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THERMO-OXIDATIVE STABILITY OF HIGH-TEMPERATURE GREASES

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Abstract. *It is established the connection between a group hydro-carbon composition of basic petroleum oils and thermooxidative properties of high-temperature lithium complex greases. 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.*

Keywords: greases; kinetic parameter; residual petroleum oils; thermooxidative stability.

1. Introduction

The aspiration to facilitate mass aircraft's units and its mechanisms determines in aircraft manufacturing the tendency of increasing loads, speeds and temperatures at which the lubricants should run longer. The friction units of aircraft flying at a speed of more than 2 M can be heated up to 200-250 °C [1].

Under these conditions, the lubrication performance determines thermo-oxidative stability of its dispersion medium – petroleum or synthetic oils, which account for 95% of the total mass of the grease. This indicator characterizes the resistance of the base oil's components and lubricating grease composition as a whole to thermal destruction and degradation under the action of oxygen. The loss of this ability leads to a miss of plasticity and thermo-strengthening of grease, the degradation of the base oil, thickener and additives [2].

High thermo-oxidative stability is one of the main characteristics of high-temperature greases [3].

In the proposed work the attempt is made to establish a link between the nature of dispersion medium and thermo-oxidative stability of high temperature lithium complex greases (kLi-greases).

2. Analysis of research

To study the process of oxidation of greases we are used 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 [4]. 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 breakage of

chains, a degenerated branching on the products of oxidation.

The study of the oxidation kinetics of greases at high temperatures raised a number of issues, namely:

- the lack of methods for a precise determination of small oxidation rates by direct measurement of the quantity of adsorbed oxygen;
- difficulty of manometric pressure measurements of pressure changes due to evaporation and gas evaluation;
- lack of reliable initiators for temperatures over 150°C capable to generate free radicals at a constant rate for a sufficiently long time.

As a theoretical basis of the method of research 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 (1)

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

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

2. The kinetics equation of hydrocarbon's autooxidation

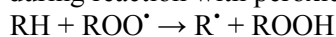
$$\Delta[O_2]^{1/2} = \frac{k_2 \sqrt{k_3} [RH]}{f \sqrt{k_6}} t \quad (2)$$

where $\Delta[O_2]$ – oxygen quantity absorbed by a grease in the mode autooxidation; t – time; k_3 – total rate constant of reactions with hydroperoxides involved; f – stoichiometric ratio of inhibition (as usual $f=2$);

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) and (3).

Parameter $a = \frac{k_2[RH]}{\sqrt{k_6}}$ defines the activity of

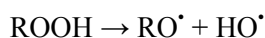
hydrocarbons during reaction with peroxide radicals:



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

Parameter $b = \frac{k_2\sqrt{k_3}[RH]}{f\sqrt{k_6}}$ characterizes the

intensification of auto-oxidation process at the expense of hydro-peroxides' disintegration by the reaction:



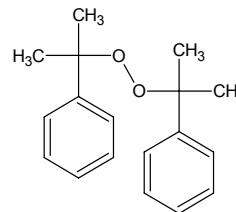
The more active ROOH in reactions of oxidation chains' development, the more is the value of b parameter and less stable is the system as a whole.

For measuring the oxygen absorbed by a grease and calculation of quantitative kinetic parameters we use a special installation [5]. 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 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. 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 ($4OH^- \rightarrow 2H_2O + O_2 + 4e^-$; $2H^+ + 2e^- \rightarrow H_2$). H_2 is released into the atmosphere, and O_2 enters the system until full compensation of adsorbed oxygen with a 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. To calculate initial rate of oxidation (W_H) the method is proposed for determining W_H after absorbing $1,5 \cdot 10^{-2}$ mol/l of oxygen with a grease, when virtually in all of model samples a natural inhibitor would be fully depleted. For the induction period (τ) it 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.

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 within the temperature range 100-145°C

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

where T – temperature in Kelvin degrees.

