagern. Gesellschaft für Tribologie, Fachtagung Göttingen, 1998.
11. Totten, G. E.; Westbrook, S. R.; Shah, R. J.: Fuels and lubricants handbook: technology, properties, performance, and testing, ASTM International, 2003.
12. Thiede, K-U., Deters, L.: Schmierungsverhalten bei oszillierenden Gleit- und Wälzbewegungen, FVA 315 II 2003.
13. Karbacher, R.: Fettschmierung von Wälzlagern bei oszillierender Beanspruchung, Tribologie und Schmierungstechnik, 45 (15), 1998, pp 1-24

Evaluation of Frictional Properties of Lubricating Greases

Nahid Parveen, V.P. Deshmukh & .K. Sachdeva
Siddharth Petro Products,
Gurgaon, Haryana

Abstract

Lubricating grease Industry is constantly looking forward for eco friendly and heavy metal free additives to be used in lubricating greases. Antiwear additives and friction modifiers play an important role in reducing the friction and wear there by improving the performance of the greases. Lithium greases being the widely used greases in India, the paper describes the evaluation of eco friendly antiwear additives in lithium and lithium complex greases. For comparison, the commercially popular antiwear additive ZDDP (Zinc dialkyl dithiophosphate) and a metal containing antiwear additive have also been evaluated for their frictional properties such as coefficient of friction and wear scar dia on a Four Ball Tester. The various combinations of these additives have also been tested to check their synergistic action.

INTRODUCTION

The main function of lubricating grease is to reduce friction and wear. Conventional greases contain various types of additives in amounts depending upon the operating conditions under which the grease is to be used to impart some desirable characteristics to the greases such as oxidation stability, load carrying ability, corrosion resistance, friction reduction, tackiness etc. The extreme pressure/antiwear additives normally used are zinc salts such as zinc dialkyl or diaryl dithiophosphate, borates, substituted thiodiazoles, amine phosphates, sulphurised fats, organo phosphates etc.

Where friction is there, heat is generated indicating that some energy is lost. Wear and friction reduction in greases are such important parameters that in some high performance greases minimum levels of friction modifiers and antiwear/extreme pressure agents are specified.

It has been shown that the lubricating grease compositions with Lithium soaps and polyurea thickener and friction modifiers show improved results in coefficient of friction and wear scar dia. Addition of zinc napthanate to molybdenum sulfide plus ZDDP results in substantial reduction in friction coefficient and wear scar dia in lithium and polyurea base greases.(1) It has been reported that ZDDP and functionalized irradiated PTFE in combination gives synergistic effect in wear properties.(2) Similar studies have been carried out by So, H and coworkers and indicated that only the additives that can produce chemical films on rubbing surfaces can reduce friction more effectively. PTFE neither improves anti wear performance nor reduces friction substantially on the rubbing surfaces of steel.(3)

Friction Modifiers and Antiwear Additives Functions and mechanism

Friction modifiers are materials that modify the frictional properties of lubricants. These additives perform in mixed film lubrication regime. They interact with surfaces either by physical adsorption or chemical adsorption depending upon their reactivity. Friction modifiers are used to decrease or increase friction depending upon the application. Wide varieties of friction modifiers are reported in the literature. Organic friction modifiers are long chain molecules with a polar end group and a non polar linear hydrocarbon chain. The polar groups either physically adsorb on to the metal surface or chemically react with it while the hydrocarbon chains extend into the lubricant. These chains associate with one another and the lubricant to form a strong lubricant film.(4)

Most antiwear and extreme pressure agents contain sulphur, chlorine, phosphorus, boron or combination thereof. The use of S and P containing compounds as antiwear additives in lubricant compositions is known. In general, the sulfur and phosphorus compounds comprise alkyl acid phosphates and their amine metal salts.[5,6] With the use of sulfurised hydrocarbons such as sulfurised di isobutylene with higher sulfur content as the major component in the formulations it was inferred that active sulfur in such compounds reacted with rubbing surfaces to produce thick iron sulfide films responsible for producing lower wear and supporting heavier loads. [7, 8]

Both antiwear and extreme pressure additives function by thermal decomposition and by forming products that react with the metal surface to form a solid protective layer. This solid metal film fills the surface cavities and facilitates effective film formation, thereby reducing friction and preventing welding and surface wear.

It has also been shown that antiwear properties of sulfurised fatty oils are better than that of molybdenum dithiocarbamate, dithiophosphate and thio-carbonate.[9]

The Zinc in ZDDP, a well known antiwear agent is an environmental contaminant and the lubricant industry is under pressure to find a good, environmentally friendly alternative antiwear agent.[10]

This paper compares the frictional properties of four (A, B, C & ZDDP) commercially available antiwear agents. The antiwear agents A & B are S, P, N & Zn free and are environmentally acceptable additives. Antiwear agent C contains S & P. The performances of these three additives have been compared with ZDDP. The effect of addition of EP additive in these antiwear agents is also studied. The frictional properties are determined using of Four Ball Test machine.

MATERIALS

Base Greases : Lithium base grease was prepared using mineral oil with a viscosity of 110 cSt at 40°C. The lithium complex grease was prepared using mineral oil of viscosity 160 cSt @ 40°C and boric acid is used as complexing agent.

The properties of both the base greases are given in table 1.

Table 1 – Base Grease Properties

S.No.	Characteristics	Lithium	Lithium Complex
1.	Appearance	Smooth, Homogeneous	Smooth, Homogeneous
2	Color	Creamish yellow	Creamish yellow
3	Thickener	Lithium	Lithium complex
4	NLGI Grade	3	3
5	Drop point, °C	196	256
6	Base oil viscosity @ 40°C, cSt	130	155

ADDITIVES

We have used three (A,B,&C)commercially available anti wear agents along with the well known anti wear agent ZDDP (Zinc dialkyl dithiophosphate) and one commercial EP additive for our studies. The additives A and B are S, P and Zn free additives. All the three anti wear additives and ZDDP were used at 0.5% level to have the uniformity in comparison. The EP additive was used at 1% level. These additives were blended in lithium and lithium complex base greases.

