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THE OVERBASED LUBRICATING GREASE: REGULARITIES AND PECULIARITIES OF PROPERTIES

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Abstract. Physicochemical and tribological properties of overbased phenolate lubricating greases were studied in the comparison with analogous sulfonate and alkylsalicylate greases. Overbased components were extracted from the grease model systems and also researched. The scheme and parameters of the real micelles' carbonate nuclei are discussed.

Keywords: overbased grease, extracted overbased component, micelle, carbonate nuclei.

1. Introduction

Overbased complex greases are a new form of high performance lubricating greases [1, 2]. It is known that high-based additives, mainly of sulfonate and alkylsalicylate types [3-5], were used for the improvement of motor oils detergent properties. The changes in parameters of carbonation process allow to obtain overbased sulfonate [6-8] and alkylsalicylate [9] complex greases. Molecules of calcium metaborate added to the grease composition penetrate into the surface layer of the carbonate nuclei and soften the gel structure. At the same time, attempts to produce overbased greases based on bisphenolic additives or Mannich's bases appeared to be ineffective. It is evident that acidity of various calcium phenolates is not optimal for the formation of stable colloidal systems with carbonate nuclei.

However, as was determined [10] in the process of overbased alkylsalicylate complex greases synthesis, the situation is changed with the addition of the second surfactant component. This allows to believe that phenolate complex systems on Mannich's bases may also form overbased complex greases. Indeed, the overbased phenolate complex grease, which has the particles of colloidal calcium carbonate modified with molecules of Mannich's base named as "Borin" additive, [11] was pro-

duced [12]. Introducing calcium 12-hydroxystearate into ordinary overbased calcium phenolate results in a drastic improvement of carbonate nuclei lyophilization and strengthening of a colloidal system. This is indicative of a synergism between Mannich's base and calcium 12-hydroxystearate in the process of lyophilization.

As in the cases of sulfonate [13] and alkylsalicylate [10] systems the calcium metaborate and 12-hydroxy stearate initiate the changes in the composition of micelles of overbased calcium phenolate. In contrast to calcium metaborate, molecules of calcium 12-hydroxystearate assist in the composition of micelle' adsorbed envelope and impart the additional aggregative stability to the thixotropic system that has a great importance for the phenolate systems. As a result, the overbased component in the phenolate complex grease consists of micelles which include the colloidal particles of calcium carbonate doping of calcium metaborate molecules, and adsorbed envelope of calcium salts of Mannich's base and 12-hydroxystearate acid [14] (Fig. 1).

At the same time the structure of the micelles of the overbased systems is a result of their self-organization during the carbonate formation process and reaching of equilibrium between the structures of micelle nucleus and envelope. The concentration of calcium carbonate and accordingly base number are the main characteristics of the overbased greases. It is interesting that the overbased components extracted from the greases considerably differ by total base number, and the overbased phenolate component has the largest number [10, 13, 14]. So, further to our investigations the revelation of regularities and peculiarities of overbased grease properties is a topical problem.

The aim of this work is to determine the differences and similarities in structure and properties of the overbased phenolate greases in comparison with the overbased sulfonate and alkylsalicylate greases.

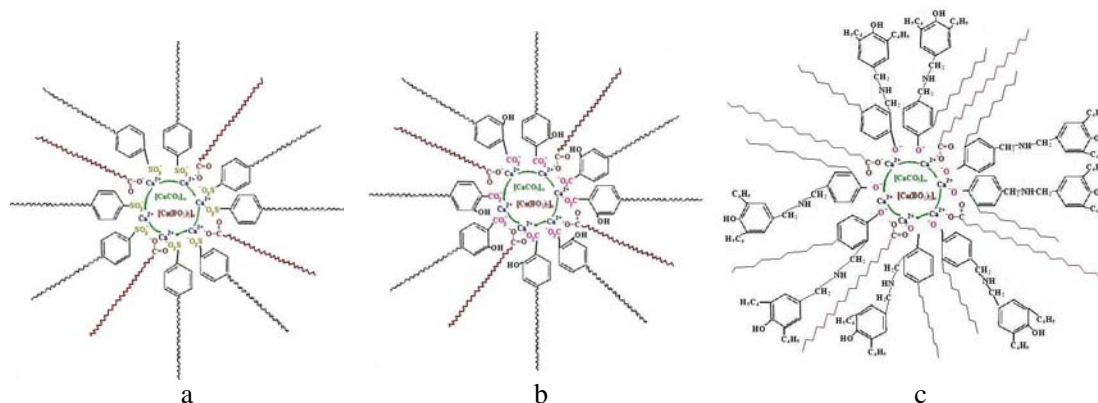


Fig. 1. Micelles of various overbased lubricating systems: sulfonate (a) [13]; alkylsalicylate (b) [10] and phenolate (c) [14]. (The proportions are not preserved)

2. Experimental

The properties of the overbased phenolate greases were studied according to the procedure [14], which was used for the researches of high-based sulfonate additives in oils [15], and later – of overbased sulfonate [13] and alkylsalicylate [10] complex greases.

