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NLGI India

## Extreme Pressure Performance of Greases: Testing and Additive Solutions

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### Abstract

For more than 100 years, grease developers and formulators have sought solutions to raise the load carrying capacity (LCC) of products. Sulfur was first used as an extreme pressure (EP) additive in the 19th century and it was later followed by lead additives, chlorinated paraffins and sulfurized whale-oil products.

The traditional test methods for determining the LCC or EP properties of grease, namely the sliding 4-ball and the Timken OK load methods, were first standardized in the 1960s. Both are still in use today and at least one of them features in all EP grease standards.

Since lead, chlorinated paraffins, and sulfurized whale-oil were banned from most grease formulations, it has become a significant challenge to maintain or increase the LCC of EP greases. Solid lubricants such as molybdenum disulfide ( $\text{MoS}_2$ ) are used in many applications, but owing to considerable volatility in its pricing and availability,  $\text{MoS}_2$  is not often the best choice. Consequently, in many applications, calcium carbonate, graphite, solid potassium or sodium borates are used as alternatives. Antimony dithiocarbamates have been used widely. Sulfurized organic compounds containing up to 45% of sulfur are widely used alone, or in combination with other additives like antimony dithiocarbamates or calcium sulfonates, but these can have issues with odor and corrosivity. Sulfur-phosphorus and sulfur-nitrogen compounds are also used but many of these have issues with seal compatibility.

This paper discusses the test method appetites and outlines some of the potential solutions to today's grease formulator for increasing the EP properties of lubricating greases.

## **Introduction**

High load carrying capacity (LCC) or extreme pressure performance is an important grease characteristic focused on the ability of the grease to serve as a lubricant for mating metal surfaces in motion and under heavy load to avoid scuffing or seizure. In 2010, Fish and Ward (1) reviewed the various test methods for evaluating the extreme pressure (EP) performance of greases and the many and varied additive solutions to improve the extreme pressure performance of grease. Test methods discussed included the Timken OK load test, the differing international versions of the sliding 4-ball EP test, the Falex pin and vee block test, the SRV step load test, and the FZG gear test. A wide variety of chemistries impacting these various test methods were also discussed.

## **EP Testing**

The majority of rigs used currently to determine the LCC of greases are essentially modifications to the standard test methods used for oils. There is a clear difference between testing lubricating grease and oils in the response of the lubricant to the contact conditions. As outlined in the earlier paper, the two most important test methods are the Timken OK load test (2) and the ASTM 4-ball EP (3). The IP 239 and DIN 51350 4-ball EP testers and the SRV step load test are widely used in Europe.

### **The Timken OK Tester**

The Timken OK load tester was first developed in the 1930s but not standardized until 1966 as ASTM D2509 (2). It is a joint method with the Energy Institute as IP 326. A hardened steel block is loaded against the outer surface of a tapered roller bearing cone and run for 10 mins at 2.05 m/s with a constant grease feed until either the test reaches its time limit and stops or scuffing occurs and the rig is stopped. The test blocks are visually inspected for scuffing, and the OK load is determined as being the highest load used in which scuffing did not occur. By general consensus, a grease with a 40 pound OK load is considered to be an EP grease. However, in some cases a 35lb OK load is accepted. The test ring and the test block have the same specified hardness (58 – 62 HRC) and roughness ( $R_a = 0.51$  to  $0.76 \mu\text{m}$ ). The contact patch is a line contact. It is difficult to determine what the effective peak stress is as under the conditions of the test; the block can wear significantly and reduce the stress. With some EP additives the amount of wear is very large, and this goes a long way in supporting the load and preventing scuffing from occurring. A grease may give a wear scar of 1mm width and at 70 pounds load will have a contact stress of 36,000 psi (248MPa) while one which wears to 2mm would be only 10,000 psi (68.9MPa). If neither scuffed, both would be a 70 pound OK load, but the former would have the better load carrying capacity. In many cases high wear additives give higher OK loads, but the wear can be a cause for concern. From general discussions with various marketers and developers within the grease industry, it is acknowledged that the Timken test is variable, yet when studying commercial product data sheets, it is observed that many EP greases include a Timken OK result as a demonstration of high LCC grease product performance. The high Timken OK load serves as a way of differentiating products' performance.

### **The Sliding 4-ball EP**

The sliding 4-ball EP was first developed in the 1930s but not standardized until 1967 as ASTM D2596 (3). Variations in local electricity, motors, steel and thinking led to the development of the three quite different tests that exist today. Efforts were made to standardize practice, but these did not succeed. A comparison of the three widely used methods, ASTM D2596, IP 239 and DIN 51350 parts 1 & 4 is

included in table 1 below. The triangular loading of the three lower balls gives three point contacts. At 250 kg load, the applied load generally considered to be the threshold of EP performance, the Hertzian stress at each of the contacts is more than 5.0 GPa. At these contact pressures, plastic flow occurs and the actual peak stresses seen by the surfaces are much lower than calculated.

Method	Ball steel	Ball hardness (HRC)	Rotational speed (rpm)	Step duration (seconds)	Loading
ASTM D2596	AISI 52100	64 - 66	1770	10	6, 8, 10, 13, 16, 20, 24, 32, 40, 50, 63, 80, 100, 126, 160, 200, 250, 315, 400, 500, 620, 800 kg
IP 239	ISO 683-17	58 – 67 (60±2)	1450 - 1500	10 or 60	10kg steps to 100kg then 25kg steps to 300kg then 50kg to 800kg
DIN 51350 part 1 & 4	100Cr6	63±3	1420	60	2000N then steps of 200N to 5000N then 500N to 8000N

Table 1 Comparison of 4-ball EP test methods

As wear is a significant issue in EP contacts, the sliding 4-ball wear test method (4) is used to supplement the EP test results.

In Europe, the accepted level of EP performance is not so clear. In DIN 51825(5), the standard talks about demonstrating the anti-wear performance of grease by running DIN 51350 part 5 method E (6). Run under a 1000N load, this a heavily loaded 1 minute wear test in which the surfaces cannot seize and the wear scar cannot be wider than 1.8mm. This is equivalent to contact stress of 4.12 GPa and a contact patch diameter of 0.37mm. Greases without EP additives will normally seize under these conditions. ISO 6743 part 9 (7) asks the question if the greases contains EP additives. If the answer is yes it is determined to be an EP grease and should be tested by either IP 239 European standard EP test (8) or by ASTM D2596 (3), but no limits are given as to what minimum weld point is required.

Subsequent to the publication of the first paper it was suggested that we had missed an important EP test from the list, the Brugger test (9). This is a cylinder on ring test. A 25mm diameter ring manufactured from 1.2436 through hardened tool steel is coated with grease or oil and rotates at 860rpm. Against this is loaded an 18mm diameter cylindrical roller bearing manufactured out of through hardened bearing steel. The test load is 400N and the test runs for 30s, starting at room temperature. The wear scar dimensions on the cylinder is measured and from this the load carrying capacity is determined and reported as N/mm<sup>2</sup>. In DIN 51347 it states that it can be used to measure the load carrying properties of hydraulic fluids and gear oils, but not grease. It is occasionally seen in grease specification requirements, but as with the other minor tests, no significant body of specifications exist with it incorporated.

## **Grease Component Influences on LCC Properties**

### **Base Grease Influences**

Based on the experiences in the authors' own test department, the load carrying capacity of simple lithium 12-hydroxystearate base greases without EP additives is typically poor. Timken OK loads of only 10 to 20 pounds or less are typical. Under 4-ball EP testing using ASTM D2596, weld loads of 80 to 126 kg are typically obtained. Under the SRV step load test, base greases will typically weld at between 50 and 200 N. The base oil viscosity seems to have only a minor influence on behavior as does consistency, with grease being close to the NLGI 2 grade. Lithium complex greases seem to perform slightly better than lithium greases typically giving 1 load stage higher on the 4-ball (to 160 kg) and up to 10 pounds better on Timken.

Anhydrous calcium greases have been seen to behave similarly to simple lithium soap thickened greases. Calcium complex greases containing either in-situ reacted calcium acetate or using preformed calcium acetate in oil have much higher base lines. Calcium complex greases with no additional EP additives have been seen with 40 pound Timken OK loads and 250 kg weld loads.

Overbased calcium sulfonate greases with their higher loading of calcium carbonate, and typically containing a small amount of free lime, have been shown to give 4-ball weld loads of up to 620 kg and 70 pound Timken OK load passes.

Aluminum complex greases for food grade applications typically give Timken OK loads of only 10 to 20 pounds and using ASTM D2596, weld loads of 80 to 126 kg are typically obtained

Simple urea greases, however, seem to be the worst base grease available with some giving 4-ball weld loads of 50 kg to 80 kg and only 10 pounds on the Timken test. If it is necessary to give the urea grease a higher basic LCC, then the normal way of doing it is to make the grease a urea complex by adding a calcium grease to the urea. Historically, up to 5% calcium complex grease was added into urea greases containing 8 to 12% urea thickener. This typically boosted the LCC to a minimum of 200 kg by 4-ball EP and 40 pounds OK load by the Timken Tester. Today, typical calcium complex greases, which would have been used in this type of application, are no longer widely available. Instead, grease formulators are using overbased calcium sulfonate greases as EP boosters in urea greases. The use of this type of additives in grease will be discussed later.

### **Additive Influences**

Most of the literature published before 1990 demonstrated the efficacy of lead and chlorine additives. The vast majority of the literature is based on gear oils and not on lubricating grease. The typical situation for grease is that it is assumed that if the EP additive works in oil it will work in grease, but this is not always the case. Based on this understanding, the literature for additives was reviewed and work investigated covering mostly oils, but with some more recent information on EP additives in grease.

Elemental sulfur was the first LCC enhancing additive used, but owing to its corrosivity to yellow metals other sulfur-containing additives were developed. In 1948, Greenhill (10) reported that suitable sulfur-containing additives offered good load carrying when operated at temperatures from 20 to 300 °C. Prior to 1980, sulfurized sperm oil was widely used as an EP additive but was replaced by sulfurized synthetic

varieties, sulfurized esters and vegetable oils. Sulfurized olefins with up to about 45 %wt S were also introduced as replacements for the lower sulfur containing vegetable oils.

Ashless dithiophosphates are the most common form of non-organo metallic sulfur-phosphorus compounds. Some are available as thiophosphate esters but more commonly as the amine salts. The activity and performance of the amine thiophosphates are known to be influenced by the chain length of the alcohol used to make the thiophosphoric acid and by the nature of the amine used for the salting.

It is actually more common to make mixtures of sulfur and phosphorus—the sulfur additives for high LCC and phosphorus additives to prevent excessive wear—especially when operating under non-EP conditions. Phosphorus compounds have been used as LCC additives for more than 80 years. In 1940, Beeck et al (11) published an investigation into the behavior of various phosphorus additives including tricresylphosphate (TCP). Using an early type of 4-ball wear machine, they looked at the relative wear rates of compounds and concluded that TCP was a very good antiwear additive. They concluded that it worked by corroding high spots on the surface and by laying down metal phosphide reaction films. They also observed that EP additives such as dibenzylsulfide increased the amount of wear that occurred but did reduce the onset of seizure. Based on this and much later published work, phosphorus only compounds would be better considered to be antiwear rather than EP additives.