FOUR BALL TEST APPARATUS

A Four Ball test apparatus is used to measure the friction and wear characteristics of lubricating oils and greases. In four ball tester three 12.7 mm diameter steel balls are clamped together and covered with lubricant to be evaluated, a fourth ball of same dia referred to as top ball is held in a special collet inside spindle, rotated by AC motor. The top ball is rotated in contact with three fixed bearing balls, which are immersed in grease sample. Inside the ball pot, the balls are held in position against each other by a clamping ring and force applied by tightening lock nut, additional provision to heat and control temperature of grease sample is also provided at bottom of ball pot. Normal load is applied on the balls by loading lever and dead weights placed on loading pan. The ball pot is supported above the loading lever on the thrust bearing & plunger and beneath plunger a load cell is fixed to loading lever to measure normal load.

The frictional torque exerted on the three balls is measured by frictional force load.

The four ball wear tests conducted at load 40 Kg and 75°C for duration of one hour at 1200 rpm.

TEST RESULTS AND DISCUSSION

The frictional properties of the greases were tested using Four Ball Test machine and determining the wear scar dia and coefficient of friction under the condition Load 40 Kg., 1200rpm, 75 °C and 1 Hr.

We have taken two base greases one normal Lithium base Grease and another Lithium Complex base grease.

Normal Lithium base grease was fortified with anti wear additives A, B, C and ZDDP and their combination with ZDDP. One EP additive was also evaluated in combination with anti wear additives. The same process was followed for Lithium Complex Grease.

The data generated for lithium base grease is given in Table 2 and for lithium complex is given in Table 3.

Table 2 : Lithium Grease with additives

S.No.	Additives					WSD, mm	µ
	ZDDP, %	A,%	B,%	C,%	EP,%		
1.	-	-	-	-	-	0.69	0.08743
2.	0.5	-	-	-	-	0.42	0.07135
3.	-	0.5	-	-	-	0.48	0.07784
4.	0.5	0.5	-	-	-	0.37	0.05343
5.	-	-	0.5	-	-	0.53	0.06990
6.	0.5	-	0.5	-	-	0.43	0.05912
7.	-	-	-	0.5	-	0.37	0.0346
8.	0.5	-	-	0.5	-	0.38	0.06940
9.	-	0.5	-	-	1	0.38	0.07484
10.	-	-	0.5	-	1	0.42	0.05912
11.	-	-	-	0.5	1	0.38	0.04848

Table 2 : Lithium Complex Grease with additives

S.No.	Additives				WSD, mm	µ
	ZDDP, %	A,%	B,%	C,%		
1.	-	-	-	-	0.54	0.07953
2.	0.5	-	-	-	0.45	0.08995
3.	-	0.5	-	-	0.49	0.09340
4.	0.5	0.5	-	-	0.46	0.07477
5.	-	-	0.5	-	0.52	0.09810
6.	-	-	-	0.5	0.47	0.07981

Figure 1 gives the comparative frictional properties of additive A in combination with ZDDP. The additive A in combination with ZDDP gives the lowest wear scar dia and coefficient of friction as compared to base grease with additive A and ZDDP alone. This shows that additive ZDDP gives synergistic effect with additive A to give the lowest wear scar dia and coefficient of friction.

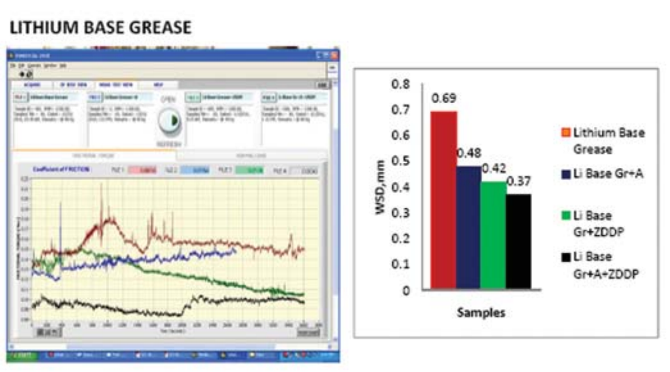


Fig. 1

Figure 2 gives the comparative frictional properties of additive B in combination with ZDDP. The additive B in combination with ZDDP gives similar results in wear scar dia. However, the combination of B and ZDDP gives lower coefficient of friction as compared to ZDDP alone. This shows that additive B also gives better frictional properties in combination with ZDDP.

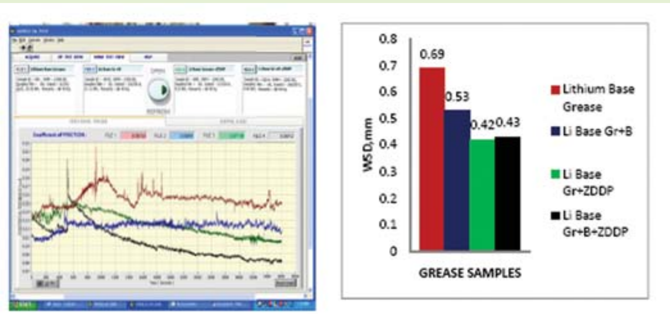


Fig. 2

Figure 3 gives the comparative frictional properties of additive C in combination with ZDDP. The additive C alone gives the best frictional properties or lowest coefficient of friction and wears scar dia. The addition of ZDDP increases coefficient of friction indicating that ZDDP has antagonistic effect in combination with additive C.

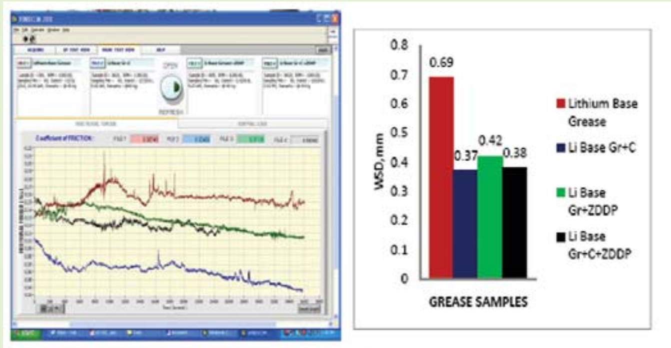


Fig. 3

Figure 4 gives the comparative frictional properties of additive A, B, C & ZDDP. The additive C gives the best performance in terms of wear scar dia and coefficient of friction among all the antiwear additives studied.