Overbased calcium phenolate is formed in the process of carbonation under certain conditions and in the presence of a promoter [14]. For the comparison of various overbased complex systems, also the samples of overbased calcium sulphonate and overbased calcium alkylsalicylate were examined. So, the following model lubrication systems were prepared for the researches:

- PhG-1 – the ordinary thixotropic overbased calcium phenolate;
- PhG-2 – the system of PhG-1 and calcium metaborate;
- PhG-3 – the system of PhG-1 and calcium 12-hydroxystearate;
- PhG-4 – the complex system which contains the ordinary thixotropic overbased calcium phenolate, calcium metaborate, and calcium 12-hydroxystearate;
- SG-4 – the complex system which contains the ordinary thixotropic overbased calcium sulphonate, calcium metaborate, and calcium 12-hydroxystearate;
- AG-4 – the complex system which contains the ordinary thixotropic overbased calcium alkylsalicylate, calcium metaborate, and calcium 12-hydroxystearate.

For the study of internal structures of the model lubrication systems the overbased components were extracted from them by the re-precipitation from the methanol-toluene mixture in the same way as for the sulfonate and alkylsalicylate greases [10, 13-15]. The following overbased components of the model systems were also prepared:

- OPh-1 – the overbased phenolate component extracted from the model system PhG-1;

- OPh-2 – the overbased phenolate component extracted from the model system PhG-2;
- OPh-3 – the overbased phenolate component extracted from the model system PhG-3;
- OPh-4 – the overbased phenolate component extracted from the model system PhG-4;
- OS-4 – the overbased sulphonate component extracted from the model system SG-4;
- OA-4 – the overbased alkylsalicylate component extracted from the model system AG-4.

Generally, the samples listed above are the same as in the researches presented in [10, 13, 14]. In this paper we extend the previous investigations.

The mass of surfactants in the model systems as well as the mass of calcium carbonate were determined by the methods of liquid chromatography and potentiometric titration. Then the ratio of the calcium carbonate mass to the surfactants' mass in molar units was calculated. By analogy to the model systems these values were studied also for the overbased components.

Some physicochemical and tribological properties of the model lubrication systems were studied in accordance with the following standards: penetration (GOST 5346), dropping point (GOST 6793), oil separation (GOST 7142), wear scar diameter (ASTM D 2266), and four-ball extreme-pressure characteristics (GOST 9490). Friction coefficient was researched at the end of 1 hour friction procedure conducted according to ASTM D 2266. Total base numbers for both the model lubrication systems and their overbased components were determined by the method of potentiometric titration in accordance with GOST 11362.

The overbased components were also investigated by the methods of infrared absorption spectroscopy (IRS) and x-ray diffraction (XRD). Wear scar surfaces for ASTM D 2266 test balls were studied by the methods of scanning electron microscopy (SEM) and Auger electron spectroscopy (AES).

3. Results and Discussion

The data on compositions and various properties of the researched model systems are shown in Table 1. The physicochemical properties of the samples and EP characteristics of the phenolate samples reiterate from [10, 13, 14]. Analysis of the presented data shows that the compositions considerably influence the majority of physicochemical and tribological properties of the lubrication systems. The total base number of the overbased calcium phenolate model systems increases proportionally to the mass of calcium carbonate in them, despite the fact that the mass of surfactants varies considerably. The content of colloidal calcium carbonate is 15–21 % in all phenolate model systems; it is practically on the same level as sulfonate and alkylsalicylate model systems.

Results of investigations of a composition of the overbased components of the model systems [10, 13, 14] are given in Table 2. It should be noted that during the extractive procedure the molecules of surfactants which form the adsorbed envelope of overbased micelle are partially removed to the alcohol-toluene solution as a result of re-precipitation of the model systems. Less lyophilized

carbonate nuclei are left in overbased components. That is why the micelles of all model systems (Table 1) differ from the micelles of their overbased components (Table 2).