The most common sulfur-nitrogen compounds used are thiadiazole derivatives. At low treat levels they can passivate yellow metals and at higher levels act as EP additives. The most common additives are mercapto-derivatives with sulfur bonded to the heterocyclic ring. This is illustrated in Figure 1. The commercially available products utilize either substituted single rings or dimerized sulfur bridged compounds, which are yellow solids. With greases, the oil insoluble dimer versions are easily dispersed into grease. By extending the length of the alkyl groups to about a minimum of 8 carbon atoms, the products become oil soluble. One of the challenges of DMTD derivatives is that they can attack elastomers and may cause a loss in sealing.

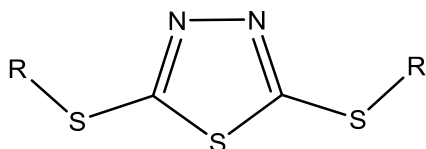


Figure 1 Di-mercapto-thiadiazole (DMTD)

In 1970, Forbes (12) published a review on EP additives on behalf of the Institution of Mechanical Engineers. Surprisingly for 1970, there is no mention of lead additives but chlorinated paraffins are included. When introduced in the 1950s (13), as an enhancement over lead naphthenate, lead dithiocarbamate (PbDTC) contained sulfur and lead on the same molecule. The LCC of PbDTC was higher and at a lower effective treatment level. Antimony (SbDTC) and later bismuth dithiocarbamates (BiDTC) were introduced as lower toxicity alternatives to lead. Ward et al (14) described previously the behavior of SbDTC and Rohrs et al (15) promoted the use of BiDTC.

### Solid Lubricants

A significant amount of literature has been published on the performance and behavior of metal disulfides and sulfides as solid additives to boost EP performance. Risdon (16) is a good review of the topic.

Generally, MoS<sub>2</sub> is used as a reference by which to judge other solid additives. MoS<sub>2</sub> is written into many specifications as a solid load-carrying EP additive at treatment levels of 3 - 5 %wt in the finished grease, although there are greases with higher solids contents marketed.

### **Boron Compounds**

Potassium, sodium and calcium borates are all available in today's marketplace. As none of the borates are soluble in oil, they are supplied either as solids or as dispersions in oil. Historically, potassium borates have been sold as LCC boosters, especially if high Timken OK loads are required.

### **Calcium Salts – Carbonates, Oxide and Acetates**

It was observed that complexing a calcium grease with acetic acid to form calcium acetate not only increased the dropping point but also the EP properties. In calcium sulfonate greases, layers of calcium oxide as well as calcium carbonate have been observed on Timken blocks run in the test (14).

### **Potential Solutions**

Formulating grease for a particular application is generally more complicated than simply adding one additive component to the finished grease formulation. It involves working with multiple components to provide the desired overall performance. It is useful to apply the various EP additives with either other components or a formulated core additive to produce the desired effect in the various tests aforementioned as a measure of extreme pressure performance. With this in mind, potential chemical and physical solutions can be proven using comparative testing.

### **Sulfurized Additives**

In terms of today's market, sulfur containing additives are available from a wide variety of suppliers and with a variety of activities, colors, odors and performance. It is easiest to incorporate high percentages of sulfur into polysulfides. These can be sourced with up to around 50 %wt. The typical challenge being that the higher the sulfur content, the less thermally stable the products are, the more likely they are to give off noxious odors and the more corrosive they are to copper. They are used both as the primary EP additive in many commercial grease packages or partial packages and also as EP boosters at low treat levels. This type of product is also often used in metal working applications. With sulfurized esters, it is difficult to incorporate more than about 20% sulfur into the molecules. They are however typically lower odor and light colored and have much lower copper activity.

### **Phosphorus and Phosphorus-Sulfur Compounds**

Phosphorus and phosphorus-sulfur additives are used in conjunction with other components to deliver increased LCC. Timken LCC tends to be weak with sulfur compounds and with ZnDTPs as was reviewed. One way to increase the OK load is to use phosphorus or phosphorus-sulfur compound as co-additive with the components. For example, figure 2 shows a comparison of proprietary P/S (phosphorus-sulfur), dialkyldithiophosphate ester, phosphate ester amine salt, triarylthiophosphate, and dialkyl hydrogen phosphate compounds formulated in a P/S additive formulation at equal phosphorus level with other components held constant, including sulfur EP, which is an integral part of the formulation. The proprietary PS represents field-proven additive technology. As can be seen, directional differences in LCC were found suggesting that improvements may be made by component substitution. In practice, other factors such as package compatibility against separation, odor, and antagonism to other performance requirements must be carefully considered before implementing such changes.



## Antimony Compounds

One of the most reliable and frequently used ways to increase LCC capacity is through the use of antimony dialkyldithiocarbamate (SbDTC). This can be accomplished as an individual additive or as a component with other additives. Ward, et al (14) analyzed the wear scars of blocks from the D2509 Timken test. They showed relatively thin tribochemical films suggesting that the mechanism of SbDTC is one of erosion/abrasion of the film over time at steady state. Table 2 shows the impact of adding SbDTC to grease formulated with ZN/P/S additive. The OK load was dramatically improved over the baseline with ZN/P/S additive alone. At a higher level of SbDTC the weld load was also increased by two load stages from 315 kg to 500 kg.

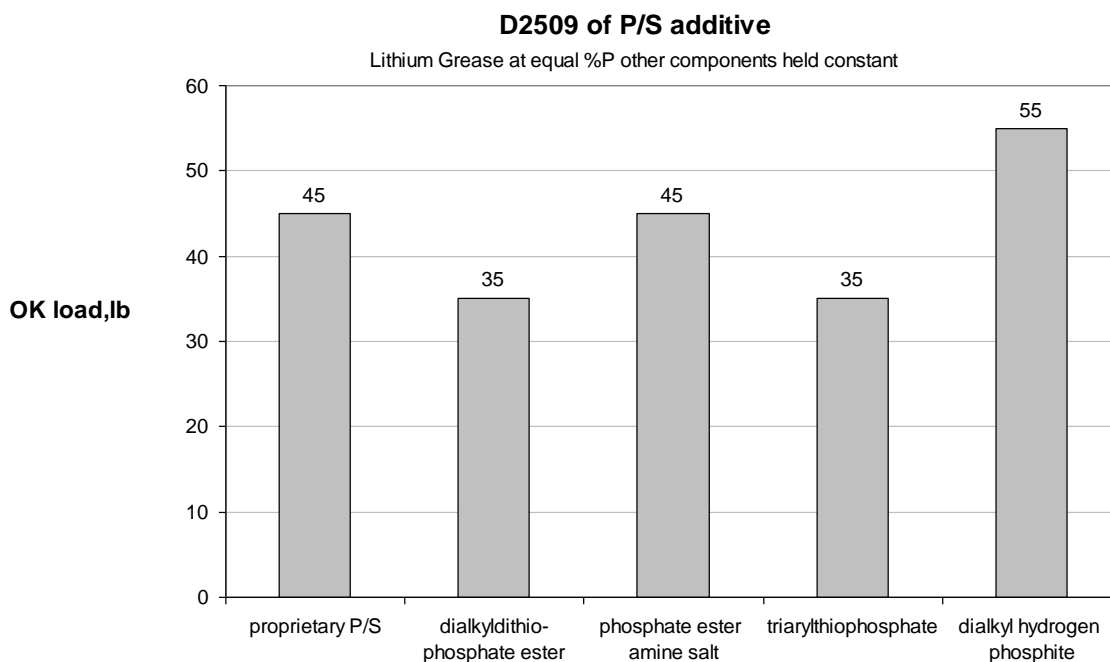


Figure 2. Phosphorus and phosphorus-sulfur additives in core package containing S-EP

Table 2 SbDTC impact on OK load and weld point

Additives	Timken OK load (lb)	4-Ball Weld load (kg)
ZN/P/S	25	315
ZN/P/S + 2% SbDTC	45	315
ZN/P/S + 4% SbDTC	100	500

## Passive EP Additives

A passive extreme pressure (PEP or passive EP) additive refers to the combination of overbased metal sulfonates used with sulfur EP compounds. The phrase, “Passive Extreme Pressure” related to a previous trademark applied to industrial oils and greases as a family of metal working additives used as passive extreme pressure agents (17). Past work covered their evaluation, metal reaction and chemistry (18).

Previous work on PEP additives consisted of evaluations of alkaline and alkaline earth metal overbased alkylated sulfonates in combination with sulfurized olefin. The main focus was on the use of 400TBN sodium, calcium, and magnesium alkylarylsulfonates. The overbased sulfonates and sulfurized olefins were evaluated in a tapping test machine used to cut internal threads in 1020 steel and to thread 304 stainless steel pipe. Test results of 304 stainless steel showed that when only using a sulfurized olefin the tap would break while when using the overbased sulfonates the tapping could complete with better efficiency. Synergy to boost the tapping efficiency occurred when the combination of overbased sulfonate and sulfurized olefin were employed (18). Sodium and calcium overbased sulfonates were most effective.

In this work, four different passive EP component additives were used to conduct combination studies, including two 400TBN overbased calcium sulfonates and two sulfurized olefin based compositions. Both natural and synthetic sulfonate substrates were tested for comparison. The two sulfur EP compounds consisted of a higher sulfur content sulfurized isobutylene and a lower sulfur content sulfurized mixed olefin-unsaturated ester. The higher sulfur content additive is well-known to provide EP performance in 4-ball EP testing, while the lower sulfur content additive is better known for lubricity performance more representative of a friction modifier. The target was to try to achieve a 60 pound Timken OK load in an NLGI 2 lithium grease.

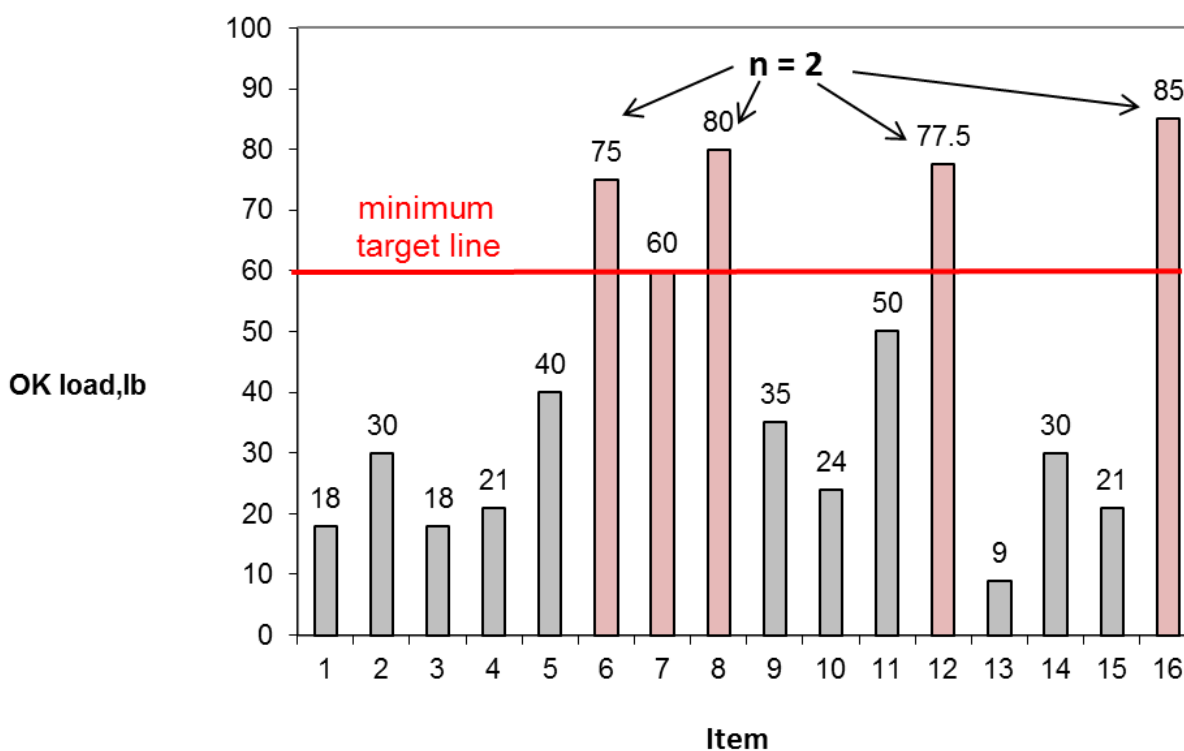


Figure 3. Passive EP Timken test results in an NLGI 2 lithium grease

Table 3. Best PEP matrix greases with supplemental EP and wear data

Item	Sulfur-EP	Calcium Sulfonate	Ca/S ratio	Treatment Level	D2509, OK load lb	D2596, weld point, kgf	D2266, scar mm
16	mid	natural	1:1	4x	85	315	0.46
8	high	synthetic	2:1	4x	80	315	0.44
6	high	natural	1:1	3x	75	315	0.51
12	mid	natural	2:1	4x	77.5	250	0.41
7	high	natural	1:1	4x	60	250	0.51

Using a very high level of passive EP components enables high levels of Timken OK loads to be achieved, but 4-ball weld tests gave slightly lower than expected weld points.