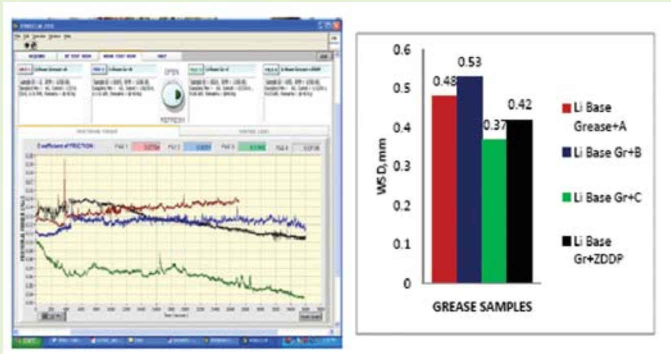


Fig. 4

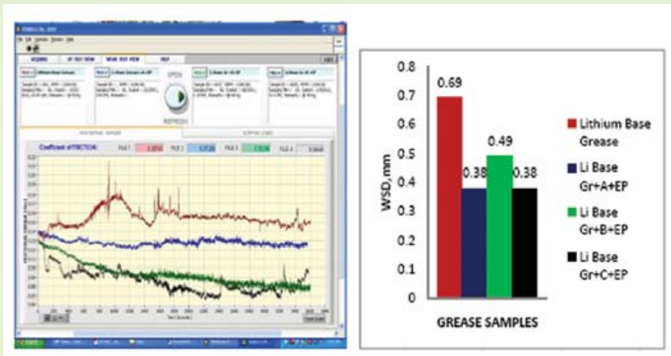


Fig. 5

Figure 5 gives the comparative frictional properties of antiwear agents A, B & C in combination with EP additive. It shows that additions of EP additive reduces the coefficient of friction and wear scar dia compare to addition of these additives alone. The reduction is different for additive A, B, and C. Athough the additive C gives the best frictional properties in combination with EP additive its coefficient of friction has gone up by addition of EP additive.

Fig. 6

Lithium Complex Grease

Figure 6 shows the comparative frictional properties of additive A in combination with ZDDP in lithium complex grease. The additive A in combination with ZDDP gives the best results as compared to base grease in combination with additive A and ZDDP alone. This shows that ZDDP gives synergistic effect with additive A in lithium complex grease too. The addition of additive A and ZDDP increases the coefficient of friction of the base grease although reduces the wear scar dia.

Fig. 7

Figure 7 shows the comparative frictional properties of additives B, C & ZDDP in lithium complex grease. Here also it is observed that additive C gives best result. The addition of additive B to base grease has increased coefficient of friction although there is slight reduction in wear scar dia. The additive C has given lower scar dia although there is not much change in coefficient of friction.

SUMMARY

The three commercially available anti wear additives were evaluated for their frictional properties and these were compared with the known widely used anti wear additive ZDDP. The combination of additives were also tested to arrive at the best combination to get the least frictional properties. Since the normal greases often contain EP additive, a combination of anti wear and EP was also evaluated. The results have been tabulated.

CONCLUSION

Based on the studies carried out it is observed that when the coefficient of friction is reduced the wear scar dia may not get reduced and vice a versa. The anti wear agent C gives the lowest coefficient of friction and wear scar dia when tested alone with base grease. The ZDDP gives synergistic effect in combination with additives A and B. Sulphur, phosphorus containing antiwear agents and ZDDP give slightly better results in frictional properties as compared to S and P free antiwear additives A and B. Additives antiwear agents A and B give very good frictional properties as compared to base grease alone although their performance is slightly inferior as compared to S,P containing antiwear agents.

ACKNOWLEDGEMENT

The authors are thankful to the management of Siddharth Petro Products for giving the permission to publish this work.

REFERENCES

1. European Patent EP0850290 The use of friction reducing additive combination in lubricating oil composition. Fletcher Robert Anthony
2. US Patent 7754662 High performance lubricants additives for crankcase oils, greases, gear oils and transmission oils.
3. Effects of Friction Modifiers on Wear Mechanism of some Steels under Boundary Lubrication Conditions, SO H., Hu C., National Taiwan University, Taipei, Source: STP (1404 EB) 10504.
4. A Comprehensive Review Of Lubricant Chemistry, Technology, Selection and Design, pp154
5. Spikes H., Trib. Lett. 2004, 17, pp469
6. Bansal V., Dohhen K., Sarin R., Sarpal A., Bhatnagar A., Trib. Int., 2002, 35, 819
7. Tomaru H,Hironaka S,Sakurai T., Wear ,1977,41,pp141
8. Rounds F.G. ASLE Trans.1964, 7, pp11
9. Anand O.N., Vijay Kumar, Singh A.K., and Bisht R.P.S., ICIT 2004 pp140
10. Najman M., Kasari M., G Ban croft, Trib. Lett. 2004, 17, pp217.

Molecular Engineering of High Performance Synthetic Base Stocks by Spectroscopic Techniques

A. S. Sarpal*, M. I. S. Sastry, Ravindra Kumar, Kavita Rai, Sanker Bhadhavath, V. Bansal, and M. B. Patel

Indian Oil Corporation Limited,
Research & Development Centre, Sector-13, Faridabad.
Email: sarpalas@iocrd.co.in

ABSTRACT

This paper describes the structure-property relationship of synthetic pentaerythritol polyol esters (PEE) and Poly Alpha Olefins (PAO) as explained by the diffusion and mobility measurement results by NMR & IR spectroscopic techniques. The diffusion coefficients (D) have been found to be dependent upon the molecular structure, alkyl chain length, shape and size, hydrodynamic volume and alignment of molecules on surface. The viscosity-temperature and viscosity-pressure properties such as Viscosity Index (VI), Pour Point (PP), Elasto Hydro Dynamic (EHD) film thickness, pressure-viscosity coefficient (PVC) and hydrodynamic volume/ radius have been explained on the basis of variation of "**D'** with temperature, and tilt angle on the smooth surfaces. The study has enabled to propose a molecular structure of a synthetic molecule which can be molecularly engineered for meeting high performance physico-chemical properties.