Total base number of the phenolate overbased components changes in the range of 677 to 896 mg KOH/g. It is higher than total base numbers of sulfonate and alkylsalicylate overbased components. In contrast to the model lubricating systems, the content of calcium carbonate (52–76 %) in the overbased phenolate components is also much higher than in sulfonate and alkylsalicylate overbased components. In general, a total base number (Table 2) of all overbased components is proportional to a content of calcium carbonate in them, but this number has no evident correlation with total base number and calcium carbonate mass for their previous lubricating systems (Table 1).

The last circumstance is connected with regularities of the interaction of absorbable envelope and carbonate nucleus of micelle and requires taking surfactants into consideration. Using our results [10, 13, 14], let us analyze this interaction as a correlations between the values of total base number TBN , overbased components and ratios r_{gr} , and molar masses of the calcium carbonate and the surfactants in the lubricating systems (Fig. 2).

Table 1

Physicochemical and tribological properties
of the model lubrication systems

Characteristics	PhG-1	PhG-2	PhG-3	PhG-4	SG-4	AG-4
Total base number, mg KOH/g	187	249	210	278	280	220
Mass of the overbased component in the model system, wt %	23.7	28.9	32.2	39.1	49.8	37.6
Mass of calcium carbonate* in the model system, wt %	15.2	20.7	15.6	21.3	20.0	17.3
Mass of surfactants** in the model system, wt %	7.8	7.9	16.4	17.8	15.6	18.7
Ratio of the molar masses of the calcium carbonate and the surfactants in the model system r_{gr} , mol-to-mol	10.0	13.5	4.8	6.1	15.3	7.4
Penetration P , $m \cdot 10^{-4}$	348	467	260	244	202	217
Dropping point, K	>503	466	>503	>503	>503	>503
Oil separation, %	3.0	Leakage	1.9	1.3	1.1	1.4
FB EP characteristics N						
– weld point WP	2450	3280	2070	3280	4640	3280
– last non-seizure point $Ln-SP$	1230	1470	1040	1470	1960	1470
– load-wear index LWI	580	609	418	634	690	645
Wear scar diameter D , mm	0.55	0.53	0.57	0.50	0.50	0.50
Friction coefficient f	0.040	0.025	0.042	0.038	0.036	0.038

* Calcium carbonate is mixed with calcium metaborate in the samples of OPh-2, OPh-4, SG-4, and AG-4.

** Neutral calcium phenolate and calcium 12-hydroxystearate.

Table 2

Characteristics of the overbased components extracted from the model systems [10, 13, 14]

Characteristics	OPh-1	OPh-2	OPh-3	OPh-4	OS-4	OA-4
Total base number TBN , mg KOH/g	896	877	677	781	576	606
Mass of calcium carbonate* in the overbased component C_{CaCO_3} , wt %	76.4	74.4	51.9	57.2	46.3	48.0
Mass of surfactants** in the overbased component, wt %	16.7	20.0	44.1	40.8	32.1	48.8
Ratio of the molar masses of the calcium carbonate and the surfactants in the overbased component r_{ov} , mol-to-mol	23.5	19.0	7.0	7.2	17.2	7.9
Ratio of the effective molecular weights of the surfactants and calcium carbonate a	5.14	5.11	5.95	5.14	11.92	8.03

* The calcium carbonate is mixed with calcium metaborate in the samples of OPh-2 and OPh-4.

** There are neutral calcium phenolate and calcium 12-hydroxystearate.

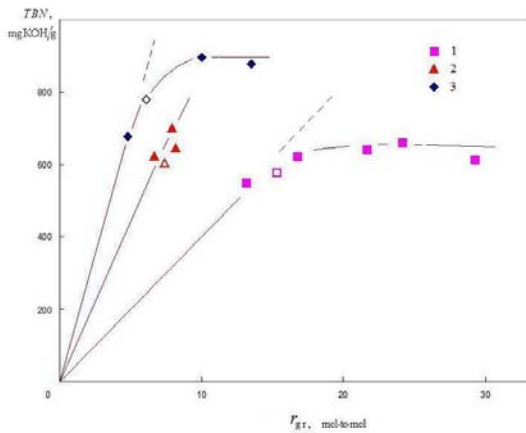


Fig. 2. The base properties of the overbased components as a function of the ratio of molar masses of the calcium carbonate and the surfactants in various lubricating systems: sulfonate (data from [13]) (1); alkylsalicylate [10] (2) and phenolate [14] (3). The light markers indicate the results for SG-4 and OS-4, AG-4 and OA-4, PhG-4 and OPh-4 samples (Tables 1 and 2)

Analysis of these results suggests a common logarithmic approximation for all overbased systems:

$$a \cdot TBN = a_0 TBN_0 \ln\left(\frac{r_{gr}}{r_{gr,0}}\right) \quad (1)$$

where a is the ratio of the effective molecular masses of the surfactants and calcium carbonate for the overbased components (Table 2); r_{gr} is the ratio of the molar masses of the calcium carbonate and the surfactants in the model lubrication systems (Table 1); a_0 , TBN_0 and $r_{gr,0}$ are the constants.