### Solid Lubricants

Solid lubricants offer an opportunity to improve the LCC of grease. It is a common practice to use molybdenum disulfide ( $\text{MoS}_2$ ) in grease for this purpose. There are many OEM specifications that require the use of  $\text{MoS}_2$  in grease formulations as a countermeasure for anti-seizure. It is useful to run the  $\text{MoS}_2$  as a baseline reference to understand the usefulness of other potential solid and related inorganic additives to improve LCC. There has been work done on various solids with EP additives or co-additives. The authors have evaluated a number of different solids and solid/inorganic dispersions that will be summarized below as potential solutions for increased LCC.

### Calcium and Magnesium Solids

Calcium and magnesium solids were evaluated for their LCC in lithium complex grease by D2509 and D2596 tests as summarized in table 4. It is a common practice to add calcium carbonate to grease to increase LCC. Table 3 shows that both calcium hydroxide and magnesium hydroxide did not increase OK load over 3%  $\text{MoS}_2$  baseline.  $\text{CaCO}_3$  (as calcite) increased the LCC by the D2509 Timken test, but the D2596 weld load decreased by two load stages from 315 kg to 200 kg. This makes calcite an option for increasing LCC for some applications.

Table 4. Effect of Solid Additives in Lithium Grease

Solid Additive, 3% Solids in NLGI#2 Lithium Grease	$\text{MoS}_2$	$\text{Ca}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$	$\text{CaCO}_3$
D2509, OK load (lb)	<20	<20	<20	60
D2596, Weld load (kg)	315	250	160	200

### Boron Compounds

Borates represent one additive class that is known to provide extreme pressure properties. Boron compounds include solids, solid dispersions, inorganic dispersions, and organic compounds. Some borates may be considered a physical solution and some a chemical solution depending upon how the additive interacts with surfaces that are lubricated, i.e., whether a tribochemical film is formed at the interface or not. Figure 4 shows comparative weld load results for greases containing a variety of different borate compounds in the ASTM D2596 4-ball EP test. The grease used in this study was a lithium complex made using 12-hydroxy stearic acid and azelaic acid in a 2 to 1 molar ratio. For comparison, a grease containing no additive was evaluated to show the EP activity of the different borates, and a

reference grease containing MoS<sub>2</sub> was evaluated to show how the different borates compare to a well-known industry standard solid lubricant. The results showed that metaboric acid, potassium tetraborate tetrahydrate, and potassium pentaborate tetrahydrate provided equivalent weld point of 400 kg to the MoS<sub>2</sub> and significantly above having no added solid at all.

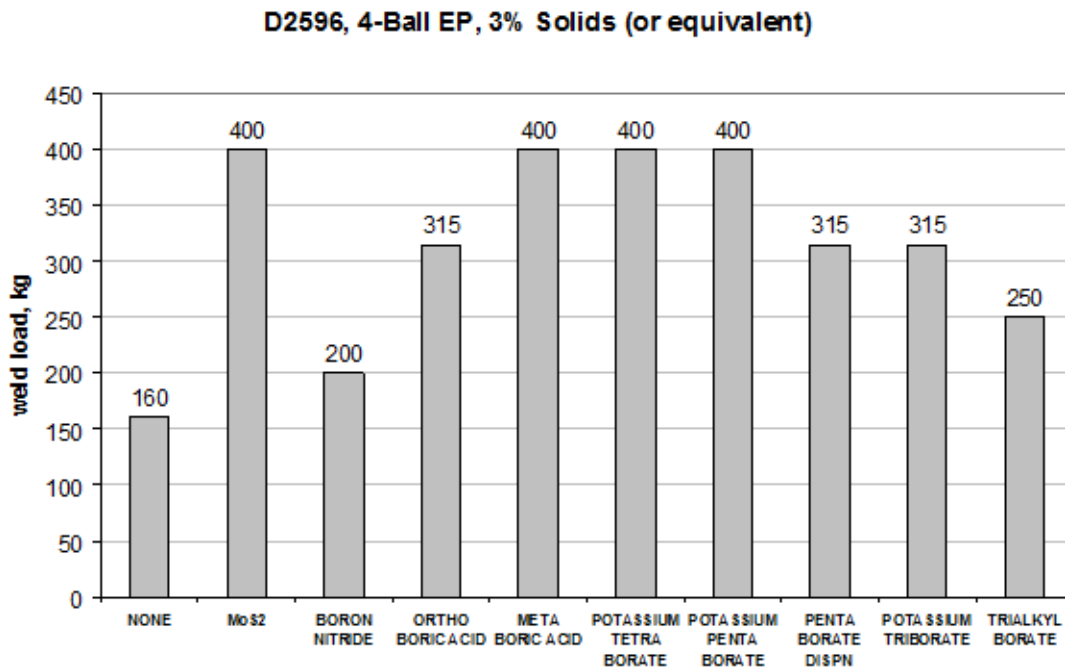


Figure 4. 4-ball weld points of boron compounds

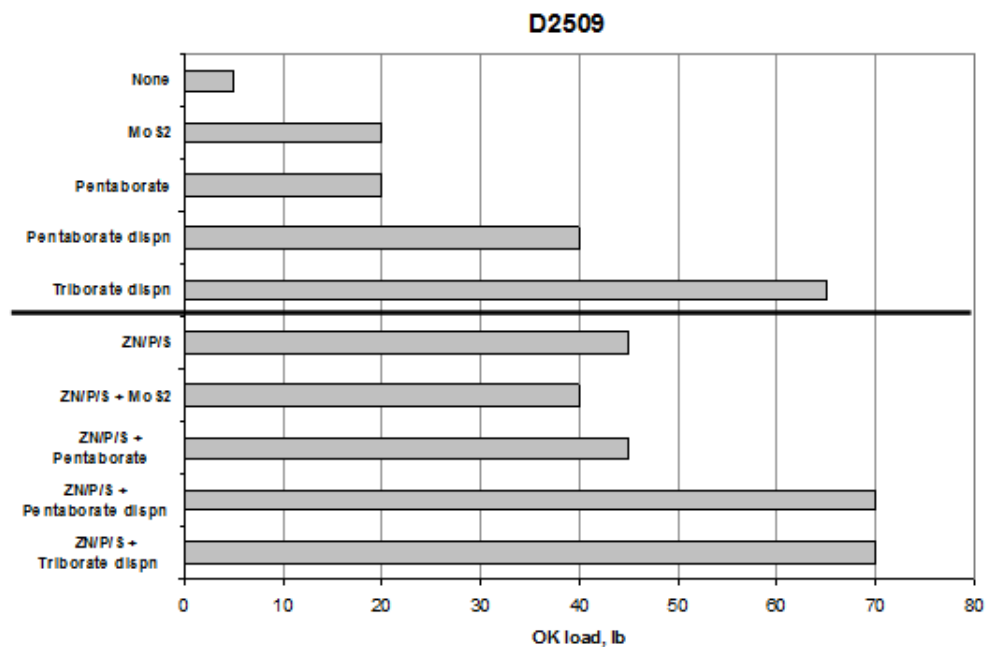


Figure 5. Borate dispersion impact on OK load

Figure 5 shows that when it comes to Timken OK load, the borate dispersions outperform MoS<sub>2</sub> as individual components and when formulated as a Zn/P/S additive package where the solids/inorganics were added at 3 %wt solids in the greases. This data on the triborate agrees well with results published previously by Ward, et al (12) on triborate dispersion additive chemistry. The triborate dispersion was found to give extremely thick and tenacious tribochemical film in the wear scars of Timken blocks as compared to sulfurized olefin, zinc dialkyldithiophosphate, and antimony dialkyldithiocarbamate additive chemistries. The borate solid in oil dispersions provide a way to increase LCC when formulated in a responsive grease. The data show the efficacy of a ZN/P/S additive to provide an EP level of protection and the borate dispersions to increase the LCC to a higher level without antagonizing the overall formulation to lower LCC.

## **Summary**

Today the two main standard methods used for determining the LCC of greases are the Sliding 4-Ball EP test and the Timken OK load test. However, based on the examinations of a heavily loaded industrial application, it would appear that none of today's standard test methods wholly relate to EP conditions seen in this type of application, although, at least one the current test methods have been written into almost all EP grease specifications.

For increasing the LCC when using the Sliding 4-Ball EP test, increasing the sulfur content of the grease either through using a polysulfide or SbDTC can easily be applied but care needs to be taken with copper corrosion issues. Solid lubricants such as MoS<sub>2</sub> or borates can also be used in conjunction with or as EP boosters for antiwear packages

For the Timken OK test, polysulfides on their own do not perform as well as DMTD or SbDTC additives. Borates and MoS<sub>2</sub> also can act as boosters on top of antiwear packages.

## **Conclusions**

There are multiple solutions to achieving high LCC, but care needs to be taken when choosing one as all potential solutions have issues that need to be considered. How the LCC is determined also has an influence as to what solution should be chosen.

## **Acknowledgements**

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## Rheological Studies of Lubricating Greases using Lincoln Ventmeter

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**ABSTRACT-** Rheological properties of lubricating greases play an important role in the selection of greases specially those greases which are to be used in centralized lubrication system. There are various test equipments to study the rheological properties of greases. But Lincoln Ventmeter test is the simple and fast test which can be used to decide the suitability of greases for a particular centralized lubrication system. The paper describes the Lincoln Ventmeter study of different types of greases with different base oils, different NLGI grades etc.

The rheological property of grease depends upon various factors like the type of grease, its structure, consistency, base oil viscosity, temperature etc. Various greases have been studied with different thickeners, different NLGI grades and different base oil viscosities. The results obtained are discussed.