INTRODUCTION

Poly Alpha Olefins (PAO) and synthetic esters are designated into group-IV and V base oils respectively representing an important segment of lubricants (1-8). The basic natures of synthetic esters are polyol ester of short and long chain acids, i.e. Esters of normal and iso alcohols with long alkyl fatty acids (Viz., Neopentyl glycol (NPG), Pentaerythritol (PE), Trimethylol Propane (TMP)), and dibasic esters of Adipic and Palmitic etc. Because of their availability in high to low viscosity grades and excellent physico-chemical properties such as high VI (120-170), low pour point (<-30°C), low Noack volatility (<10), improved detergency and dispersancy, lubricity and highest biodegradability (>90%), excellent additive solubility and outstanding compatibility with seal material make these esters suitable stocks for high performance lubricants in a variety of applications (1, 5). The structure of these polyol esters, especially the chain length, branching in the acid & alcohol part and its molecular weight, plays a very important role in determining its physical characteristics (1, 9-12). Lighter acids such as Valeric acid (C5) with higher alcohols are desirable for reducing low temperature viscosity. Branches on the acid part on the carbon alpha to the carboxyl group have superior resistance towards hydrolysis, whereas multiple branches are useful for building viscosity and improving low temperature flow (11). In order to establish structure-property relationship, it is important to elucidate the structure of polyol esters with regard to nature and chain length of the acid part (9, 12).

The impact of chain branching on physico-chemical characteristics, particularly viscosity, VI and pour point of PEE and hydrocarbons, have been explained on the basis of hydrodynamic volume occupied under pressure and temperature (7, 9). The molecular chain architecture for a polyol ester with desired physico-chemical properties can be modeled based on diffusivity results of a number of branched hydrocarbons including fatty acids. These studies guide syntheses of an 'ideal' molecular structures for a given performance of a lubricant base stock for improved properties at the extremes of low temperature and high pressure required in many lubrication applications (7). The pressure-viscosity-temperature properties (EHD film thickness, PVC, VI, PPt) of mineral and synthetic base stocks are entirely dependent on the nature of branched chain hydrocarbons in mineral oil and nature of fatty acids of in synthetic esters (2-6, 9, 10, 12-15). NMR and IR spectroscopic techniques are widely used to determine these structures and properties including estimation of hydrodynamic volumes to establish structure- property relationship of hydrocarbons and lubricant system (8, 9, 15-17).

The objective of the present studies focus on the molecular engineering of a pentaerythritol ester molecule with high VI, low pour point and appropriate viscosity pressure characteristics from the self diffusion coefficient, hydrodynamic volume, tilt angle and shape of the molecules at variable temperature (300-350^{o}K) estimated from the multipulse NMR Diffusion Ordered Spectroscopy (DOSY)(8) and Grazing Angle IR spectral studies.

EXPERIMENTAL

Base Oils:

Four synthetic esters, viz., pentaerythritol esters PES11, PE320, PE507, and PE307 and PAO4 with different physico-chemical properties are employed for the studies (Table-1). The nature of the acid and polyol part of the ester has been confirmed by ^{1}H and ^{13}NMR spectral analyses (1).

Materials

- Stainless steel specimens
- Emery papers 0, 1, 2, 3, 4 grades

Sample Preparation

The stainless steel specimens were machined and ground to give steel specimens with dimensions of 20 x 15 x 2 mm. The samples were mechanically polished using 1, 2, 3, 4 grade Emery papers and then finally polished with Grade-I Lavigated alumina to give shiny or mirror finish. The samples were then placed in acetone for 1-hr to remove all polishing debris and then dried in air for nearly 1-hr to generate a natural thin film of oxide/ hydroxide. The steel specimens (substrate) were then dried in stream of dry nitrogen for 15 minutes and preserved in dessicator, ready for deposition of SAM. ~200 mmol solutions of synthetic base oils in iso-octane are prepared in iso-octane and used for deposition of the SAMs. The steel specimens were dipped in the solutions of various samples for 24 hrs, then taken out, rinsed and washed with iso-octane to remove excess and physically adsorbed layers. The steel specimens were stored in desiccators prior to subjecting them to IR spectral experiments.

IR Spectral Recording:

The IR spectra reported here are recorded using IR reflection-absorption spectroscopies (IRRAS) employing a Perkin-Elmer (Spectrum GX) FT-IR spectrometer. The instrument is equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The variable temperature measurements for the monolayers are carried out insitu using a refractor-reactor (Harrick Scientific Corporation, USA) accessory with an incident angle of 75° from the surface normal. The sample chamber and the heating accessory are purged using high purity nitrogen during initialization of the equipment. The system is not purged during the experiment. The background is collected using a High reflecting mirror. All spectra are averaged over 500 scans with a resolution of 4 cm^{-1} and referenced to reflecting mirror background. The spectral analysis is carried out using spectrum 3.02-version (Perkin-Elmer) software. The temperature range used in the study is 303–423 K (i.e. 25 to 150 °C). The sample is heated uniformly and is allowed to equilibrate at each temperature for about 5 min before the spectrum is recorded.

For isotropic bulk spectra, the IR spectra of the samples are recorded as thin films between KBr windows in transmittance mode.

Kinematics Viscosity and Density Measurements:

The kinematic viscosity values at 27 to 100 ^{0}C are calculated as per ASTM D445 test procedure using a Canon automatic viscometer. Viscosities at different temperatures have been calculated using the viscosity-temperature relationship using software. Densities at different temperatures have been determined to calculate the absolute viscosities at various temperatures. These values have been used to estimate pressure-viscosity coefficient. The kinematic viscosity and density values at different temperatures are given in Table-1.

