Influence of hydro-carbon composition of basic petroleum oils on the oxidation of high temperature greases

L.V. Zheleznyi

Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine,
1, Murmanska Str., Kyiv 02660, Ukraine, Tel./Fax: (044) 573-25-52;
leonid_zhelezny@mail.ru

New procedure that considers and quantitatively characterises all diversity of the oxidation reactions with natural inhibitors and without them was used for the research into the resistance of high temperature greases to the oxidation. The connection between a dispersion medium's composition (group hydro-carbon composition of basic petroleum oils) and thermooxidative properties of high-temperature lithium complex greases was established and distillate and residual base oils that were the most stable under those conditions were also determined. Differences in thermooxidative properties of model greases were explained. Greases on the residual oils were characterised by high anti-oxidative properties over a wide range of application temperatures and could be used as the main component of a dispersion medium of high temperature greases.

1. Introduction

Among the main characteristics of high-temperature plastic greases [1], influencing the efficiency and durability of friction unit operation, a special place is occupied by thermooxidative stability. It determines resistance of base oil 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 the grease to resist the changes in its initial chemical composition. The loss of this ability leads to degradation of the base oil, thickener and additives, to the increase of evaporation and grease viscosity. Oxidation products destroy the structure of grease which results into loss of plasticity and thermohardening [2].

The proposed paper attempts to establish a link between the composition of base oil (dispersion medium) and thermooxidative properties of the complex lithium greases (*c*Li-grease), and to reveal the most stable base oils under these conditions.

2. Experimental

Model samples of *c*Li-greases are prepared on the base of petroleum oils with different nature of the oil, method of purification and composition of hydrocarbons: sample 1 – distillate oil of phenol purification, deep dewaxing and contact cleaning up; 2 – distillate oil of acid-alkaline purification; 3 – residual oil of selective purification with deasphalted tars of crude oils; 4 – residual oil of selective purification of low-sulfur crude oils; 5 – residual oil, paraffin-naphthenic.

Group hydrocarbon composition of dispersion medium is determined with adsorption chromatography (GOST 11244). Structural-group chemical composition of the oils, studied by a range of physical and chemical methods, namely: liquid chromatography, infrared spectroscopy and mass spectrometry is presented in Table 1.

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

Properties of base oils and cLi-greases on their base are presented in Table 2.

Oil, dispersion medium of greases, is a mixture of hydrocarbons. Therefore, to study the process of oxidation of greases and to develop ways of oxidation inhibiting we use the chain theory of liquid-phase oxidation of complex multicomponent systems and techniques that allow to obtain quantitative information on the kinetics of the process [3]. In the first approximation to the actual mechanism of the oxidation, the complex system is considered as an integral 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 breakage of the chains, a degenerated branching on the products of oxidation, as well as the retarding of the process with natural inhibitors.

As a theoretical basis of the method for research of 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) on the rate of initiation (1)

$$W_K = \frac{k_2[RH]}{\sqrt{k_6}}\sqrt{W_i + W_{io}} \qquad (1)$$

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 reaction rate constant with peroxide

Table 1. **Structural-group composition of petroleum crude oils**

Type of compounds	Empirical formula	Content in oil, %				
		1	2	3	4	5
Paraffines:	C_nH_{2n+2}	12.4	25.8	12.0	22.6	37.8
Naphthenes:		47.4	55.9	27.8	49.4	61.9
mono	C_nH_{2n}	20.7	26.8	6.9	14.4	24.5
di	C_nH_{2n-2}	16.4	15.4	6.1	16.1	22.7
tri	C_nH_{2n-4}	7.0	8.5	5.7	9.3	9.6
tetra	C_nH_{2n-6}	3.3	3.6	6.2	6.3	4.9
pentacyclic	C_nH_{2n-8}	–	1.6	2.1	2.1	0.2
hexacyclic	C_nH_{2n-10}	–	–	0.8	0.2	–
Aromatic hydrocarbons:		39.4	17.7	54.0	26.3	–
- light		14.6	8.5	35.4	21.6	–
alkylbenzenes	C_nH_{2n-6}	9.4	6.4	19.2	15.7	–
indans and tetralins	C_nH_{2n-8}	4.0	2.1	9.4	4.6	–
dinaphthenbenzenes	C_nH_{2n-10}	1.2	–	6.8	1.3	–
- middle I group		19.7	3.9	10.2	2.4	–
naphthalenes	C_nH_{2n-12}	15.4	0.9	4.9	0.8	–
acetonaphthens	C_nH_{2n-14}	3.2	2.0	3.7	1.2	–
fluorenes	C_nH_{2n-16}	1.1	1.0	1.6	04	–
- middle II group		5.1	2.1	5.3	1.7	–
phenanthrenepes	C_nH_{2n-18}	5.0	1.2	3.0	1.6	–
naphthenophenanthrenes	C_nH_{2n-20}	0.1	0.9	2.3	0.1	–
- heavy		–	2.6	3.1	0.6	–
pyrenes	C_nH_{2n-22}	–	2.6	2.2	0.6	–
chrysenes		–	–	0.9	–	–
Sulfur-containing compounds:		0.2	0.6	2.5	0.2	–
benzthiophenes		0.1	0.4	1.5	0.2	–
dibenzthiophenes		–	0.2	0.2	–	–
Naphthalenebenzthiophenes		0.1	–	0.8	–	–
Resinous compounds		0.6	–	3.7	1.5	0.3