## **Introduction-**

Although, lubricating grease is defined by ASTM D-288 as “Solid to semisolid product of dispersion of a thickening agent in a fluid lubricant”, this definition is not complete. This could be useful for production purpose; it is hardly adequate to describe grease which is a complex product. Rheologically, a more appropriate definition has been given by Sinitsyn (1) “a lubricant which under certain loads and within its range of temperature application exhibits the property of a solid body, undergoes plastic strain and starts to flow like a fluid should the load reach the critical point and regains solid body property after the removal of stress” This indicates that the grease is both solid and liquid depending on the physical condition of temperature, stress etc. This gives grease an additional property i.e. Yield Value, the threshold level of shear stress or strain. The grease structure is held together by internal bonding forces giving the grease a solid character by resisting positional change. This rigidity is referred as Consistency. (2)

Below the yield stress, greases behave like solids and do not flow. The yield stress depends upon the rigidity of the soap fiber network. However, when the load exceeds the yield point, grease starts flowing like lubricating oil. This is due to the rupture of the weakest junction in the network thus making flow possible. (3)

The rheology of greases appears to be typical of viscoelastic materials possessing a certain degree of internal structure and memory (thixotropy) and there exists an obvious correlation between the pumpability and rheological characteristic of greases at all temperatures.(4)



It has been observed that besides base oils, thickeners & additives, the flow properties of lubricating greases also depends upon the structural network of its soap fibers.

### **Equipment & Test-**

Lincoln Ventmeter is often used to predict the flow property of lubricating greases. As shown below, the Lincoln Ventmeter consist of a 25 ft coil of  $\frac{1}{4}$  inch copper tubing with a gauge at one end and a grease fitting at the other end of the test coil. With valve no 1 closed, and valve no 2 open, the grease to be tested is pumped into the ventmeter by a lever gun until the grease begins to flow from valve no. 2, thus eliminating any air entrapped in the tube. At that point, the temperature is adjusted to the test temperature. Valve no 2 is then closed and lever gun is operated until the pressure builds to 1800 psi. Equilibrium of at least 30 minute is required. The pressure is then vented and the venting rate is timed; the pressure at the end of 30 sec is recorded as ventmeter reading or ventmeter viscosity.



The major advantage of Lincoln Ventmeter is that due to its small size ventmeter readings can be obtained at low temperatures by keeping the ventmeter in ice box or at high temperature by placing it in an oven.

Since the action of ventmeter is similar to venting a lubricating system, it can be used to specify the size of supply lines or knowing the different diameters and lengths of supply lines, predict which grease will be most suitable. A supply line chart as generated by the supplier is shown in Table.

Table SL-1&SL-11 Supply Line Chart

NLGI Grde	Lincoln Ventmeter Reading(psi)	Nominal pipe size or ID of Tube or Hose(in)	Max. supply line length (Ft)
#0	0-100	2.00	1100
	0-100	1.50	875
	0-100	1.25	700
	0-100	1.00	575
	0-100	0.75	430
	0-100	0.50	270
	0-100	0.38	200
	0-100	0.25	130
#1	100-200	2.00	500
	100-200	1.50	400
	100-200	1.25	350
	100-200	1.00	270
	100-200	0.75	210
	100-200	0.50	140
	100-200	0.38	110
	100-200	0.25	50

#2	200-300	2.00	350
	200-300	1.50	280
	200-300	1.25	235
	200300-	1.00	180
	200-300	0.75	140
	200-300	0.50	90
	200-300	0.38	70
	200-300	0.25	40
#2	300-400	2.00	280
	300-400	1.50	200
	300-400	1.25	175
	300-400	1.00	140
	300-400	0.75	100
	300-400	0.50	70
	300-400	0.38	50
	300-400	0.25	30
#3	400-500	2.00	230
	400-500	1.50	170
	400-500	1.25	140
	400-500	1.00	140
	400-500	0.75	100
	400-500	0.50	70
	400-500	0.38	50
	400-500	0.25	30
#3	500-600	2.00	190
	500-600	1.50	140
	500-600	1.25	120
	500-600	1.00	90
	500-600	0.75	65
	500-600	0.50	45
	500-600	0.38	36
	500-600	0.25	15

This supply line chart can indicate most suitable grease at specific temperature, knowing the diameter and length and determining the ventmeter reading. If the readings are taken at different temperatures graph of ventmeter reading against temperatures can be plotted. This graph then can be used to determine which grease is suitable at a particular temperature for centralized lubrication system.

Lincoln ventmeter can also be used to determine the apparent viscosity of greases at different temperatures. For this the amount of grease coming out of ventmeter in 30 sec is to be determined.

It has been established that Poiseuille's equation for laminar flow in pipes can be used for grease flow calculations over a wide range of operating conditions with sufficient accuracy for most engineering uses.

Poiseuille's equation for laminar flow in pipe is

Apparent Viscosity ( $\eta$ ) = Shear Stress( $Y$ )/Shear Strain( $S$ )

$$\eta = Y/S$$

$\eta$ =Apparent Viscosity, dynes/cm<sup>2</sup>

$Y$ =Shear Stress, lbs/in<sup>2</sup>

$S$ = Shear Strain, (s<sup>-1</sup>)

Shear Stress =  $PR/2L$

Shear Strain =  $4Q/\pi R^3$

$$\eta = \pi PR^4/8LQ$$

$P$  = Pressure drop in dynes/cm<sup>2</sup>

$R$ = Radius of pipe in cm.

$L$  = Length of pipe in cm.

$Q$  = Flow rate in  $\text{cm}^3/\text{sec}$

So knowing the pressure drop, length of tubing, its diameter and the flow rate in Lincoln Ventmeter, the apparent viscosity of the grease can be determined at that temperature.

The centralized lubrication systems are used in big plants where no. of lubrication points are to be lubricated regularly at certain frequency and the right amount of grease to be applied at right time. The performance of the plant vastly depends upon the successful operation of centralized lubrication system. Lincoln ventmeter testing will determine the suitability of particular grease at particular temperature for a particular centralized system.

Ventability is defined as a measure of residual pressure (psig) where grease ceases to flow through a length of coiled tubing of coiled  $\frac{1}{4}$  inch (6mm) diameter tubing 25 ft (7.62 meters) in length after a pressure of 1800 psig (122.5 atm) is applied and vented.(5)

Ventmeter can be used to

- determine what type of grease can be used in a given grease supply line for use in a centralized automatic lubrication system.
- determine what diameter of line should be used for a type of grease and supply line length in a centralized lubrication system.
- determine at colder temperatures, when to switch a grease to a lighter NLGI grade so the system will continue to operate correctly at those lower temperatures.

The apparent viscosity test results obtained by Lincoln Ventmeter are comparable with the results obtained by ASTM D-1092. Apparent viscosity has been accepted by application engineers in sizing pumps and designing lubrication systems. (6)

Grease with a ventmeter reading of above 600 psi would not be suitable for use with automatic lubrication system. (7)

The paper describes the effect of various factors such as grease thickeners, type of base oils, viscosity of base oils and consistency of grease on the ventability.

### **Experimental –**

In big steel plants, Power plants, Cement plants etc. normally lubricating greases are being applied through centralized lubrication systems which can deliver the grease through long pipe lines to various lubrication points. Lubrication frequency can be adjusted by multistage dispenser which delivers specific quantity of grease in specific time. Hence, the greases to be used in these plants should not only have all the suitable attributes such as high temperature capability, high load carrying ability, high water resistance etc. but in addition they also should have good pumpability for working in centralized lubrication systems. Hence, in this rheological study only those types of greases are included which are normally suitable in centralized lubrication systems.

This study has been divided into five parts.

In the first part, lithium base greases (A1,A2, A3,A4,A5) with the same base oil viscosity but with different NLGI Grades have been tested.

Table 1

In the second part, Lithium complex greases (B1, B2, B3, B4, B5) with same base oil viscosity but different NLGI Grades are tested. Table 2 This is similar to part I except for Lithium Complex soap.

In the third part, lithium base greases with the same base oil viscosity and same NLGI Grades but different types of base oils (C1,C2,C3,C4)i.e. paraffinic, naphthenic and synthetic oil are used. Table 3

In the fourth part, greases (D1, D2, D3, D4, D5) were prepared with same base oil viscosity, same NLGI Grades but different types of thickeners are used. Table 4

In the fifth part, same thickener of grease, (E1, E2, E3, E4,) same NLGI Grade, same type of base oil but different viscosity grades are used. Table 5

All the ventmeter tests have been carried out at 25 deg. C.

### **Results and discussions-**

In the first experiment lithium base greases were prepared by the normal procedure using same mineral base oil VG-100 and tested for Lincoln ventmeter test. The results are given in Table 1

Table 1

Grease	Thickener	Base Oil Viscosity Grade	NLGI Grade	Worked Penetration	Lincoln Ventmeter Reading, psi
A1	Lithium soap	VG-100	3	242	450
A2	Lithium soap	VG-100	2	285	275
A3	Lithium	VG-100	1	325	260

	soap				
A4	Lithium soap	VG-100	0	361	125
A5	Lithium soap	VG-100	00	405	100

In the second experiment Lithium complex greases were prepared using VG-220 base oil.

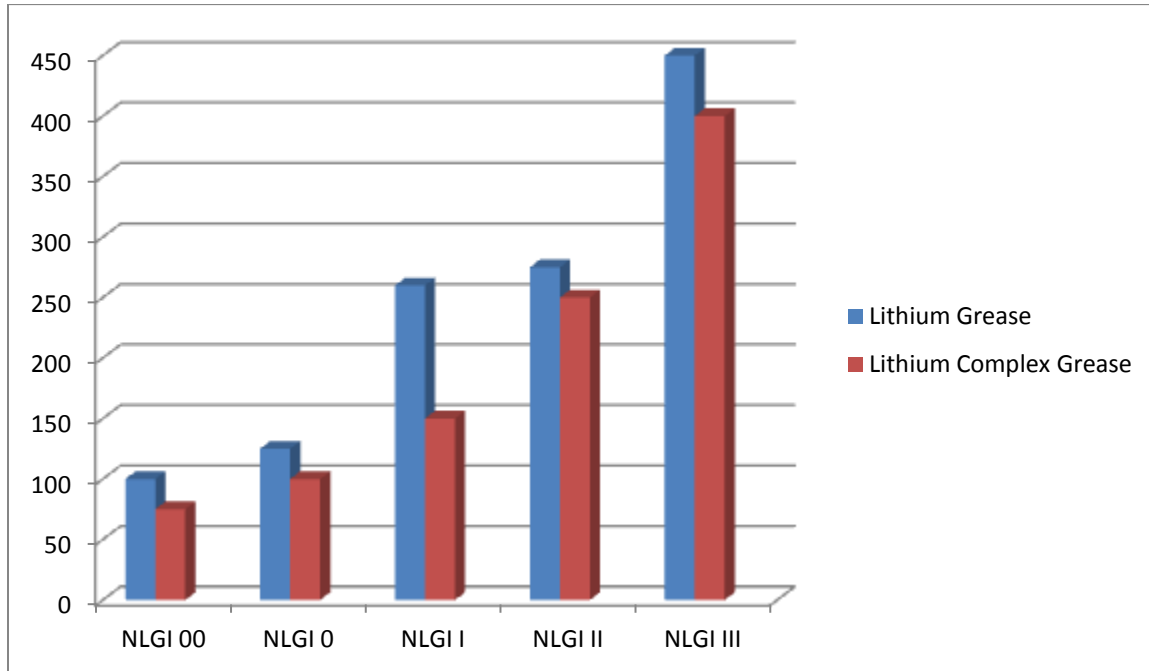
Table 2

Grease	Thickener	Base Oil Viscosity at 40 deg C, cSt	NLGI Grade	Worked Penetration	Lincoln Ventmeter Reading, psi
B1	Lithium Complex soap	220	3	245	300
B2	Lithium Complex soap	220	2	285	250
B3	Lithium Complex soap	220	1	324	150
B4	Lithium Complex soap	220	0	360	100
B5	Lithium complex soap	220	00	410	25



Fig 1

### Ventility of Greases with different NLGI Grades



The fig.1 indicates that the softer greases have better flow properties. The yield stress for softer greases is low, which facilitates them to flow. Amongst the lithium and Lithium complex greases, other things like consistency, type of base oil and temperature remaining same, lithium complex greases have better flow properties than normal lithium greases.