The same dependence takes place also in the case of examination of overbased components only.

$$a \cdot TBN = a_{01} a_0 TBN_0 \ln\left(\frac{r_{ov}}{r_{ov,0}}\right) \quad (2)$$

where r_{ov} is the ratio of the molar masses of the calcium carbonate and the surfactants in the overbased components (Tab. 2); a_{01} and $r_{ov,0}$ are constants.

Eqs. (1) and (2) testify to strong connections between the properties of extracted overbased components and previous lubricating systems. On the other hand the correlations between other characteristics of the lubricating systems and the overbased components are rather complex. For example, the dependency of weld point versus calcium carbonate concentration has a maximum at the middle value of carbonate concentration (Table 1). However, further study of the experimental data (Table 1), taking into account Eq. (1), finds evident liner dependencies between the characteristics of lubricating systems and the value of “ $aTBN$ ” for corresponding overbased components (Fig. 3).

These dependencies may be written as the following equations:

$$F_i = k_i a TBN \quad (3)$$

$$C_i = b_i (a TBN - a_{02} TBN_0) \quad (4)$$

where F_i is one of the extreme pressure characteristics, WP , $Ln-SP$, or LWI (Table 1, Fig. 3a); C_i is one of the following: penetration P , antiwear characteristic D , or antifricition characteristic f , (Table 1, Fig. 3b); k_i and b_i are the constants in the cases with the corresponding characteristics (Table 1, Fig. 3); a_{02} is a constant.

The liner correlation (4) for the penetration (Fig. 3b) characterizes the effect of overbased component on the strengthening of complex lubricating systems, and therefore the value of $aTBN$ is connected with the effective grain sizes of overbased components in lubricating systems.

Let us take the maximum total base number for calcium carbonate as the TBN_0 value:

$$TBN_0 = \frac{100}{n} \sum_{l=1}^n \left(\frac{TBN}{C_{CaCO_3}} \right)_l \quad (5)$$

where C_{CaCO_3} is the calcium carbonate concentration in the overbased component (Tab. 2) for sample l ; n is the number of all samples.

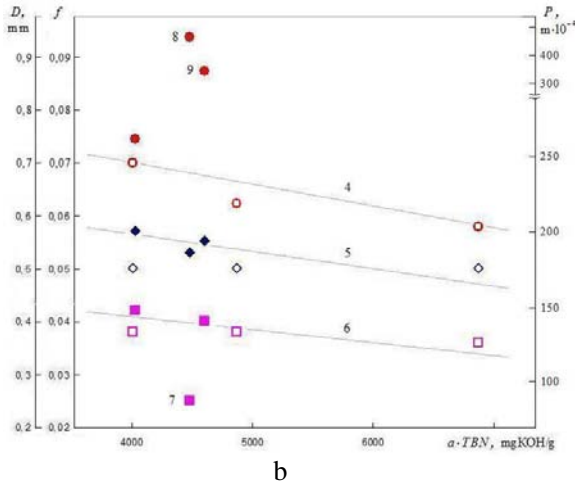
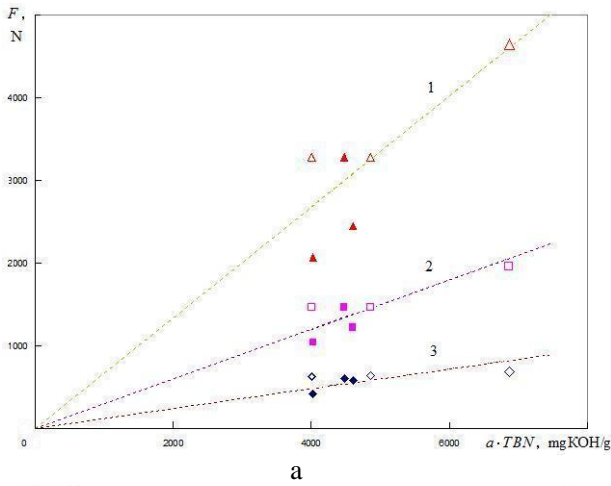