radicals; k_6 – recombination reaction rate constant ($ROO^\bullet$ + $ROO^\bullet \rightarrow$ molecular products);

2. The equation of oxidation chain length $v = W_K / W_i$.

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 (2)

$$W_H = W_i + \frac{k_2[RH]}{fk_7[InH]} W_i \qquad (2)$$

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
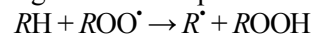
$$[InH] = \frac{\tau \cdot W_i}{f}$$

where τ – induction time of oxidation;

Oxidation resistance of model samples is evaluated by the value of kinetic parameters that represent certain ratios of constant of elementary reactions rates.

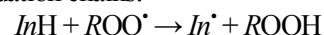Parameter $a = \dfrac{k_2[RH]}{\sqrt{k_6}}$ defines the activity of hydrocarbons during reaction with peroxide radicals:

$$RH + ROO^\bullet \rightarrow R^\bullet + ROOH$$

The more stable the grease is, the lower the value of parameter a.

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

$$InH + ROO^\bullet \rightarrow In^\bullet + ROOH$$

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

Kinetic parameters a and c are calculated by graphical solution of equations (1) and (2).

The collective of the above presented kinetic parameters, in our opinion, characterizes fully enough the oxidation process of complex multicomponent mixtures and is a basis for the research of antioxidative stability of

Table 2. **Properties of** cLi-grease**s with the dispersion medium on petroleum oils**

The properties of petroleum oil and lubricant-cLi based on it	Sample				
	1	2	3	4	5
Petroleum oil					
Flash Point, ºC	190	165	270	240	188
Pour point, ºC	-45	-45	-10	-18	-30
Viscosity at 100 ºC, mm²/s	4.7	3.2	29.0	22.0	13.4
cLi-*grease*					
Dropping point, ºC	>230	>230	>230	>230	>230
Penetration at 25 ºC, m 10^{-4}	230	240	200	220	225
Oil separation, % of separated oil under load 1000 g	8.1	8.6	4.6	7.5	7.5
Wear spot diameter (Dw) on 4-ball friction machine at P=392 H, 1 hour, mm	0.60	0.65	0.40	0.55	0.75

greases and establishment of model systems to study the effectiveness of antioxidants.

To measure the oxygen absorbed by the grease and to calculate the quantitative kinetic parameters we used a special installation [4]. The main unit of the installation is the reactor of original design executed in the form of a planetary mechanism. All details of the reactor are in fixed positions and are positioned relative to each other at a certain gap. Pinion shaft rotation is transmitted to two rolls. Revolving simultaneously around their axes 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 ensure continuous renovation of the surface layer of the grease. Design of the reactor simulates the real conditions of grease operation in a roller bearing. The reactor is involved in an enclosed sealed system with forced circulation of oxidative agent. Gaseous products formed during oxidation are frozen out, and oxygen purified in such a manner is fed to the reactor. As a result of absorbtion of the oxygen with the grease, the pressure in the system drops below atmospheric pressure. To restore the oxygen pressure in the system, an electrolyzer unit is provided. The electrolyte level in electrolyzer varies depending on the pressure in the system. With pressure falling, a contact is closed. As a result of electrolysis reactions, oxygen is evolved at the anode, and hydrogen is evolved at the cathode ($4OH^- \rightarrow 2H_2O + O_2 + 4e; 2H^+ + 2e \rightarrow H_2$). H_2 is released into the atmosphere, and O_2 enters the system until full compensation of adsorbed oxygen with grease is achieved. This quantity is registered with an automatic potentiometer as a kinetic curve.