NMR Recording:

The $^{1}H/^{13}C$-NMR spectral recording have been carried out on a 300 MHz FT-NMR using $CDCl_3$ as an internal reference. The quantitative ^{13}C-NMR spectra have been recorded in a 30% solution prepared in $CDCl_3$ containing 0.1M chromium acetyl acetonate as the relaxation agent (2, 3). A total of 10,000 scans with a relaxation delay time of 5.0 sec. were given for achieving the best S/N ratio for obtaining the quantitative ^{13}C spectra.

The diffusion coefficient (D) at variable temperature range of 300 ºK to 350 ºK have been measured by NMR using the spin echo diffusion sequences (PGSE pulse sequence) described by Cotts et al (4) and DOSY sequence(8,15). Samples were recorded neat using external DMSO-d6 in a sealed capillary. The maximum gradient strength was adjusted by optimizing the gradient pulse duration (Δ) and gradient distance time (δ) for attenuated echo signal and echo decay. For better results the value of 4 ms and 50 ms respectively for Δ and δ was achieved and used for measurement of diffusion coefficient.

EHD Film Thickness Measurement:

The EHD film thickness measurements for synthetic base oils (Table-1) at 40, 60, 80 and 100 ^{0}C were made using an optical interferometer with speed of the disk varying from 0.01m/sec to 4.37m/sec. The specimen properties and contact conditions between a steel ball and coated glass are given in the table.

Based on the parameters in the table, the value of $k=2.69KR^{0.46}W^{-0.067}E^{-0.073}$ (where K is a geometric parameter equal to 0.706 for circular point contacts) was estimated to be 3.0954 mm Pa/N.

Glass disk		Steel ball			
Elastic modulus	75 GPa	Elastic modulus	207 GPa	Effective modulus, E	116.9GPa
Poisson's ratio	0.220	Poisson's ratio	0.293	Effective radius, R	9.525 mm
Ra roughness	10 nm	Radius	10 nm	Load, W	20N
		Ra Roughness	10 nm	Max. Hertzian Pressure	0.53 GPa

Pressure-Viscosity Coefficient (á):

The film thickness was measured as a function of entrainment speed at various temperatures (40, 60, 80 and 100 °C) at constant load of 20N. The EHD film thickness (Log(Hc)) versus entrainment speed (Log(u)) plots were plotted (Figs. 1 to 3). In most of the cases the curves are linear at high speed and are in accordance with EHD theory. Regression analysis on the plots has been carried out to get the relationship between film thickness and entrainment speed (see Eq.1 below). From the relationships, the pressure–viscosity coefficients at different temperatures for the synthetic fluids have been estimated and given in Table-2.

$$\mathbf{Log(Hc) = Log(a) + 0.67{*}Log(u) — 1}$$

$$\mathbf{and\ a = k(\eta)^{0.67}\alpha^{0.53}}$$

where, "k" is constant dependent on test geometry, "u" is entrainment speed (m/s), "h" is the lubricant film thickness (nm), "η" is dynamic viscosity at ambient atmospheric pressure (cP), and "α" is pressure-viscosity coefficient (GPa-1) at the test temperature.

RESULTS AND DISCUSSIONS

Characterization of Base Oils:

The physico-chemical data on the synthetic base oils is given in Table-1. The PAO4 is a hydrocarbon richer in paraffins and isoparaffins, whereas, the remaining three are synthetic esters of different chemistries. PES11 is pentaerythritol ester of mixed acids i.e., C_7 to C_{12} (mainly heptanoic acid, octonoic acid and decanoic acid). PE507 is pentaerythritol ester of 3,3,5,-trimethyl hexanoic acid. PE320 is pentaerythritol ester of 2-ethyl hexanoic acid and 3,3,5-trimethyl hexanoic acid. PE307 is neopentyl glycol ester of 2-ethyl hexanoic acid. As the chemistries vary, one will expect variations in physico-chemical properties. From Table-1, it is evident that PAO4 and PES11 are having high VI and PE 307 is having low VI. PE507 is having high viscosity at room temperature, where as PE320 which is ester of mixture of two branched acids is showing low viscosity.

Molecular Diffusion Measurement:

The hydrocarbon mobility, and characteristics of liquids can be explained by the measurements of molecular dynamics parameters such as relaxation time (mobility) (T1), reorientation correlation time and diffusion coefficient (D) (2, 4, 5). The molecular mobility parameters of various methyl branched structures describe motion of the normal and isoparaffins including long alkyl chain attached to aromatics or naphthenes. In order to account for the contribution of each towards the molecular dynamics of a system, diffusion coefficients (D) of the synthetic base oil samples as such have been determined by the application of DOSY/^{1}H-PGSE techniques (4, 8, 15). The diffusion coefficients reported by these experiments represent the average motion of all the types of hydrocarbons chain attached to paraffins. The results presented here are due to average motion of CH_3 (signals at 0.64 ppm of ^{1}H-NMR spectra) of normal and isoparaffin carbon chain and at 3.8 ppm due to ester. The relationship of diffusion coefficient with temperature i.e. 'Log (D) vs 1/T' is shown in Fig. 4 for all the base fluids for the peak at 3.8 ppm. The energy of activation for the diffusion process as estimated from the slope of this curve is given in Table-3.

EHD Film Thickness (Hc) and PVC results:

The pressure viscosity coefficient (á) describes the film generating capabilities of a lubricant and allows the calculation of a film thickness at EHD contacts in tribological contacts. The higher value of 'á' implies thicker film formation compared to other fluids under study and 'á' decreases with increase in temperature. However, larger fall in the values at higher temperature correspond to thinner film at that temperature. The behavior is similar to VI characteristics depicted for base fluid. The pressure viscosity coefficient (á) is determined by the methods based on (a) change in the viscosity as a function of pressure using high pressure apparatus and (b) indirectly by measuring EHD film thickness in an optical interferometer (9, 10, 15)

The EHD film thickness plots i.e., log (H_c) (film thickness) versus log (u) (entrainment speed), for all the samples at different temperatures are plotted and are shown in Figs. 1-3. The plots display a number of important features. First, the film thickness increases with increasing entrainment speed. Second, the film thickness displays a dramatic decrease with temperature. The effect of temperature on film thickness is attributed to the effect of temperature on viscosity. Increasing the temperature decreases viscosity which leads to the formation of thinner films.