3. Experimental part

Model samples of kLi-greases are prepared on residual petroleum oils with different nature of the oil, method of purification and composition of hydrocarbons: sample 1 – selective purification with deasphalted tars of crude oils; 2 – selective purification of low-sulfur crude oils; 3 – paraffin-naphthenic.

Group hydrocarbon composition of dispersion medium is determined with adsorption chromatography (GOST 11244).

Model samples of kLi-greases have been prepared on the technology including the following stages:

- interaction of fatty component and acid-complex forming compounds with lithium hydroxide in oil medium;
- dehydration of oil-soap suspension;
- thermotreatment of oil-soap suspension, cooling and isothermal crystallization of half-finished grease;
- grease homogenization.

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

Properties of base oils and kLi-greases based on them are given in Table 1.

Table 1. Properties of kLi-greases with the dispersion medium on petroleum oils

The properties of residual petroleum oil and lubricant-kLi based on it	Sample		
	1	2	3
<i>Petroleum oil</i>			
Hydrocarbon composition % mass.	39,8	72,0	99,7
– Paraffins and naphthenes	54,0	26,3	–
– Aromatics hydrocarbons	6,2	1,7	0,3
– Resins and sulfure containing compounds			
Flash Point, °C	270	240	188
Pour point, °C	–10	–18	–30
Viscosity at 100 °C, mm ² /s	29,0	22,0	13,4
<i>Grease</i>			
Dropping point, °C	>230	>230	>230
Penetration at 25 °C, m 10 ^{–4}	200	220	225
Oil separation, % of separated oil under load 1000 g	4,6	7,5	7,5
Wear spot diameter (Dw) on 4-ball friction machine at P=392 H, 1 hour, mm	0,40	0,55	0,75

4. Results and Discussion

Value of parameter a , which characterize the initial stages of greases oxidation after depletion of natural inhibitors, for temperatures $> 135^{\circ}\text{C}$ were calculated by Arrhenius logarithm dependence of the parameter and the temperature ($\lg a - 1/T$), taking into account the test data at $115\text{--}135^{\circ}\text{C}$. For oil 1 – $\lg a = 3.52 - 2070.4 / T$, for oil 2 – $\lg a = 3.61 - 2086.6 / T$, for oil 3 – $\lg a = 9.85 - 4372.55 / T$. The lower the values of the coefficients A and B in the equation

$\lg a = A - B/T$, the higher is the antioxidative stability of greases.

It is suggested [6] that naphthenes and paraffins of residual oils, the oil 2 in particular, contain higher 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 antioxidative stability of hydrocarbons. The availability of quaternary carbon atoms shields -C-H group, interferes 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) of residual oils are more stable to oxidation due to the greater stability of heavy alkanocyclanes which are typical for PNH fractions of residual oils.

The most stable to oxidation was a grease on oil 1. With rise in temperature, it is observed the smallest, among the investigated greases, increase of the parameter a . 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 inhibiting properties of fractions of middle aromatics hydrocarbons II-nd group (5,3%), heavy aromatic hydrocarbons – derivatives of pyrene and chrysene (3,1%) aromatics and sulfure-containing compounds (2,5%) and light hydrocarbons (35,4%), because of their specific structure, are more chemically stable in comparison with light aromatic hydrocarbons of other oils.

Values of parameter a for the grease on oil 3 confirm the conclusions of some authors that fraction of the PNH has a low anti-oxidative stability [7]. In our case, the lowest among the studied dispersion media.

It is known [8] that at the joint oxidation of hydrocarbons with different energy value of -C-H bond, there appears reactions of "cross-over" continuation chain oxidation when intermediate oxidation products of each component of the mixture can interact between themselves and essential role belongs to the reaction of a chain transfer $\text{R}_1^{\cdot} + \text{R}_2\text{H} \rightarrow \text{R}_1\text{H} + \text{R}_2^{\cdot}$. As a result, easily oxidizing substances can inhibit a consumption of hardly

oxidizing compounds and vice versa. For example, a small addition of ethylbenzene stops the oxidation of n-decane, and the presence of a certain quantity of aromatic hydrocarbons without side chains reduces the ability of naphthenes to oxidation.