Kinetic curve is a bearer of information on initial and final rates of grease oxidation and the induction period of oxidation (figure 1). The kinetics of the initiated oxidation process of greases has 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 that provides for determination of W_H after absorbing of $1.5 \cdot 10^{-2}$ mol/l of

oxygen with the grease, when virtually in all model samples a natural inhibitor will be fully depleted, is proposed. ($W_H = \dfrac{1,5 \times 10^{-2} (mol/l)}{\tau(s)}$). The time point at which the grease sample absorbs the same amount of oxygen is taken as the induction period (τ). The final rate of oxidation W_K is calculated according to the tangent tilt angle to the kinetic curve drawn from the point on the x-axis that corresponds to the induction period ($W_K = \dfrac{a(mol/l)}{b(s)}$).

To create standard kinetic conditions for study of the oxidation process of greases we use dicoumilperoxide as the initiator:
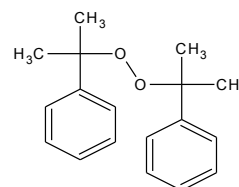
It ensures constant rate of free radicals formation within the temperature range 100–145 °C
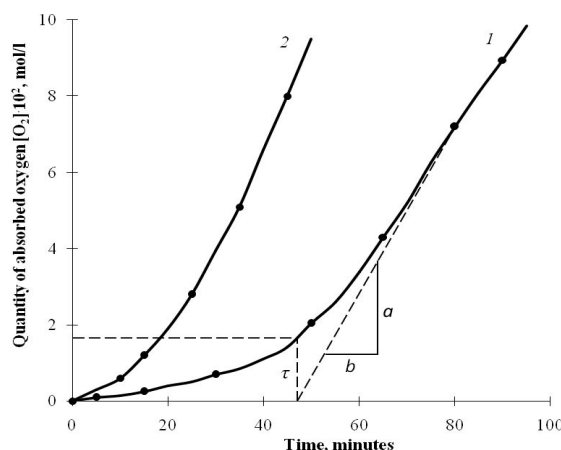
Kinetics of petroleum distillate oil of acid-alkaline purification oxidation and Li-grease on its base (135 °C): *1* – petroleum oil, *2* – Li-grease

$$\lg k_i = 14{,}88 - \frac{7580}{T},$$

where T – temperature in Kelvin degrees.

3. Results and Discussion

Oxygen uptake kinetics in the initiated oxidation of cLi-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 efficiency according to value of parameter c are presented in Table 3.

The table shows that the maximum amount of inhibitors is contained in the grease on the base of petroleum oil 3. Most likely, this is because the oil was derived from sulfur crude oils that contain significant amounts of thiophene derivatives which are well-known oxidation inhibitors. In addition, the oil contains 3.1 % of heavy aromatics with compounds that are potential natural oxidation inhibitors, and the greatest amount of resinous substances that pose the condensed systems (aromatic and naphthenic cycles) with the main content of oxygen-sulfur- and nitrogen-containing compounds. All of these substances, especially the sulfur-containing ones, can actively counteract oxidative processes.

Greases 2 and 4 based on petroleum oils contain approximately the same amount of inhibitors, although they differ by the structural-group composition of the dispersion medium. When assessing substances that can inhibit oxidation, note that number 4 oil contains 2.5 times more resinous compounds and number 2 oil virtually does not have sulfur-containing compounds. A little less natural inhibitors are contained in number 1 oil (the main share, most probably, is contained in fractions of middle aromatic hydrocarbons (MAH) that amount to 24.8 %.

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

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

Value of parameter a, which characterizes the initial stages of greases oxidation after depletion of natural inhibitors, for temperatures > 135 °C were calculated by the dependence ($lg\,a$ ($lg\,W_{io}$) – $1/T$), taking into account the test data at 115–135 °C. Table 3 shows the dependence of the logarithm of parameter a on the temperature. The lower the values of coefficients A and B in the equation $lg\,a = A - B/T$ are, the higher the antioxidative stability of greases.