As can be seen from the figures, the effect of temperature on film thickness was observed in the entire entrainment speed range, resulting more or less parallel set of lines. This parallel trend was always observed in the high entrainment speed region but not always in the low entrainment speed region. At some temperatures the film thickness values in the low entrainment speed region could be higher or lower than that extrapolated from the data trend in the high entrainment speed region. This is a very important distinction in the trend of oil film thickness in the low vs high entrainment speed regions, arising due to changes in temperature. It is evident from the Table-2 higher viscosity oil PE507 form thicker films (1551-370.41 nm) compared to low viscosity grade oils PES11 (325.63-108.14nm), PE307 (172.5-65.32nm) and PAO4 (272.01-104.73nm) as indicated by the higher PVC values of PE507 (109.64-44.34) compared to PES11 (41.43-24.43), and PAO4 (29.96-28.55) in the temperature range of 40 to 100^{o}C. The percentage fall of 39.2, 59.6 and 3.3 can be correlated to the VI values of 138, 90 and 150 respectively for PES11, PE507 and PAO4. Thus higher VI oils provide optimum film thickness and demonstrate fewer falls at higher temperature.

From the above studies, it is concluded that viscosity–temperature and viscosity- pressure behaviors are dependent upon the nature and length of alkyl chain of acid attached to pentaerythritol alcohols. In the present case normal alkyl chain of PES11 (average chain ~n-C_8), demonstrate better viscosity–temperature-pressure characteristic compared to

PE507 (iso-C_9) and PE320 (iso C_9 + C_8) (Table–2). However, between PE320 and PE507; PE320 showed an appropriate viscosity-temperature behavior. The higher branched molecular structure with C_9 (3,3,5-trimethyl hexyl) are not tightly packed both at higher and low temperature in contrast to iso-C_8 (2- ethyl hexyl) in PE320. This has also been explained by the tilt angle of these molecules on the steel surfaces estimated by IR Grazing angle spectral studies at variable temperature. The results have shown that tilt angle of C_9 branched chain with 3 methyls along the C6 chain is much higher than the tilt angle of C_8, 2-ethyl hexyl with ethyl chain near the carboxyl group; particularly at higher temperature. This has facilitated the close packing of molecules in PEE with C_8 + C_9 chain compared to PEE with highly branched iso-C_9 chain. The close packing has resulted in the occupation of less hydrodynamic volume (1664.0 A^0 to 2203 A^0) of iso-C_8 ester compared to iso-C_9 highly branched ester (1885 to 2441.2 A^0) (Table-4). The occupation of low hydrodynamic volume for iso-C_8 + iso-C_9 chain esters make the molecules more mobile or fluid at low temperature resulting in the low pour point of -37 ^{0}C for PE320 ester compared to -26 ^{0}C for PE507 ester. The activation energy Ea as estimated from the plot of log of diffusion coefficient 'D' vs 1/T is lower (35.99Kcal) for PE320 ester compared to higher (45.92Kcal) for PE507 ester. Thus the molecules of iso- C8 + iso-C9 chain esters can easily creep past molecules to overcome the low energy barrier in contrast to molecules of iso–C9 highly branched ester, which has to face higher energy barrier.

There also exist an interesting relationship between PVC (á), hydrodynamic radius(r) and Ea. The lower activation energy of 35.99 kcal for iso-C8/C9 ester PE320 allow formation of thicker film at EHD contacts. The pressure-viscosity coefficient decreases as the temperature increases for samples as shown in the Table-2. The ester with iso-C9 chain form thinner film at all temperature compared to esters of C8 (normal) and iso- C8+C9. However the PVC values are also higher for iso-C9 ester compared to other esters indicating thicker EHD film formation. The fall in the á is also higher for PE507 (59.55%) compared PE320 (40%) and PES11 (39.2%). Thus optimum films are formed for both PES11 and PE320 and also maintained at higher temperature as indicated by the results in the Table-2. This low value of Ea, 29.09 and 35.99 kcal respectively for PES11 and PE320 are indicative of less rigid ester molecules at EHD contacts at all temperatures and may occupy appropriate volume and adjustable shape to overcome the pressure experienced at higher pressure EHD contacts. These also facilitate to form optimum film thickness to provide low friction coefficient or better wear characteristics.

Hydrodynamic Volume:

The hydrodynamic volume of molecules of ester and PAO4 has been estimated from the following Einstein equation:

D= KT/6ð r Þ

Where D, K, T, r, and Þ are the self diffusivity, Boltzman constant, temperature, radius for spherical molecules/ gyration ellipsoid and viscosity respectively. The self diffusion coefficient (D) has been estimated from the NMR DOSY data as explained in the experimental section. The values of radius 'r' for three PEEs and PAO4 at variable temperatures are given in the Table-4. It is observed that the 'r' is increasing with temperature for all the esters with different branched and normal alkyl chain of the fatty esters. However, there is decrease in the 'r' for synthetic hydrocarbon base PAO4 (dimer of C10 alpha olefins) with increasing temperature. The increase in the 'r' or size of the molecules for PEE is due to the unpacking of polar molecules due to thermal effects at high temperature.

The methyl or ethyl branching of C8 or C9 in PE507 and PE320 are being unfolded and might be straightened at higher temperature resulting in the increase in the hydrodynamic volume. In case of straight chain ester PES11, the hydrodynamic volume is higher compared to branched chain ester PE507 and PE320. This is due to the fact that PES11 ester is composed of n-alky chain fatty acid with carbon number C_7 to C_{12} (average C_8). The normal alkyl chain is coiled at low temperature and not effectively packed resulting in the higher molecular volume compared to branched chain of C_9 and C_8 ester. The higher fatty acid chain is uncoiled resulting in the increase in the hydrodynamic volumes. The PAO4 is a hydrocarbon based molecules with less methyl branching along the chain (5, 6). Being non-polar, the chain experience strong Van Der Waals repulsions and molecule is longitudinally elongated compared to vertical alignment of PEE ester molecules containing bulky pentaerythritol alcohol. As the temperature is increased the repulsive forces also increased resulting in the decrease in the effective molecular volume (Table- 4) (5, 6).