It has been found [6] that aromatic hydrocarbons inhibit the oxidation of naphthenic ones, and complete removal or excessive reduction of the concentration of aromatic compounds sharply increases the ability to oxidation of oil fractions of crude oils. This most likely concerns the oil 3 obtained by adsorption removal of aromatics from a residual oil and consisting predominantly of naphthenic hydrocarbons.

In the case where the initiation largely comes from hydroperoxides' transformations, kinetics of hydrocarbons autooxidation, is defined by equation (2). By his graphical solution, kinetic parameter b which includes three oxidation rate constants (k_2 , k_3 , k_6) was evaluated.

Calculating the parameters a and b , using the formula $k_3 = \left(\frac{b}{0,5a}\right)^2$ we defined the value of

constant k_3 , characterizing several groups of processes: degenerated branching and ROOH decompositions by reactions of first and second order relative to hydroperoxides; induced decomposition; ROOH reaction with the weakest C-H-bonded components of a grease dispersion medium and compounds capable of oxidizing destruction. The k_3 value is defined at a relatively early stage of oxidation, when the reaction of degenerated branching, does not gain the maximum power. Therefore, k_3 , probably does not include all constants of speeds of theoretically possible reactions.

Quantitative kinetic parameters of kLi-greases auto-oxidation in the temperature interval 115-180°C are given in table 2. The data in table 2 show that with temperature increasing kinetic parameters of auto-oxidation are raised for all greases, especially at $t > 150$ °C. Tendency to the oxidation of oils is dependent upon ROOH behaviour under conditions of the experiment, especially on their ability to induce free radicals. The least stable grease by the parameter b (b -max) is on the oil 3, oils 1 and 2 are placed further in a series of dispersion media. It is observed the regularity inherent to anti-oxidative stability of these oils by parameter a in the initiated oxidation.

As the temperature of the experiment increases from 115 to 180 °C, the value of b parameter for all greases grows without disturbing the row of stability of greases under conditions of auto-oxidation.

The value of the constant k_3 for the mentioned greases based on the oils 1 and 2 decreases at 135 °C compared with 125 °C temperature. The fact of parameter b growth at these temperatures, indicates the presence of oxidative transformations in the system that can not only compensate for slowing down the generation of free radicals, but, by the power of radical formation, exceed it. It is difficult to clearly describe in such complex and multicomponent systems like greases, the nature of this new source of free radicals. One can assume only that at this depth of oxidation, oxygen-containing products of transformations influence on the process of degenerated.

Table 2. Kinetic parameters of kLi-greases auto-oxidation on petroleum oils within 115-180°C

Sample	T, °C	Rate of autooxidation, $W_a \cdot 10^6$, mol/l·s	Kinetic parameter $b \cdot 10^5$ (mol/l) ^{1/2} ·s	$k_3 \cdot 10^6$, s ⁻¹
1	115	0,5	0,6	0,51
	125	0,81	0,72	0,42
	135	1,49	0,88	0,32
	155	8,17	4,64	2,92
	165	18,41	10,52	8,98
	180	66,6	23,33	21,39
2	115	0,41	0,36	0,25
	125	0,63	0,56	0,33
	135	1,11	0,61	0,21
	155	5,43	3,41	2,0
	165	13,17	6,59	4,42
	180	44,91	18,02	16,36
3	115	1,53	1,06	0,35
	125	3,79	2,22	0,41
	135	10,08	5,26	0,63
	155	42,71	19,45	0,82
	165	96,15	27,13	0,54

So, overall trends in the oxidation of greases based on residual oils (except oil 3), at the stage of degenerated branching of chains on hydroperoxides within the temperature interval 115-180 °C are the following:

– at 115 °C according to the parameters b and k_3 the regularity is observed inherent to anti-oxidative stability of these greases by parameter a in the initiated oxidation;

– at 125-135 °C the value of constant k_3 is almost identical for both greases. Its growth is retarded. The main part of hydroperoxides is spent on the generation of molecular oxygen-containing products that stimulates the occurrence of new reactions for the oxidation process initiation ;

– at $t > 150$ °C constant k_3 and parameter b of greases are sharply growing . The main role in the formation of free radicals belongs to ROOH , although for each grease in this process there has been its own trend.