At temperatures 115–125 °C, the resistance to oxidation of greases based on distillate oils, by parameter a, is almost

Table 3. **The kinetic parameters of oxidation of cLi-greases on petroleum oils**

A sample of grease on petroleum oils	The concentration of natural inhibitors, $[InH] \cdot 10^3$ mol/l	The dependence of the kinetic parameter a on temperature, K	Parameter c (135 °C)
1	1.11	$\lg a = 4.44 - 2335.0/T$	5.3
2	1.35	$\lg a = 4.05 - 2234.0/T$	4.2
3	2.14	$\lg a = 3.52 - 2070.4/T$	2.1
4	1.45	$\lg a = 3.61 - 2086.6/T$	3.3
5	0.33	$\lg a = 9.85 - 4372.55/T$	20.0

identical, but as the temperature increases to 135 °C, the grease on the base of oil 2 possesses the highest stability. This trend is explained by presence of heavy aromatics (2.6 %) in the composition of this oil (while they are completely absent in oil 1), advantage in the quantity of paraffins that are more stable than naphthenes [2], as well as by the presence of sulfur-containing aromatic compounds which are potential inhibitors. In addition, oil 2 contains small amounts of light aromatic hydrocarbons (LAH), prone to oxidation. It should be noted that the basis of this fraction is constituted by the chemically sensitive compound that oxidize mainly with formation of acidic products. Products of hardening (resins) that are condensed during this process in small quantities are not involved in the inhibition of oxidation and are adsorbed on the fibres of the thickener. Heavy aromatic hydrocarbons (HAH) – pyrene and chryzene derivatives, as well as sulfur-containing compounds (SCC) of oil 2 by their stabilizing properties are superior to the middle aromatics of oil 1, the content of which is 24.8 %. For comparison, oil 2 contains 6.0 % MAH.

Oils 2 and 4 have much in common in their hydrocarbon composition (comparable quantities of paraffins, naphthenes and middle aromatics). However, oil 4 contains more light aromatics and less HAH and SCC that would adversely affect the stability of oil to oxidation, but according to parameter a, oil 4 is more stable. The advantage in the amount of resins, as the likely oxidation inhibitors, for oil 4 is not relevant, since the above mentioned kinetic parameters are calculated after full depletion of natural inhibitors. It is known [5] that naphthenes and paraffins of residual oils, oil 4 in particular, contain higher amounts of branched alkyl substituents. Moreover, the branching occurs along quaternary carbon atoms, unlike paraffin-naphthenic hydrocarbon distillate oils, where a large amount of tertiary carbon atoms is

present. An increase in the amount of tertiary carbon atoms with short radicals reduces the antioxidative stability of hydrocarbons. The availability of quaternary carbon atoms shields –C–H group, hinders the oxygen molecule to break the group with the formation of peroxide radical ROO• and enhances the ability of hydrocarbons to counteract the process of oxidation. In addition, paraffin-naphthenic hydrocarbons (PNH) of residual oils are more stable to oxidation than the distillate ones due to higher stability of heavy alkanocyclanes which are typical for PNH fractions of residual oils.

Grease on the base of oil 3 appeared to be the most stable to oxidation. With the rise in temperature, the minimal among the investigated greases increase in the oxidation kinetic parameters is observed. This cannot 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 inhibited with the properties of fractions of middle (5.3 %), heavy (3.1 %) aromatics and SCC (2.5 %) and light aromatic hydrocarbons (35.4 %), because of their specific structure, are more chemically stable in comparison with LAH of other oils (especially distillate).

Values of parameter a for the grease on the base of oil 5 confirm the conclusions of some authors that fraction of PNH has low antioxidative stability [6]. In our case, the lowest stability among the studied dispersion media.

It is known [7] that at the joint oxidation of hydrocarbons with different energy value of –C–H bond, there occur reactions of "cross-over" continuation of chain oxidation when intermediate oxidation products of each component of the mixture can interact with each other and essential role belongs to the reaction of chain transfer $R_1^\bullet + R_2H \rightarrow R_1H + R_2^\bullet$. As a result, easily oxidizing substances can inhibit consumption of hardly oxidizing compounds and vice versa. For example, addition of small amount of ethylbenzene stops the oxidation of n-decane, and the presence of a certain amount of aromatic hydrocarbons without side chains reduces the oxidability of naphthenes.

It has been found [5] that aromatic hydrocarbons inhibit the oxidation of naphthenic ones, and complete removal or excessive reduction of the concentration of aromatic compounds sharply increases the oxidability of oil fractions of crude oils. This most likely relates to oil 5 obtained by adsorption removal of aromatics from residual oil and consisting predominantly of naphthenic hydrocarbons.