The micro structural network of soap fibers may be playing a role in influencing the better flow properties of lithium complex greases. Further work is needed to confirm this tendency.

In the third experiment, Lithium base greases were prepared with different types of base oils. The base oil viscosity for all greases was

kept constant. The penetration was also kept almost same I NLGI Grade 2 range. The base oils used for making greases were mineral oil of Group I & Group II, Naphthenic and synthetic oil. The greases were prepared with similar procedure and milling was carried out in the same manner for all greases.

Table 3

Ventility of greases with different types base oils

Grease	NLGI Grade	Worked Penetration	Type of Base oil	Base Oil Viscosity @40 deg C, cSt	Lincoln Ventmeter reading
C1	2	285	Paraffinic Gr I	VG-100	275
C2	2	295	Paraffinic Gr. II	VG-100	350
C3	2	286	Naphthenic	VG-100	400
C4	2	281	Synthetic (PAO)	VG-100	425

Fig.2

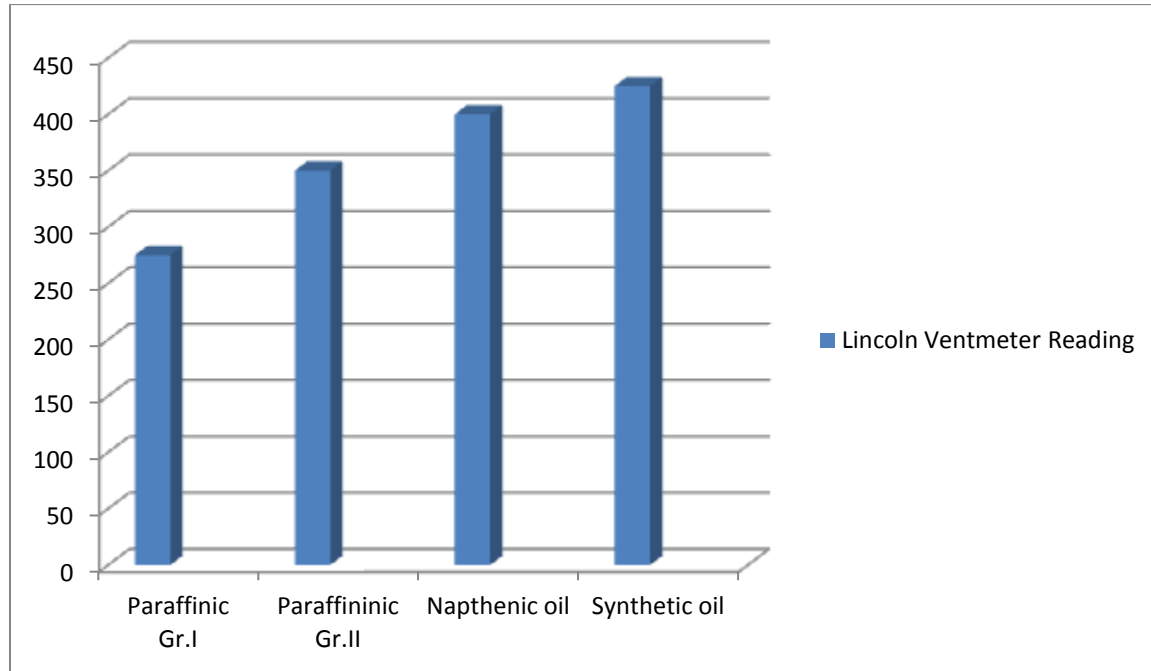


Fig. 2 shows that the grease with Group I base oil has the best flow properties even compared with naphthenic and synthetic base oils among the samples tested under the test conditions. This rheological behavior needs to be studied further by conducting few more experiments at different temperatures.

It has been observed that the thickener content in the lithium grease with Group I base oil is least among the greases tested and it is in the increasing order for Group II, Naphthenic and synthetic oil. The lower percentage of thickener means higher percentage of base oil content and this could give better flow properties to Lithium complex grease. The ventmeter readings show upward trends as the thickener content increases.

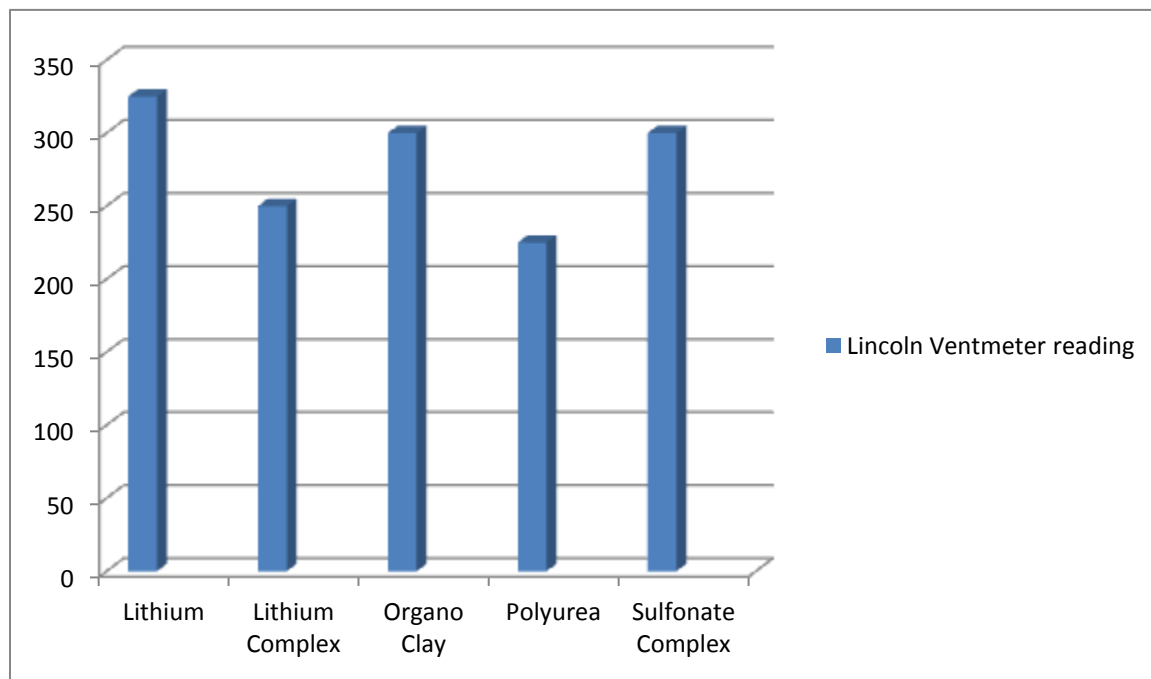
It has been established that pumpability of naphthenic greases is superior to that of paraffinic greases at temperatures between -20 and -40 deg C. The observed difference in the rheological properties of greases is attributed to differing solvencies of base oils which has a significant impact on the structure of the thickener and as a result on the rheology and efficiency of grease.(4)

Table 4

Ventility of Greases with different Thickeners

Grease	Type of Thickener	NLGI Grade	Work Penetration	Base Oil Viscosity	Lincoln Vent meter Reading
D1	Lithium	2	285	VG-320	325
D2	Lithium Complex	2	285	VG-320	250
D3	Organo Clay	2	284	VG-320	300
D4	Polyurea	2	283	VG-320	225
D5	Sulfonate complex	2	282	VG-320	300

Fig.3



In fig.3,it has been observed that among different types of greases, NLGI Grade and base oil viscosity remaining same, polyurea base grease show the least ventmeter reading indicating that among these greases studied, the polyurea base grease show the best flow properties at 25 deg. C.

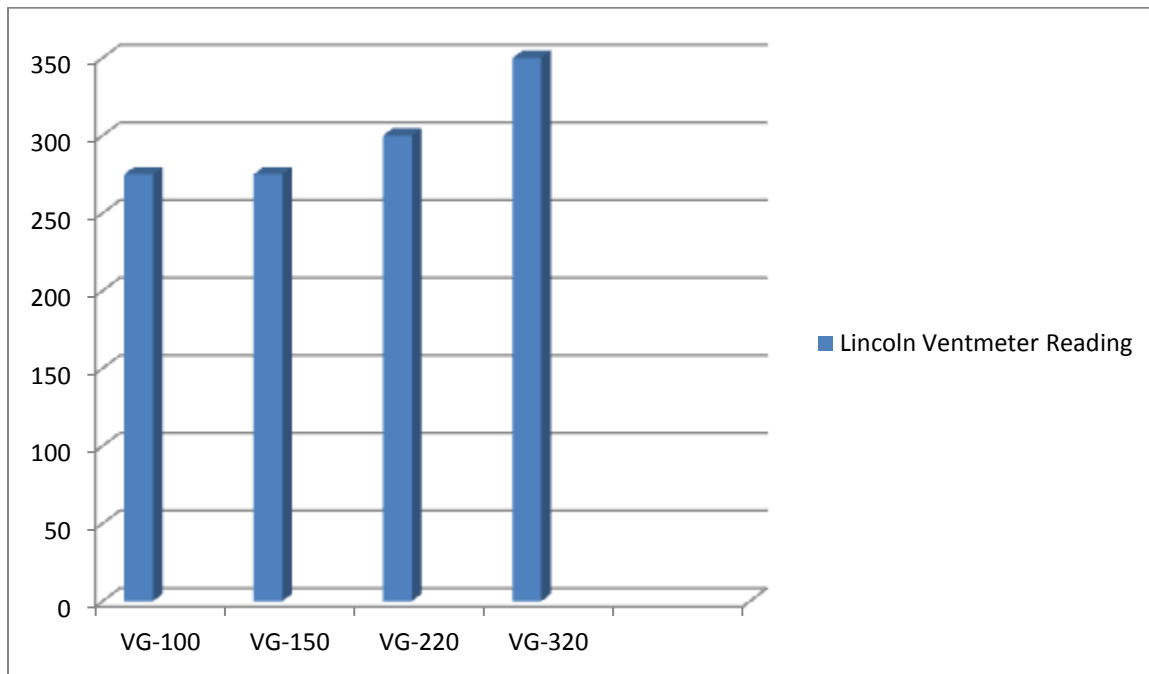
In the fifth experiment, Lithium greases were prepared with mineral oil of different VG Grades. All the greases were NLGI II grades and the consistency was kept within 280-285.The tests were carried out at 25 deg C.

Table 5

Ventility vs Greases with different base oil viscosity

Grease	NLGI Grade	Worked Penetration	Base Oil Viscosity, VG Grade	Lincoln Vent meter reading
E1	2	285	100	275
E2	2	285	150	275
E3	2	282	220	300
E4	2	285	320	325

Fig.4



In fig. 4, the ventmeter readings of Lithium base greases prepared with different base oil viscosities are shown. All the greases are NLGI Grade II with base oils of VG-100, VG-150, VG-220 & VG-320.