Fig. 3. Extreme pressure (a), physicochemical, antiwear and antifriction (b) properties of the overbased model lubricating systems: weld point WP (1); last non-seizure point $Ln-SP$ (2); load-wear index LWI (3); penetration P (4); wear scar diameter D (5); friction coefficient f (6); friction coefficient and penetration for the PhG-2 sample (7 and 8); penetration for the PhG-1 sample (9). The light markers indicate the results for PhG-4 and OPh-4, AG-4 and OA-4, SG-4 and OS-4 samples (Tables 1 and 2)

Then the value a_0 will characterize the effective (middle) valence of cations of the based compounds which is, for example, equals to 2 for pure calcium carbonate. For similar extrapolation we have the constant value $r_{gr,0}=1$ in the Eq. (1).

So, in accordance with the Eqs. (1) and (5) let us introduce the effective value a_{ef} for the characterization of colloidal structure of the overbased components:

$$a_{ef} = a \cdot \frac{TBN}{TBN_0} = a_0 \ln\left(\frac{r_{gr}}{r_{gr,0}}\right) = a_0 \ln(r_{gr}) \quad (6)$$

In this equation the ratio of the molecular weights a , characterizes also the spatial stereo-factor which is proportional to dimensions of hydrocarbon part of the surfactants in a micelle absorbed envelope. The ratio of the molar masses r_{gr} is connected with the spatial sizes of carbonate nucleus too.

From this standpoint the effective value a_{ef}/a_0 indicates the additional valence of each carbonate particle which is proportional to the ratio between the volume V , and the surface area S , of the particle:

$$\frac{a_{ef}}{a_0} = \frac{a \cdot TBN}{a_0 TBN_0} = k \frac{V}{S} = k \frac{d}{6} = \frac{d}{L} \quad (7)$$

where d is the effective diameter of the carbonate particle (the micelle nucleus); k is the proportional coefficient which is considered as a constant; $L = \frac{6}{k}$ is the characteristic size of the single package of calcite lamella.

In connection with the Eqs. (6) and (7) the diameter of the micelle carbonate nucleus of the overbased component may be written as:

$$d = L \ln(r_{gr}) \quad (8)$$

$$d = \frac{L}{a_0} a_{ef} \quad (9)$$

The Eq. (8) proves the connection between the size of carbonate nucleus of the overbased component and the composition of the previous lubricating system.

Using the Eq. (5) let us rebuild Fig. 2 in accordance with the Eq. (6). Fig. 4, taking into account expression (9) represents the following: (i) various values of carbonate nucleus diameter for sulfonate, alkylsalicylate, and phenolate overbased components; (ii) saturation phenomenon according to which the nucleus size cannot be greater than some critical value d_{max} .

In the last case the critical value r_{cr} of the ratio r_{gr} (Table 1) takes place. On reaching this critical ratio the value of a_{ef} ceases to increase higher than some critical value a_{cr} . In this connection let us note that the ratio value r_{gr} in the Eqs. (1), (6), and (8), as well as the ratio value r_{ov} in the Eq. (2) correlate only with liner dependency for logarithmic abscissa axis as in the Fig. 4.

In our opinion the critical value r_{cr} is inversely proportional to adsorbed area of a surfactant molecule, and the adsorbed area of the phenolate molecule is nearly 3.6 times ($24.2/6.7 = 3.6$) greater than of the sulfonate molecule.

From the Eqs. (2) and (6) the following expression is obtained:

$$\frac{a_{ef}}{a_0} = a_{01} \ln\left(\frac{r_{ov}}{r_{ov,0}}\right) = \ln(r_{gr}) \quad (10)$$