4. Conclusions

Thus, by the results of research of influence of group hydrocarbon composition of petroleum oils upon the antioxidative stability of cLi-greases, manufactured on their basis, the following conclusions can be drawn and some recommendations can be suggested:

– residual oil, depending on the structural-group hydrocarbon composition, have different resistance to oxidation. Therefore, some caution is needed when developing cLi-greases formulations with their participation intended for packing into friction units for the life-time lubrication;

–oil on the base of industrial fraction PNH (residual oil 5) appeared to be the least reistant to oxidation. It is not recommended for use in high-temperature cLi-greases;

– greases on residual oils 4 and 3 have high antioxidative properties and these oils can be used as the main component of the dispersion medium for high-temperature cLi-greases;

– grease on the base of distillate oil 2 due to wide spectrum of aromatics, including heavy and sulfur-containing aromatics, is proved to be stable to oxidation. But low flash point of the oil 2 complicates the process of cLi-grease manufacture and its high-temperature application. So, cLi-greases formulations can be used only as a constituent part, which increases antioxidative stability of a grease;

– grease on the base of distillate oil 1 is 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 cLi-greases only in combination with residual oils stable to oxidation, to improv certain properties, for example, low temperature properties of these greases.

1. Lyubinin J.A., Zhelezny L.V., *Friction and grease in machines and mechanisms*, 2013, (3), 21–30.

2. Ishchuk J.L., *Composition, structure and properties of greases*, Kiev, 1996.

3. Emanuel N.M., *Theory and practice of the liquid phase oxidation*, Moscow, 1974.

4. Zhelezny L.V., Butovets V.V., Nikulichev J.G., Lengyel I.V., Ishchuk J.L., *World oil*, 2006, (6), 28–30.

5. Chernozhukov N.I., Crane S.E., Losikov B.V., *Chemistry mineral oils*, Moscow, 1959.

6. Novoded R.N., Bogdanov M.V., Sokolova T.G., *Chemistry and Technology of Fuels and Oils*, 1974, (5), 24–26.

7. Mankovskaya N.K., *Modern ideas about the chemistry of oxidation of various classes of hydrocarbons*, Kiev, 1976.

8. Agabekov V.E., Denisov E.T., Mitscevich N.I., Kosmacheva T.G., *Kinetics and catalysis*, 1974, (4), 883–887.

Влияние углеводородного состава базовых нефтяных масел на окисление высокотемпературных смазок

Л.В. Железный

Институт биоорганической химии и нефтехимии НАН Украины
Украина, 02660 Киев, ул. Мурманская, 1, Тел./факс: (044) 573-25-52;
leonid_zhelezny@mail.ru

Для исследования стойкости к окислению высокотемпературных смазок использована новая методика, учитывающая и количественно характеризующая все разнообразие реакций окисления смазок с природными ингибиторами и без них. Установлена связь между составом дисперсионной среды (групповым углеводородным составом базовых нефтяных масел) и термоокислительными свойствами высокотемпературных комплексных литиевых смазок, а также выявлены наиболее стабильные в этих условиях базовые дистиллятные и остаточные масла. Объяснены различия в антиокислительных характеристиках модельных смазок. Установлено, что смазки на остаточных маслах характеризуются высокими антиокислительных свойствами в широком температурном диапазоне применения и могут использоваться как основной компонент дисперсионной среды высокотемпературных смазок.

Вплив вуглеводневого складу базових нафтових масел на окиснення високотемпературних мастил

Л.В. Желєзний

Інститут біоорганічної хімії та нафтохімії НАН України
Україна, 02660 Київ, вул. Мурманська, 1, Тел./факс: (044) 573-25-52;
leonid_zhelezny@mail.ru

Для дослідження стійкості до окиснення високотемпературних мастил використана нова методика, що враховує і кількісно характеризує все розмаїття реакцій окиснення мастил з природними інгібіторами і без них. Встановлено зв'язок між складом дисперсійного середовища (груповим вуглеводневим складом базових нафтових олив) і термоокиснювальними властивостями високотемпературних комплексних літійових мастил, а також виявлені найбільш стабільні в цих умовах базові дистилятні і залишкові оливи. Пояснені відмінності в антиокиснювальних характеристиках модельних мастил. Встановлено, що мастила на залишкових оливах характеризуються високими антиокиснювальними властивостями в широкому температурному діапазоні застосування і можуть використовуватися як основний компонент дисперсійного середовища високотемпературних мастил.