Reduction of resistance to oxidation of a grease on oil 3 with increasing temperature, as shown by kinetic parameters b and W_a , has an avalanche character, and already at $t > 165$ °C to determine these parameters is impossible. The parameter k_3 remains constant. The overall rate of reaction with ROOH participation in the naphtheno-paraffinic oil is almost unchanged, but increasingly important role is beginning to play the reaction of a chain extension that leads to a growth of constant k_2 , and ultimately – parameter b .

Hydroxide radical (ROO \cdot) reacts with molecules of one or another hydrocarbons not only by the reaction with the ROOH formation, but also by reactions that generate molecular products. There is a possibility of ROO \cdot interaction with molecules of hydroperoxides with the formation of molecules of alcohol. In addition, ROO \cdot may be subjected to intramolecular isomerization with subsequent breakage -C-C- bond weakened by the formation of intramolecular complexes, and the formation of aldehydes and alkoxylic radicals with a smaller number of carbon atoms in comparison with the original hydrocarbon.

Oxygen-containing compounds, formed as a result of all these reactions, if compared to the original hydrocarbons, have weaker -C-H-bonds particularly in -CH₂-O- hydroxymethylene groups [9]. So, they are easier to come into the reaction of a chain extension, which leads to a rapid formation and accumulation of acid molecular products. Thus, on the temperature rise, it begins the process of rapid transformation of intermediate oxygen-containing compounds to the acids with the sharp growth of parameter b .

To test this thesis, the growth of acid number (mg KOH/g) of greases' samples after their oxidation under dynamic conditions for 5 h at 155 and 165°C (table 3) was analyzed.

Results of research show that with temperature increase the proportion of acidic products in greases is also growing and the biggest development of this process is observed in the grease on oil 3. It is confirmed the assumption that the ROO \cdot interaction with RH, i.e. reactions occurring on free radical chain mechanism, leading to the accumulation of ROOH in the system is not dominated in this grease under the mode of auto-oxidation. In the naphtheno-paraffinic oil, processes are predominated, the main consequence of which is the rapid formation of acidic products.

Table 3. Acid number growth of kLi-greases' samples after oxidation at 155 and 165° C

Dispersion medium	Growth of acid number (mg KOH/g) at temperature, ° C	
	155	165
1	2.44	2,88
2	2,50	3,24
3	8,87	12,56

5. Conclusion

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

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

– the least resistant to oxidation, both under initiated and conditions of degenerated branching, is turned out to be the oil on an industrial fraction PNH (residual oil 3). At elevated temperatures the grease rapidly accumulates acidic products, which can lead to the loss of its main performance characteristics. Oil 3 is not recommended to use in high-temperature kLi-greases;

– greases on residual oils 1 and 2 have high anti-oxidative properties in a wide temperature range of application and these oils can be used as the main component of the dispersion medium for high-temperature kLi-greases.

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Л.В. Железний. Термоокиснювальна стабільність високотемпературних пластичних мастил

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Встановлено зв'язок між груповим вуглеводневим складом базових нафтових олиф і термоокиснювальними властивостями високотемпературних комплексних літійових мастил. 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.

Ключові слова: залишкова нафтова олива; кінетичний параметр; пластичне мастило; термоокиснювальна стабільність.

Л.В. Железний. Термоокислительная стабильность високотемпературных пластичных смазок

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Установлена связь между групповым углеводородным составом базовых нефтяных масел и термоокислительными свойствами високотемпературных комплексных литиевых смазок. Объяснены различия в антиокислительных характеристиках модельных смазок. Установлено, что смазки на остаточных маслах характеризуются высокими антиокислительными свойствами в широком температурном диапазоне применения и могут использоваться как основной компонент дисперсионной среды високотемпературных смазок.

Ключевые слова: кинетический параметр; остаточное нефтяное масло; пластичная смазка; термоокислительная стабильность.

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