It is observed that as the base oil viscosity increases, there is slight increase in ventmeter readings. Increase in base oil viscosity results in decrease in flow properties.

## **Conclusions:**

Based on the above study following inference can be drawn.

-As the NLGI consistency is lowered, the flow property of lithium and lithium complex greases improves. Amongst lithium and Lithium complex greases, lithium complex greases show slightly better flow property compared to lithium greases under similar conditions.

-Amongst different types of greases tested, polyurea base grease show best flow properties under similar conditions.

-If lithium base grease is prepared with different types of base oils, then grease with Group I base oil show the best flow properties compared to other base oil types.

-In lithium base greases, as the base oil viscosity is increased, the flow property decreases.

It is a preliminary rheological study of lubricating greases which we have conducted in our research laboratory using Lincoln Ventmeter. Further rheological studies of greases with Lincoln Ventmeter are planned at different temperatures and with different synthetic base fluids, thickeners coupled with other rheometers.

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### ***Oxidation's Kinematic Regularities of Complex Lithium Greases Based on Petroleum and Synthetic Oils***

Share of dispersion medium is up to 95% of the total mass of complex lithium grease (kLi-grease). The nature and properties of petroleum or synthetic oils will not only affect the structurization of grease, but also determine its performance over a wide temperature range, power and speed loads, stability in aggressive environments. Most often, petroleum oils are used in the formulations of kLi-greases.

However, the extreme conditions under which very often exploited modern technology, creating problems for the process of lubrication, which cannot be solved only by applying such dispersion media. Deficit of hydrocarbon oils with low pour points for different purposes and higher requirements to their quality are facilitated the application of synthetic lubricating fluids in the compositions of greases. Synthetic oils in many cases, by their fire resistance, thermal stability, oxidation resistance are superior to petroleum oils. In addition, a complex mix of properties, namely: slight change of viscosity and high lubricating characteristics over a wide temperature range, and chemical stability along with radiation resistance are intrinsic only to special synthetic products.

Out of a numerous class of organic compounds-bases of synthetic lubricants, as dispersion media most frequently used for greases, are polyalphaolefines, esters of different nature and polyethylsiloxane. Technical specifications are not always solved by the use of individual synthetic oils in a formulation of greases. Often the kLi-greases are manufactured on their mixtures. Mixtures of synthetic oils with petroleum ones are also applied.

Among the main characteristics of high-temperature greases, influencing on the efficiency and durability of friction unit work, a special place is occupied by thermal stability and resistance of grease to oxidation. These are the interrelated parameters which can be characterized as thermooxidative stability. It describes resistance of grease components and lubricating grease composition as a whole to thermal destruction and degradation under the action of oxygen. In other words, it's the ability of grease to resist the changes of their initial chemical composition. The loss of this ability leads to degradation of the base oil, thickener and additives, to the increase of evaporation and oil viscosity. Oxidation products destroy the structure of grease, resulting in a loss of plasticity and thermohardening.

In the proposed work the attempt is made to establish a link between the composition of a dispersion medium (group hydrocarbon composition of petroleum oils, nature of synthetic oils) and thermooxidative properties of the kLi-grease, and reveal the most stable base oils under these conditions

Model samples of kLi-greases are prepared on petroleum oils with different compositions and nature of hydrocarbons and on synthetic oils of different nature

(Table 1).

Group hydrocarbon composition of dispersion medium is determined with adsorption chromatography (GOST 11244). Structural-group chemical composition of the oils, studied over a range of physical and chemical methods, namely: liquid chromatography, infrared spectroscopy and mass spectrometry is presented in Table2.

Table 1

Petroleum and synthetic oils – dispersion media of greases

Oil	Characteristic						
	General	Temperature, °C		Viscosity at 100°C, mm <sup>2</sup> /s	Hydrocarbon composition % mass.		
		Flash point	Pour point		Paraffins & naphthenes	Aromatics	Resins & Sulfure containing compounds
1	Distillate phenolically refined, with deep deparaffinization and contact afterpurification	190	-45	4,7	59,8	39,4	0,8
2	Distillate with acid-alkaline treatment	165	-45	3,2	81,7	17,7	0,6
3	Residual selective-solvent-refined from deasphalted tower bottoms of sulfur-bearing crude oils	270	-10	29,0	39,8	54,0	6,2
4	Residual selective-solvent-refined from sweet crude oils	240	-18	22,0	72,0	26,3	1,7
5	Residual, paraffinic & naphthenic	188	-30	13,4	99,7	-	0,3
6	Polyalphaolefinic oil (PAO)	210	-55	9,3	-	-	-
7	Diisooctyl ester of sebacic acid(DOS)	215	-65	3,8	-	-	-
8	Pentaerythritol ester of fatty acids(PE)	257	-59	4,8	-	-	-
9	Polyethylsiloxane fluid (PES)	>300	-67	36,1	-	-	-
64	Mixture of PAO with oil # 4	237	-30	14,4	-	-	-
67	Mixture of PAO with DOS	215	-60	5,3	-	-	-
68	Mixture of PAO with PE	226	-56	6,3	-	-	-
69	Mixture of PAO with PES	255	-62	19,8	-	-	-

Three component lithium complex in the grease was formed with 12-hydroxy-stearic, terephthalic and boron acids.

Properties of greases on different dispersion media are presented in Table 2.

Because of the imperfections and limited coverage of traditional techniques almost all conducted to date studies of antioxidant stability of greases are not of a systemic nature and do not give a quantitative kinetic evaluation neither early nor the deep stages of oxidation. It is not possible to characterize the dynamics of the whole process and complicates the scientific substantiation of antioxidants selection. To improve the efficiency of research, it is necessary to develop and apply new methodologies that take into account and quantitatively characterizing the diversity of oxidation reactions of greases with inhibitors and without them.

Oil, dispersion medium of greases, is a mixture of hydrocarbons. Therefore, to study the process of oxidation of greases and develop ways of inhibiting it we use the chain theory of liquid-phase oxidation of complex multicomponent systems and techniques that allow you to obtain quantitative information on the kinetics of the process. In the first approximation to the actual mechanism of the oxidation, complex

system is considered as a single object, and the appropriate scheme of changes – as a formal kinetic model that reproduces the main regularities of the chain process: the initiation, growth and broken of chains, a degenerated branching on the products of oxidation, as well as the retarding of a process with natural inhibitors.

Table 2

Properties of kLi-greases with the dispersion medium on petroleum and synthetic oils

Dispersion medium	Oil separation, % (ASTM D 217)	Penetration at 25 °C, m · 10 <sup>-4</sup> (ASTM D 217)	Wear spot diameter (Dw) on 4-ball friction machine at P=392 H, 1 hour, mm, (ASTM D 2266)
1	8,1	230	0,60
2	8,6	240	0,65
3	4,6	200	0,40
4	7,5	220	0,55
5	7,5	225	0,75
6	12,0	280	0,78
68	10,8	309	0,60
67	12,0	290	0,40
69	7,4	286	1,82
64	8,0	309	0,66

\* - dropping point of all greases' samples exceeds 230 °C

To develop the theoretical basis of the method for studying kinetic regularities of greases' oxidation we use dependencies known from the chain theory of liquid-phase oxidation.

1 . The dependence of velocity of initiated oxidation in the absence of natural inhibitors in the system (the ultimate rate of oxidation) upon the rate of initiation

$$W_{\infty} = \frac{k_2 W_i}{\sqrt{k_6}} \quad (1)$$

where  $W_i$  - the rate of radicals formation from the initiator;  $W_{io}$  - the rate of radicals formation from hydrocarbons of a dispersion medium ( $RH$ ),  $W_i \gg W_{io}$ ;  $k_2$  - hydrocarbons substrate reaction rate constant with peroxide radicals;  $k_6$  - recombination reaction rate constant ( $ROO \cdot + ROO \cdot \rightarrow$  molecular products);

2. The equation of oxidation chain length

$$\nu = W_{\infty} / W_i \quad (2)$$

3. The dependence of initiated oxidation rate in the presence of natural inhibitors (initial speed of oxidation) in the system upon the rate of initiation

$$W_{\infty} = \frac{k_2 W_i}{f \sqrt{k_6}} \quad (3)$$

where  $f$  - stoichiometric coefficient of inhibition (usually  $f = 2$ );  $k_7$  - reaction rate

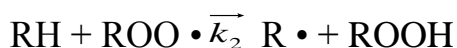
constant of oxidation chains breakage;  $[InH]$  - natural inhibitors' concentration in the system

$$[InH] = \frac{\tau \cdot W}{f} \quad (4)$$

where  $\tau$  - induction time of oxidation;

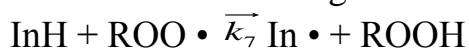
Oxidation resistance of model samples we propose to evaluate by a value of kinetic parameters representing by themselves some ratios of constant rates of elementary reactions. Kinetic parameters are calculated graphically with the solution of equations (1), (3).

Parameter  $a = \frac{k_2[RH]}{\sqrt{k_6}}$  defines the activity of hydrocarbons during reaction with peroxide radicals:



More stable the grease, the less is the value of the parameter  $a$ .

Parameter  $c = \frac{k_2[RH]}{fk_7[InH]}$  characterizes the efficiency of natural inhibitors' action in a grease by the reaction of breakage of oxidation chains:



The more effective the action of natural inhibitors in a grease, the less is the value of the parameter  $c$ .

The totality of the above presented kinetic parameters characterizes fully enough the oxidation process of complex multicomponent mixtures and is a basis for the research of antioxidative stability of greases and establishment of model systems to study the effectiveness of antioxidants.

For measuring the oxygen absorbed by a grease and calculation of quantitative kinetic parameters we made a special installation. The main unit of the installation is the reactor of original design executed in the form of a planetary mechanism (fig. 1).

All details of the reactor is in a fixed position and positioned relative to each other with a certain gap. Pinion shaft rotation is transmitted to two rolls. Revolving simultaneously around its axis and on the internal surface of the reactor, rollers distribute the grease in a thin layer on a surface of the reactor, housing, covers, shaft-gear and provide continuous renovation of the surface layer of a grease. Effective contact of a grease film with oxygen favors large surface gas-grease interface. Design of reactor simulates the real conditions of grease work in a roller bearing. The reactor involved in an enclosed sealed system with forced circulation of oxidative agent. Gaseous products formed during oxidation, are frozen out, and thus purified oxygen is fed to the reactor. As a result of absorbing oxygen with a grease, a pressure in the system drops below atmospheric. To restore the oxygen pressure in the system, an electrolyzer unit is provided. The electrolyte level in electrolyzer varies depending on a pressure in the system. With pressure falling, a contact is closed. As a result of electrolysis reactions, an oxygen is evolved at the anode, and at the cathode-hydrogen ( $4OH^- \rightarrow O_2 + 4e^- + 2H_2O$ ;  $2H^+ + 2e^- \rightarrow H_2$ ).  $H_2$  is released into the atmosphere, and  $O_2$  enters the system until full compensation of adsorbed oxygen with a grease is achieved. This quantity is registered with an automatic potentiometer

as a kinetic curve.