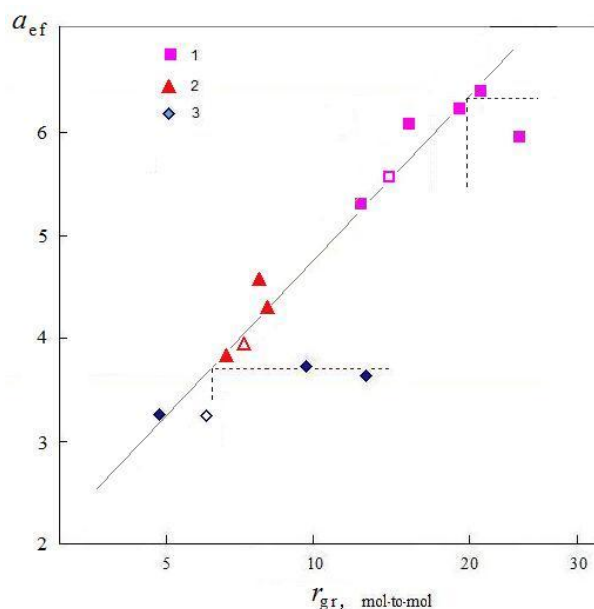


Fig. 4. Correlation dependency between the value a_{ef} for the overbased components and the ratio r_{gr} for the model systems: sulfonate (1); alkylsalicylate (2) and phenolate (3). The light markers indicate the results for SG-4 and OS-4, AG-4 and OA-4, PhG-4 and OPh-4 samples (Tables 1 and 2)

The parameter a_{01} describes the coefficient of changing of micelle nucleus sizes during extracting of the overbased components from the previous lubricating systems.

There is also an evident dependence between r_{ov} and r_{gr} values in the Eq. (10). Let us rewrite it as:

$$r_{ov} = r_{ov,0} \cdot (r_{gr})^{\frac{1}{a_{01}}} \quad (11)$$

Table 3 illustrates the results of calculations in accordance with the Eqs. (1)–(9). The initial data were taken from the Tables 1 and 2 and Figs. 3 and 4.

The analysis of the data in Table 3 proves the equality: $r_{ov,0} = a_0$. Then from (11) we get:

$$r_{ov} = a_0 \cdot (r_{gr})^{\frac{1}{a_{01}}} \approx \frac{a_0}{\sqrt[4]{r_{gr}}} r_{gr} \quad (12)$$

The extractive procedure entails both the increase of the micelle nucleus diameter ($a_{01} > 1$) and for $r_{gr} < a_0^4$ the increase of the molar ratio r_{ov} . Within the framework of our technology [8-14] a nearly 30 % dilation of micelle nucleus diameter takes place during extracting of the overbased component (Table 3).

Table 3

Manufacturing and exploitative parameters of overbased components which were extracted from the lubricating systems in accordance with the equations (1)-(9)

Characteristic	Overbased component		
	Phenolate	Alkylsalicylate	Sulfonate
TBN_0 , mgKOH/g :			
experimental		1233	
theoretical for $CaCO_3$		1120.9	
a_0 :			
experimental		2.03	
theoretical for $CaCO_3$		2	
a_{01}		1.32	
$r_{gr,0}$		1	
$r_{ov,0}$		2.03	
L , nm		7	
r_{cr}	6.7	> 8,2	24,2
a_{cr}	3.7	> 4,6	6,4
a_{ef}	3.2-3.7	3,8-4,6	5,2-6,4
d , nm	11 (for OPh-4)	14 (for OA-4)	19 (for OS-4)
d_{max} , nm	13	> 16	22
k_i , N/(mg KOH/g) :			
for WP		0.67	
for Ln-SP		0.30	
for LWI		0.12	
b_i :			
for P, m/(mgKOH/g)		$-1.26 \cdot 10^{-2}$	
for D, mm/(mgKOH/g)		$-2.85 \cdot 10^{-5}$	
for f, (mgKOH/g) ⁻¹		$-2.08 \cdot 10^{-6}$	
a_{02}		19.0	
d_2 , nm		65	

Let us return to the Eqs. (3) and (4). They may be rewritten with the account of the Eqs. (6) and (9) as:

$$F_i = k_i TBN_0 a_{ef} = \frac{k_i a_0 TBN_0}{L} d \quad (13)$$

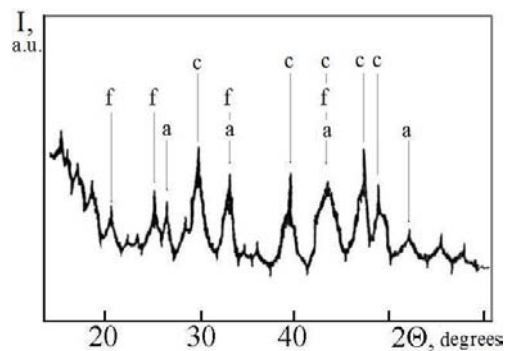
$$C_i = b_i TBN_0 (a_{ef} - a_{o2}) = b_i a_0 TBN_0 \left(\frac{d}{L} - \frac{a_{o2}}{a_0} \right) \quad (14)$$

These liner correlations between the tribological characteristics of lubricating systems and the properties of the overbased components (first of all the diameter of the micelle nucleus) confirm the mechanism of lubricity of the overbased greases with the calcite complexes according to which the deposition of calcite lamellas, as fish scales, on the friction surfaces is a very significant stage of the whole lubrication process. From the value a_{o2} (Table 3) it can be established that the best antifriction and antiwear properties of the overbased lubricating greases are achieved at the micelle carbonate nucleus diameter value of $d_2 = 65$ nm. With higher values other mechanisms of friction and wearing enter into the process. The overbased micelle may play also the role of microabrasive [16]. This last effect is very probable as in the cases of rough dispersion of other laminar fillers in the lubricating greases (molybdenum disulfide, graphite, etc. [17, 18]).