Molecular Engineering:

It is quite evident from the above diffusion, hydrodynamic volume/ radius and tilt angle results that molecular geometry or shape of the esters and PAO4 is entirely dependent on the nature of alkyl chain length; particularly number and alignment of methyl chain along the fatty acid part. The increase in viscosity from n-alkyl chain acid and ethyl group in 2-ethyl hexanoic acid to 3,3,5-trimethyl hexanoic acid has been explained on the basis of close packing of branched molecules. In order to find out the effective molecular volume under stress such as temperature and pressure, a curve of reverse of diffusivity or diffusion coefficient (1/D) and r (radius) × Þ (viscosity) has been plotted for all the esters and PAO4 (Fig.5). The slope of the curve has been found to be almost identical for these molecules. It varies from 21.50 to 24.45 × 10^{-9} A^0cSt m^2 sec between 300 and 340^{o}K. The higher tilt angle of PE507 is due to the bending of methyls towards x-axis on account of Van Der Waals repulsions. This suggest that in order to have desired viscosity and controlled variation in viscosity index (VI), methyls at the centre and at the end of the fatty acid chain will be of molecular choice. This will provide controlled diffusion of molecules at all temperature and desired physico-chemical characteristics (2-6).

REFERENCES

1. Chopra, A et al. NLGI-09(Mussorie, 2008)
2. Sarpal, A.S., Kapur, G.S., Chopra, A., Jain, S.K., Srivastava, S.P., *Fuel* 1995; 75:483.
3. Sarpal, A.S., Kapur, G.S., Mukherjee, S., Jain, S.K.. *Fuel* 1997; 76:931-937.
4. Cotts R.M., Hoch M.J.R., Sun, T., Markert J.T. Pulsed field gradient stimulated echo methods for improved NMR diffusion measurements in heterogeneous systems, *J. Magn. Reson.*, 1989; 83: 252-266
5. Kapur, G.S., Sarpal, A.S., Sarin, R., Jain, S.K., Srivastava, S.P., Bhatnagar, A.K. *J. Synthetic Lubrication.* 1998; 15(3): 177-191.
6. Kapur, G.S., Sarpal, A.S., Bhatnagar A.K. *Lubrication Science* 2000; 14(3):287-302.
7. Gordon P.A., Ind. Eng. Chem. Res. 2003; 42(26): 7025-7036
8. Cozzolino, S, Sanna, M.G., Valentini, M., Magn. Reson. Chem. 2008; 46: S16-S23
9. Pensado, A.S., Comunas, M.J.P., Fernandez, J, Eng. Chem. Res. 2006; 45: 9171-9183
10. Pensado, A.S., Comunas M.J.P., Lugo, L, Fernandez, J, Eng. Chem. Res. 2006; 45(7): 2394-2404.
11. Wang, D, Mousavi, P, Hauser, P.J., Oxenham, W, Grant C.S., Eng. Chem. Res. 2004; 43: 6638-6646.
12. Sharma, B.K., Stipanovic, A.J., Eng. Chem. Res. 2002; 41(19): 4889-4898.
13. Biresaw, G, Bantchew, G, J. Syn. Lubrication 2008; 25: 159-183.
14. Biresaw, G, Bantchew G, J. Syn. Lubrication 2008; 20: 283-297.
15. Sarpal, A.S., Sastry, M.I.S., Kapur, G.S., Bansal, V., Mehta, A.K., and Bhatnagar, A.K., Lubrication Science, 2004.,16-4, 361-375.
16. Valentini, M; Vaccaro, A; Rehor, A; Napoly, A; Hubbell, J.A. and Tirelli, N; J. Am. Chem. Soc., 2004, 126(7), 2142- 47
17. Ihre, H, Hult, A and Soderlind, E. J. Am. Chem. Soc., 1996, 118(27), 6388-6395.

Table 1 : Physico-chemical properties of synthetic base fluids

Sample	Kinematic Viscosity at different Temperatures					VI	Density at different Temperatures				
	27	40	52	67	77		25	40	52	67	77
PES11 (R=n-C8-C12	40.42	23.95	15.91	10	8.052	138	0.9832	0.9738	0.9662	0.9568	0.9505
PE507 (R=Iso C9)	519.4	220	113.2	50	38.17	90					
PE320 (R=IsoC9 + IsoC8)	138.8	68	39.23	21	15.96	88	0.9508	0.9414	0.9338	0.9244	0.9181
PE507 (R=IsoC8)	11.5	7.5	5.38	-	3.09	65					
PAO-4	53.4	30.66	19.89	14	9.68	150	0.8127	0.8019	0.7932	0.7823	0.7750

R= Carbon Chain length and nature, n=normal, iso= branched

Table 2: Estimated PVC coefficient values of base fluids at different temperatures

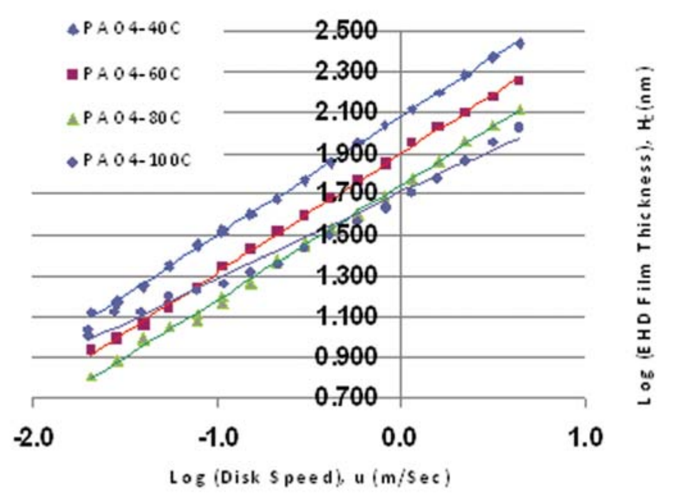
Sample	Pressure-Viscosity Coefficient ( ) at different Temperatures			
	40	60	80	100
PES11	41.43	37.18	25.33	24.45
PE307	33.86	24.28	21.50	25.93
PE507	109.64	88.33	59.15	44.34
PAO4	29.60	28.55	29.34	51.37