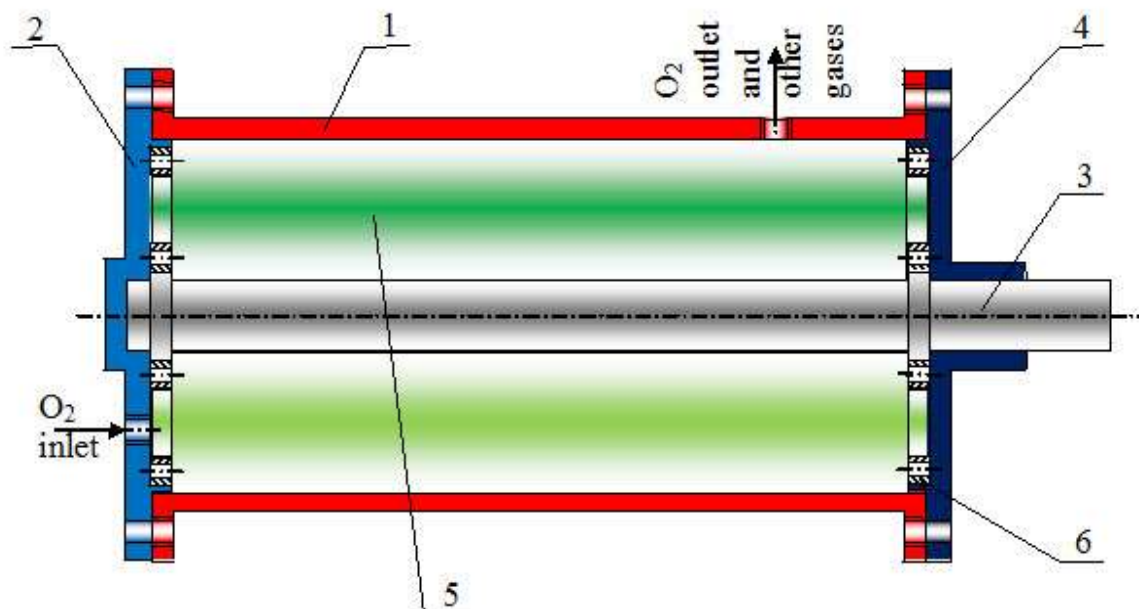
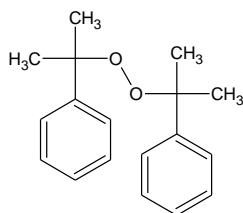


Figure 1. Reactor of the installation to determine antioxidation stability of a grease under dynamic conditions: 1 – housing, 2 – front end cover, 3 – shaft-gear, 4 – back cover, 5 – rollers

Kinetic curve is a bearer of information on initial and final rates of grease oxidation and the induction period of oxidation. The kinetics of the initiated oxidation process of greases is of a non-linear character in the initial period, due to the presence of natural inhibitors in hydrocarbon oils. To calculate initial rate of oxidation ( $W_H$ ) the method is proposed for determining  $W_H$  after absorbing with a grease  $1.5 \cdot 10^{-2}$  mol/l of oxygen, when virtually in all of model samples a natural inhibitor would be fully exhausted. For the induction period ( $\tau$ ) is taken a moment in time at which a grease sample absorbs the same amount of oxygen. The final rate of oxidation ( $W_K$ ) is calculated according to the tangent tilt angle to the kinetics curve drawn from the point on the x-axis, corresponding to the induction period (fig. 2).

To create standard kinetic conditions to study the oxidation process of greases we use dicoumilperoxide as the initiator:



It provides constant rate of free radicals formation ( $W_i$ ) within the temperature range 100-145° C

$$k = 1.88 \frac{75}{T} \quad (6)$$

where T- temperature in Kelvin degrees.

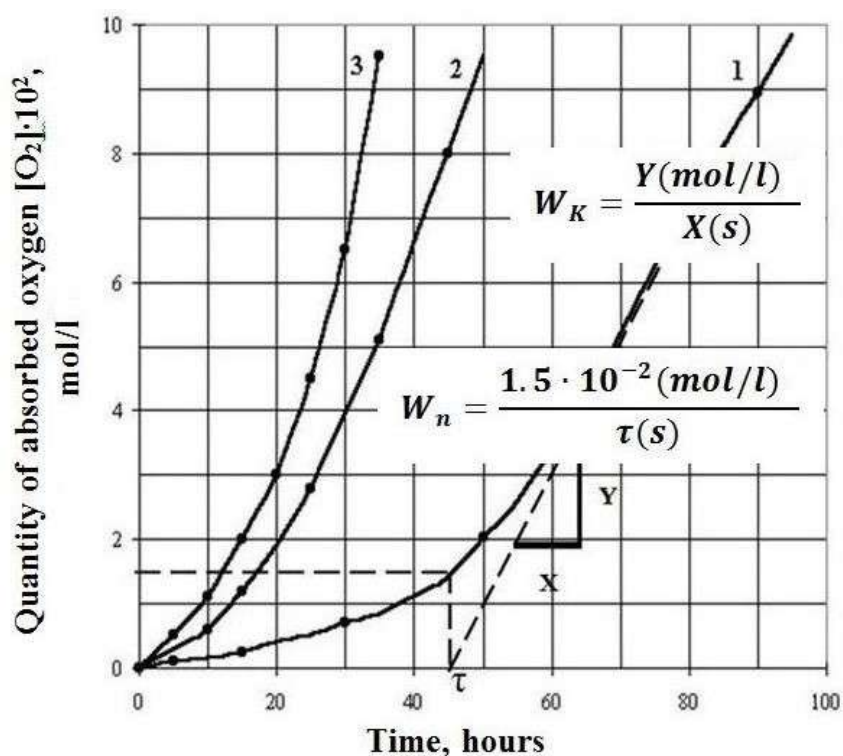


Figure 2

Oxygen uptake kinetics in initiated oxidation of kLi-greases based on petroleum oils has a non-linear character at the initial period, due to the presence of natural inhibitors in oils which are capable to inhibit the process of oxidative transformations. The concentration values of natural inhibitors and their effectiveness according to a parameter value  $c$  are presented in Table 3.

The table shows that the maximum number of inhibitors contained in a grease based on oil 3. Most likely, this is because the oil derived from sulfur crude oils containing significant amounts of thiophene derivatives - a well-known oxidation inhibitors. In addition, the oil contains heavy aromatics with compounds-potential natural oxidation inhibitors; resinous substances that represent condensed systems (aromatic and naphthenic cycles) with the main content of oxygen-, sulfur-, and nitrogen-containing compounds. All of these substances, especially sulfur-containing, can actively counteract to oxidative processes.

Table 3

Concentration of natural inhibitors ( $[InH]$ ) and their effectiveness in kLi-greases based on petroleum oils at  $125^\circ C$

Dispersion medium	$[InH] \cdot 10^3$ , mol/l	$c$
1	1,11	2,9
2	1,35	2,2
4	1,45	2,1
3	2,14	1,2
5	0,33	10,0

Greases 2 and 4 based on petroleum oils contain approximately the same number of inhibitors, although by the structural-group composition of a dispersion medium are different. Assessing substances that can inhibit oxidation, it should be noted that number 4 oil composition contains 2,5 times more resinous compounds in comparison with number 2 oil and 3 times more sulfur-containing compounds. A little less natural inhibitors is contained in number 1 oil (the main part, most probably, in fractions of middle aromatic hydrocarbons (MAH).

The total content of sulphur-containing compounds and resins in oil 1 represents only 0.8%, and heavy aromatics is absent at all. Interestingly, the effectiveness of inhibitors of these three oils are almost the same, although heavy hydrocarbons and resins better inhibit oxidation with temperature rise.

Low content of natural inhibitors in lubricating oil 5 is confirmed with structural-group composition of this oil (99.7% of PNH and 0.3% of resins). At 135°C inhibitors were almost completely depleted, perhaps even during the warmup of the installation before the start of experimental data registration.

By the initial rate of the autooxidation, after the end of the period of full inhibition with natural inhibitors, the rate of free radicals nucleation is calculated:

$$W_o = (W_a/a)^2 \quad (6)$$

This parameter is numerically characterized the "starting" a potential process for a grease oxidation after the period of full inhibition.

Values of parameters  $a$  and  $W_{io}$ , which characterize the initial stages of greases oxidation of after depletion of natural inhibitors, for temperatures  $> 135^\circ \text{C}$  were calculated by hydrogen dependences ( $\lg a$  ( $\lg W_{io}$ ) -  $1/T$ ), taking into account the test data at 115-135° C. Table 4 shows the dependence of the logarithms of  $a$  and  $W_{io}$  on temperature. The lower the values of the coefficients A and B in the equations  $\lg a$  ( $W_{io}$ ) = A - B/T, the higher is the antioxidative stability of greases.

Table 4.

Dependence of kinetic parameters  $a$  and  $W_{io}$  on temperature

Dispersion medium	Dependence $a$ on $T$ (K)	Dependence $W_{io}$ on $T$ (K)
1	$\lg a = 4,44 - 2335,0 / T$	$\lg W_{io} = 0,37 - 3621,8 / T$
2	$\lg a = 4,05 - 2234,0 / T$	$\lg W_{io} = -0,28 - 3393,9 / T$
4	$\lg a = 3,61 - 2086,6 / T$	$\lg W_{io} = -0,88 - 3170,7 / T$
3	$\lg a = 3,52 - 2070,4 / T$	$\lg W_{io} = -1,99 - 2757,8 / T$
5	$\lg a = 9,85 - 4372,55 / T$	$\lg W_{io} = 1,93 - 4148,9 / T$

At temperatures 115-125° C, the resistance to oxidation of greases based on distillate oils by parameters  $a$  and  $W_{io}$  is almost identical, but with increasing the temperature up to 135° C most stable is the grease on oil 2. Explanation of this trend is a presence of heavy aromatics in the composition of this oil (in the complete absence of them in oil 1), advantage in the quantity of paraffins, more stable than naphthenes, as well as the presence of sulfur-containing aromatic compounds which are potential inhibitors.

Oil 2 and 4 have a lot in common in their hydrocarbon composition (comparable quantities of paraffins, naphthenes and middle aromatics). However, oil 4 contains more light aromatics that would adversely affect the stability of oil to oxidation, but according to parameters  $a$  and  $W_{io}$  the oil 4 is more stable. The advantage in quantity of resins, as the likely oxidation inhibitors, for the oil 4 is not relevant, since the above mentioned kinetic parameters are calculated after full depletion of natural inhibitors. It is suggested that naphthenes and paraffins of residual oils contain high amounts of branched alkyl substituents. With branching taking place along Quaternary carbon atoms, unlike paraffin-naphthenic hydrocarbon distillate oils, where there may be a large number of tertiary carbon atoms. An increase in the number of tertiary carbon atoms with short radicals reduces the antioxidant stability of hydrocarbons. The availability of Quaternary carbon atoms shields -C-H Group, interferes with the oxygen molecule breaking it with the formation of peroxide radical  $ROO \cdot$  and enhances the ability of hydrocarbons to counteract the process of oxidation. In addition, paraffin-naphthenic hydrocarbons (PNH) residual oils are more stable to oxidation than distillate ones due to the greater stability of heavy alkanocyclanes which are typical for PNH fractions of residual oil.

The most stable to oxidation was a grease on oil 3. With rise in temperature, it is observed the smallest, among the investigated greases, increase of the oxidation's kinetic parameters. This can not be explained only by the predominance of quaternary carbon atoms in PNH fraction because the content of PNH fraction in oil is less than 40%. Perhaps this is the case when the driving force in counteracting the aggression of oxygen is inhibiting properties of fractions of middle and heavy aromatics and light aromatic hydrocarbons, because of their specific structure, are more chemically stable.