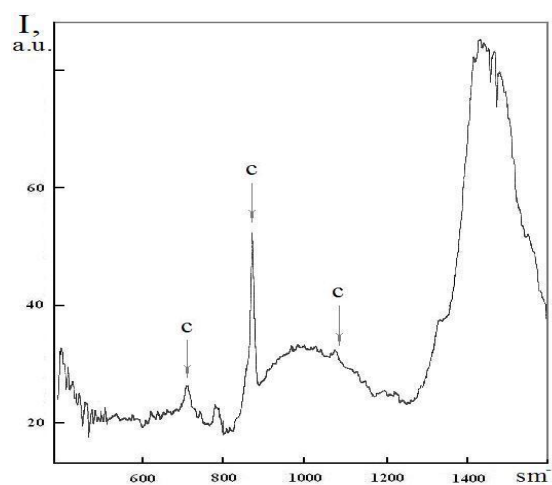
The deviation of some points in Fig. 3 from the extrapolation lines probably testifies to the presence of impurities and non-calcite phases in micelle structure of the overbased components (Fig. 1). As a proof Fig. 5 illustrates the results of XRD and IRS study of the structure and composition of the samples (Table 2). In the XRD diagram (Fig. 5a) the reflexes of calcite phase have the highest intensity. But the reflexes of the vaterite and aragonite phases are also considerable. In the IR spectrum the strong absorption band at 874 cm^{-1} (Fig. 5b), the weak peak at 713 cm^{-1} , and the overtone at 1084 cm^{-1} indicate the calcite structure of micelles' carbonate nuclei with a small admixture of vaterite structure.

Similarity of anti-wear and antifriction properties of such high-performance lubricating systems as PhG-4, SG-4, and AG-4 are evident (Table 1, Fig. 3b). Therefore, the depth profiling of wear scar surfaces of steel friction pairs after ASTM D 2266 testing was performed for the above systems (Fig. 6). The analysis of the relations of elements concentrations detected calcium oxide and calcium hydroxide surface layers on the steel surfaces after friction. It is obvious that these surface layers are caused by the deposition of the overbased components on the friction surfaces and are of tribochemical origin [19-22].

Hence, after the friction process the pre-surface micro-volumes of steel consist of a thin outer carbonate (and surfactants) layer, a considerably thicker (nearly 45 nm) milled layer of calcium oxide and hydroxide, and a deeper calcium-iron-oxygen diffusion layer.



a



b

Fig. 5. XRD data for the OS-4 sample [13] (a) and IR-spectrum for the OPh-4 sample [14] (b): c – calcite; f – vaterite; a – aragonite

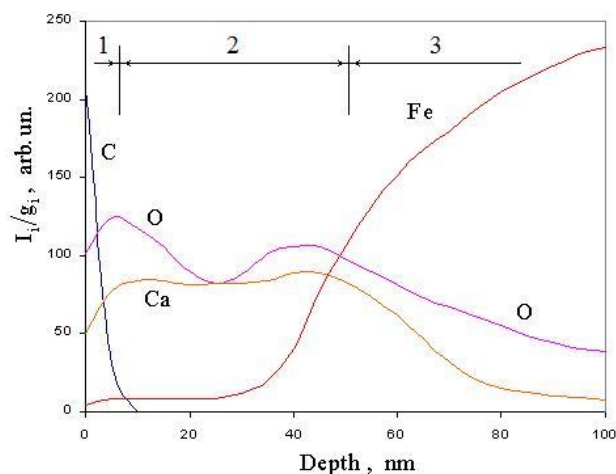


Fig. 6. Depth profile of chemical elements concentrations in the surface layers of ball wear scar after ASTM D 2266 test of the PhG-4 sample: carbonate and surfactants layer (1); calcium oxide and hydroxide milling layer (2) and calcium-oxygen-iron diffusion layer (3)

Therefore, a micelle of the colloid overbased components contains some quantity of undissolved calcium hydroxide which takes the position probably [1] in the center of a micelle nucleus and is protected against the further CO₂ action with a spherical envelope of calcium carbonate in vaterite phase. These composite nano-particles become the germs of grows of polycrystalline lamella calcite phase (Fig. 7) outer diameter d of which ensures exploitative characteristics of overbased lubricating greases. The greater the final thickness of calcite phase in the micelle nucleus, the stronger the effect of its lamellar properties (Eqs. (13) and (14)).