Table 3: Energy of activation for the diffusion process for synthetic base fluids

Samples-->	PES 11	PE 320	PE 507	PE507 (N)	PAO4	PES 11	PE 320	PE 507	PE 507(N)
Property	Energy of Activation for Peak at 4.1ppm					Energy of Activation for Peak at 0.9 ppm			
Ea (JK-1mol-1)	29.09	35.99	45.92	30.61	37.67	32.13	72.09	72.13	93.29
Ea (Cal/deg/mole)	6.95	8.60	10.97	7.32	9.00	7.68	17.23	17.24	22.29

Table-4: Hydrodynamic radius and Energy of Activation Values of Synthetic Base Oils

Sample	Hydrodynamic radius, r(A^0) at T(^oK)				Ea (KJ/mol)	VI	Pour Point (ppt ^oC)
Temp, °K	300	325	340	350			
PES11	2710.6	2971.4	3158.1		29.09	138	-57
PE507	1885.5	2287.9	2441.2	2211.5	45.92	90	-26
PE320	1664.0	2203.1	1824.4		35.99	88	-37
PAO4	1291.2	1024.5	912.93	963.6	37.67	136	-60



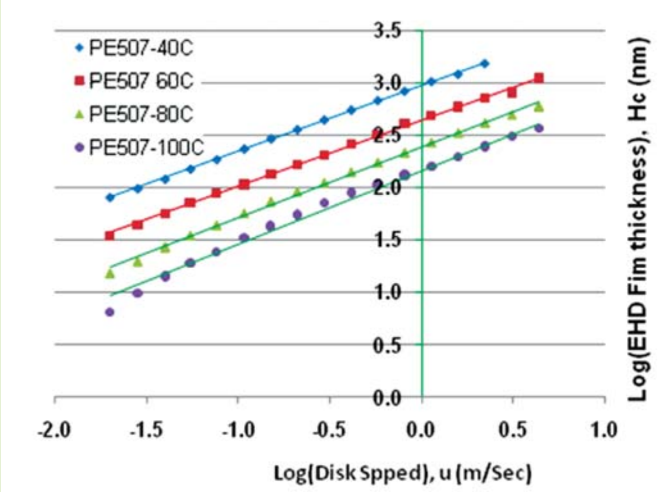
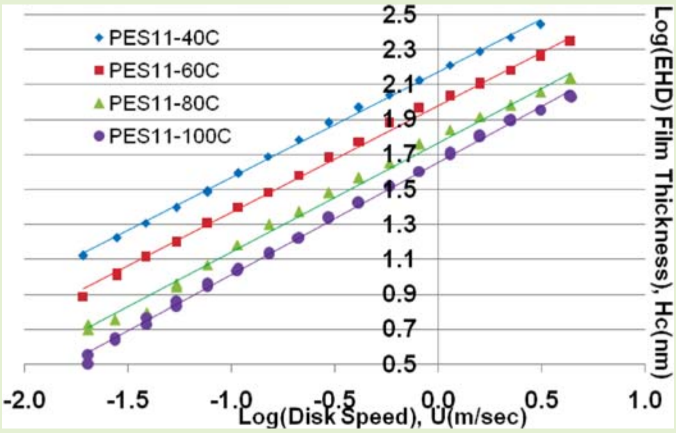


Fig. 1: EHD Film Thickness Vs Rolling Speed for PAO4 Base Oil at Different Temperatures

Fig. 2: EHD Film Thickness Vs Rolling Speed for PE507 synthetic Base Oil at Different Temperatures



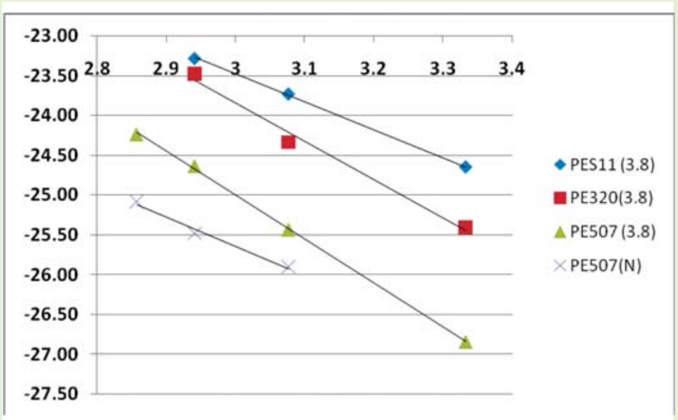


Fig. 3: EHD Film Thickness Vs Rolling Speed for PES11 synthetic Base Oil at Different Temperatures

Fig. 4: LN (D) versus 1000/T plat for synthetic base fluids for the peak at 3.8

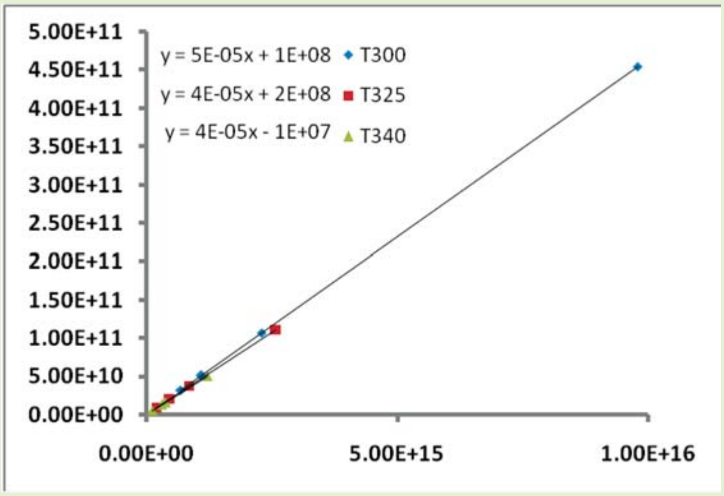


Fig. 5: 1/ D (Diffusion Coefficient and r*Þ (radius and viscosity)