PNH fraction (oil 5) has the lowest antioxidative stability among studied dispersion media. It was found that aromatic hydrocarbons inhibit the oxidation of naphthenic and complete removal or excessive reduction of the concentration of aromatic compounds sharply increased the ability to oxidation of crude oils fractions. This is most likely refer to the oil 5 obtained by the adsorption removal of aromatics from a residual oil and consisting predominantly of naphthenic hydrocarbons.

Thus, according to the results of group hydrocarbon composition research of petroleum oils influence on antioxidant stability of kLi-greases, manufactured on their basis, the following conclusions can be drawn and some recommendations suggested:

- residual oils, depending on the structural-group hydrocarbon composition, have different resistance to oxidation. Therefore, some caution is needed when kLi-greases' formulations are generated with their participation and the end application in friction units for life-time lubrication;
- the least resistant to oxidation appears the oil on industrial fraction PNH (residual oil 5). At elevated temperatures the grease rapidly accumulates acidic products, which can lead to the loss of its main performance characteristics. Oil 5 is not recommended for use in high-temperature kLi-greases;
- grease on residual oils 4 and 3 have high antioxidant properties in a wide temperature range of application and can be used as the main component of the



dispersion medium for high-temperature kLi-greases;

- grease on ditillate oil 2 because of a specific group hydrocarbon composition (presence of a wide spectrum of aromatics, including heavy and sulfur-containing) proved to be stable to oxidation. But low flash point of oil 2 complicates the process of kLi-grease manufacture and its high-temperature application. That is why, in the kLi-grease formulation it can be used only as a part which increases antioxidative stability of grease;
- grease on ditillate oil 1 is not notably resistant to oxidation, probably due to the high concentration of naphthenes and light aromatics. These types of oils can be used in the formulations of high-temperature kLi-greases only in combination with stable to oxidation residual oils. They improve certain, for example, low temperature properties of such greases.

In cases where the kLi-grease is intended for application in a wide temperature range and under sever conditions of high speeds and power loads , synthetic oils or their mixtures are included in the composition of their dispersion media. Due to a number of beneficial properties, the main component of synthetic oil mixtures – dispersion media of kLi-greases are PAO. Studying the kLi-greases based on PAO mixtures of greases with a certain number of other synthetic oils, you can compare the influence of mixture on oxidation resistance of the system as a whole, as well as determine the most stable synthetic oil.

In a project initiated by the oxidation of greases are oxidized samples with avtouskorenim, kinetic curves there are periods, due to the presence of induction even in synthetic oils (relatively homogeneous in composition) of natural inhibitors (fig. 3).

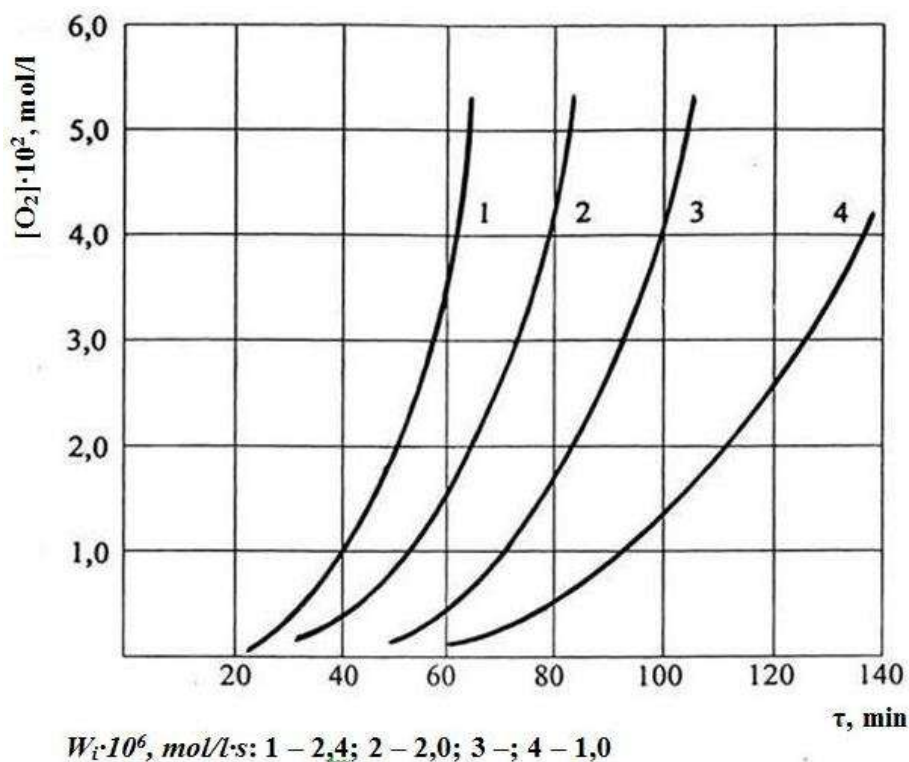


Figure 3. Kinetic curves of oxygen absorption with kLi-grease based on the mixture of PAO with PES (69) in the mode of initiated oxidation at 115 °C

Concentration and efficiency of substances-natural inhibitors, and the other, initiated by the oxidation, kinetic parameters calculated with a graphical solution of equations 1 and 3 are shown in table 5. Results of research show that the grease on PAO is characterized by low antioxidative stability. The introduction in its composition of a small amount of the initiator causes a rapid loss of ability to resist oxidative conversions already at 115° C . The content of inhibiting impurities in the oil is insignificant (~ 0.12 mol/l), and the effectiveness of their actions is extremely low ( $c \sim 52$ ). For comparison: the antioxidative stability of grease based on paraffin-naphthenic hydrocarbons fraction (oil 5) is nearly 2.5 times higher than in the grease on PAO.

Table 5

Kinematic parameters of initiated oxidation of kLi-greases based on synthetic oils at 115° C

Dispersion medium	$a \cdot 10^2$	$W_{io} \cdot 10^9$ , mol/l·s	$c$	$[InI] \cdot 10^6$ , mol/l
<b>6</b>	9,09	6,14	51,52	0,12
<b>68</b>	2,97	2,64	1,86	1,93
<b>67</b>	4,57	3,24	3,86	1,05
<b>69</b>	1,12	1,69	0,92	3,34
<b>64</b>	3,25	4,25	3,03	1,30

It is well-known that products of alpha-olefin polymerization because of the significant amount of residual double bonds (i.e. not entering into a reaction) is easily oxidized. The reaction runs through an intermediate stage of radical hydroperoxide formation in the  $\alpha$ -position of the double bond. Finished molecular products of the reaction are mainly oxides, unsaturated alcohols and carbonyl compounds; acid are formed at the deep stages of oxidation.

To eliminate residual unsaturation of PAO, a variety of methods is used namely: hydrogenation, aromatization, reaction with izoparaffines. Due to the fact that impurities not only of the inhibitory nature, but also which catalyse the ROOH decomposition into radicals by hydrogenation of the initial oligomer remain in the system, it is impossible to reduce the oxidation ability of products to the level of antioxidative stability of heavy saturated hydrocarbons. More efficient way of reducing the concentration of double bonds is the aromatization when additives-inhibitors are formed and remained in the system. The oil 6, judging by its high ability to oxidation, is not subjected to a special treatment in order to eliminate residual unsaturation in the process of its manufacturing.

Shown in Table 5 kinetic parameters indicate that greases on oils' mixtures are differentiated by higher antioxidant stability in comparison with the grease on PAO. The most intensively PAO oxidation in kLi-grease is inhibited with a silicone fluid (9) (parameter  $a$  by an order of magnitude smaller in comparison with the grease on PAO). This supports the data that siloxanes' resistance to oxidation is higher than individual hydrocarbons, their mixtures, ethers, or other compounds.

Silicone fluid (oil 9) is mainly a linear polymer with a general formula  $(C_2H_5)_3Si-[-O-Si(C_2H_5)_2-]_n-O-Si(C_2H_5)_3$ . It is known that the lateral hydrocarbon chains of polyethylenesiloxanes are subjected first to destructive changes under the action of high temperatures and oxidizing agents; and the destruction occurs on a weak methylene group.

In the grease on the mixture (69), along with the ROOH formation by polyalphaolefines and their decomposition at high temperatures under the influence of oxygen, it is generated siloxil- and silylradicals, and this eventually leads to the formation in polysiloxane molecules of cross-linked bonds and to the generation of new polymeric aggregates and gels. Under the influence of water and oxygen-containing ionogenic products formed ROOH as a result of oxidation transformations Si-O-links stability decreases. This creates the conditions for a realignment of linear molecules into cyclical three- and tetrasiloxanes that reduces the grease viscosity and increases its evaporation.

Addition of 40 % of residual petroleum oil 4 (parameter  $a = 3$ ) improves antioxidative stability of the grease on PAO in three times. On the nature of inhibiting mixtures in oil 4 was mentioned earlier. We can only note that oxidation resistance of hydrocarbon oils depends on the group hydrocarbon composition and is determined mainly by the presence of heavy aromatics, tar and sulphur-containing compounds in the oil.

For mixtures consisting of synthetic oils with petroleum ones, at a concentration of petroleum oils more than 15%, the most characteristic form of molecules' existence is their mixed complexes with molecules of a variety of hydrocarbons of petroleum oil. In our case, unstable to oxidation polyalphaolefines, being in the composition of complexes, particularly with molecules of heavy aromatics sulfur-containing compounds and resins of oil 4, are experienced much smaller oxidation transformations.

The stability to oxidation of esters 7 and 8, used as dispersion medium for kLi-greases, is investigated in detail. Attention to them is explained because these products have long been used as aircraft oils with high upper temperature limit of application ( $> 200^\circ C$ ).

We found that the grease on ester 8 is in 1.5 times more stable by parameter  $a$  than the grease on ester 7. Differences in esters reactivity can be explained by steric factors. Oximethylene and methylene group of ester (7), though fewer in number, are spatially more accessible to aggression of oxidizing agents (oxygen, radicals, products of hidroperoxide transformations), and the destruction of the molecules (7) runs faster.

Summarizing the results of the research on the antioxidative stability of kLi-greases using dispersion media on synthetic oils, the following conclusions can be drawn and some recommendations given:

- lowest antioxidative stability has the grease on PAO, possibly because of the large concentration of the double bonds in it. Use of such oil in kLi-greases formulations without prior removal of residual unsaturation can be up to  $125^\circ C$ ;
- addition to PAO 40% of synthetic oils of different classes or residual petroleum oil increases the stability of kLi-grease;

- maximum stability to oxidation under conditions of experiment is characterized the grease with dispersion medium on the mixture of PAO with PES. It is advisable to use polysiloxane fluids in formulations of high temperature kLi-greases designed to operate under conditions of relatively low loads and speeds in certain friction pairs;
- esters of different nature mixed with PAO have different antioxidative stability. By this parameter, pentaerythritol ester due to the peculiarities of the structure of exceeds dialkylsebacate. In a wide temperature range and severe conditions of application the use of PAO with PE mixture in formulations of kLi-greases is the most perspective;
- high resistance to oxidation is also demonstrated a mixture PAO with hydrocarbons of residual oil 4, due to the formation, in this system, mixed complexes of molecules of synthetic and petroleum oils which are resistant to the action of oxygen and high temperatures.

In general, the results can be a scientific basis for the creation of high-temperature multipurpose greases with high stability to oxidation.