On the other hand, the smaller the micelle diameter, the higher the activity of the hydroxide inner nucleus in reducing-oxidation surface reactions, especially in the case of long-lasting friction processes [21, 22].

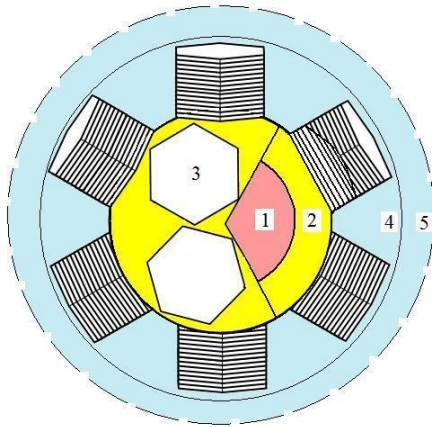


Fig. 7. Scheme of a real micelles carbonate nuclei: hydroxide core (1); vaterite type calcium carbonate inner layer (2); single calcite lamella packet (3); calcite type calcium carbonate outer layer (4) and adsorbed envelope of calcium salts of various surfactants (5)

Hence, the similar structures of overbased components in phenolate, sulphonate, and alkylsalicylate lubricating greases, which consist of micelles and include the complex calcium carbonate nucleus lyophilized by various surfactants, cause a great dependence of all researched characteristics on the diameter of the micelle carbonate nucleus. The nature of anion in adsorbed envelope around the nucleus considerably influences the thickness of calcite phase in outer envelope of the micelle nucleus. The deviations of the characteristics of lubricating greases are called by the structural addition of calcium hydroxide into calcium carbonate nucleus. Generally, the effectiveness of overbased lubricating greases is of two kinds: first of all, the adsorbed envelopes ensure antioxidant and anticorrosive properties of greases; on the other hand, carbonate nuclei contribute to the formation of the grease structure and reacting to a friction zone pressure ensure tribological properties of the greases.

4. Conclusions

Correlated results of potentiometric titration, X-ray diffraction, infra-red spectroscopy, Auger electron spectroscopy, tribological tests, and mathematical calculations allow to make the following conclusions.

- The tribological and physicochemical characteristics of the overbased lubricating greases of phenolate, sulfonate, and alkylsalicylate types are improved proportionally to diameter of carbonate nucleus in the overbased component micelles. This dependency for tribological properties is broken as a result of the action of the calcium hydroxide structural addition which is located in the center of a carbonate nucleus.

- The micelle nucleus grows during extracting procedure nearly 30 % in diameter. In the same time the ratio of the molar masses of carbonate phase and surfactant envelope increases regularly as compared to its value in the greases.

- As the result of the potentiometric titration and following mathematical calculations it has been established that the diameter of micelle nucleus increases in the range of various types of adsorbed envelope: phenolate→alkylsalicylate→sulfonate. It has been discovered that the ratio of the nucleus diameter values for the sulfonate and phenolate overbased micelles is 1.72. The calcium salt of the Mannich's base in the presence of the calcium 12-hydroxystearate has the molecule adsorptive area 3.6 times greater than the sulfonate molecule. At the same time the phenolate overbased component has the maximum total base number in comparison with alkylsalicylate and sulfonate overbased components.

- The tribochemical formation of pure calcium oxide layer on the friction surface is probably of the highest degree for the phenolate overbased lubricating grease, whose overbased component has the micelles with minimal nucleus diameter.

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НАДЛУЖНЕ МАСТИЛО: ЗАКОНОМІРНОСТІ ТА ОСОБЛИВОСТІ ВЛАСТИВОСТЕЙ

Анотація. Досліджено фізико-хімічні та трибологічні властивості надлужних фенолятних мастил в порівнянні з аналогічними сульфонатними та алкілсаліцилатними мастилами. З мастильних модельних систем були вилучені і досліджені надлужні компоненти. Розглянуто схему та параметри карбонатного ядра реальних міцел.

Ключові слова: надлужне мастило, міцела, карбонатне ядро.