1. Introduction

Oligo-butadienes (OB) of different structure and viscosity are widely applied as a binding base for liquid no-solvent ebonite compositions. Such compositions are used to produce anticorrosive coatings for equipment that is operated in highly aggressive chemical media – acids, solutions of salts, alkalis [1]. Ebonite dust, kaolin, technical carbon, powder asbestos, etc. are applied as traditional fillers for ebonite compositions [2]. Choosing the appropriate filler depends on which combination of properties of the composite is the most important to the consumer. The introduction of technical carbon to OB improves the initial structural viscosity of compositions and provides them with the required thixotropic properties in order to obtain coatings uniform in thickness [3]. The main disadvantage of carbon fillers is the contamination of surfaces in the manufacturing process and the application of the compositions.

We propose to employ as a filler for ebonite compositions with anticorrosive properties the chemically resistant polymer material ftorlon powder F-2M (Russia), which is a difluoroethylene polymer.

2. Literature review and problem statement

Liquid ebonite compositions are a blend of OB with vulcanizing agents and fillers. Technological properties of
ebonite compositions depend on the rheological characteristics of OB binder, the type and amount of filler. Studying the elastic properties of compositions is needed in order to develop a technology for their production and application on the surfaces that are protected. Article [4] examined the impact of molecular weight of OB on their rheological characteristics. It was shown that OB with low molecular weight ($M_w = 1950$–$5050$ g/mol) did not exhibit the properties of the structured polymers. The character of their flow in the temperature range from 20 to 80 °C is close to the Newtonian with the viscous flow activation energy magnitude of 17.6–19.5 kJ/mol. The sulfur, introduced to OB as a vulcanizing agent, does not change the nature of its rheological behaviour. Mixtures of OB with sulfur do not display the properties of a structured system and flow similar to the unfilled OB as the Newton fluids. The compositions on the base of these OBs, filled with kaolin, exhibit properties of the weakly-structured systems that are easily destroyed under the action of homogeneous shear and temperature [5].

In order to ensure structural viscosity and developed structure of coagulation, the compositions based on OB are recommended to be introduced with thixotropic additives, for example, aerosil [6]. An undeniable prerequisite that positively influences the resistance of polymers to the action of aggressive media is the choice of a filler, chemically inert to the aggressive environment. The introduction of a filler is effective in the case when it does not enter chemical interaction with the aggressive medium and is wetted with it worse than the binding rubber. This decreases the volume content of rubber [7]. The most common aggressive media in the chemical industry are aqueous solutions of electrolytes, in particular the solutions of mineral acids. Special features of sorption of the aqueous solutions of electrolytes by polymer materials are determined by their greater affinity with water, which is why the patterns of sorption are characterized primarily by the amount of absorbed water and the form of its distribution in a polymer [8].

The most chemically resistant polymer materials are flonlons (fluoroplastics) – polymers and copolymers of ethylene and propylene fluorine derivatives. High strength of bonding of the atoms of fluorine and carbon and specific structure of molecules determine the combination of valuable chemical and physical properties of fluoropolymers, which are not recreated by any other materials. Fluoropolymers possess high thermal resistance [9], exceptional inertness to chemical effect [10], a fairly high strength, excellent dielectric and antifriction properties, and are as well capable of maintaining these properties in a very wide range of temperatures [11].

Fluoropolymers with a varying content of fluorine atoms are widely used in tool and instrument manufacturing, automotive, aviation, chemical, oil refining and other sectors of industries as construction materials and protective coatings [12].

The largest producers of fluoropolymers in the world are the firms DuPont (USA), 3M (USA), and Daikin Industries (Japan) [13]. The fluorine elastomers “Viton” are designed for operation under conditions of high temperatures and corrosive chemicals. They are used in the production of sealants and protective coatings, valves, seals, cuffs, plugs, diaphragms, when manufacturing the hoses, tubes for hot aggressive liquids and gases, the insulation of wires and cables, containers for storing the fuel and other products that are operated in contact with oils, oxidizers and other aggressive media at 200 °C and higher [14], as the electrically insulated and heat-resistant coatings [16]. The shortcoming of fluoropolymers of these brands is their high cost, which limits their application by domestic equipment manufacturers. In addition, in order to obtain coatings of the paint and varnish type out of floron varnishes, a significant amount of fire and explosion hazardous and toxic organic solvents is required (up to 92 %).

A wide range of fusible powder fluoroplastics are used to obtain protective coatings by the spraying method. These materials do not contain organic solvents, which is important both from the environmental and sanitary-and-hygienic point of view. The spraying of powder fluoropolymers is conducted using a specialized spray gun by applying from three to nine layers during thermal treatment at high temperature [17].

The shortcoming of fluorine coatings, obtained by the method of spraying, is low adhesion, which requires the use of specialized primers, adhesives, and considerable labor-intensity of the application technology as well.

Commercially available are the floron powder materials F-2M, F-4D, F-4 MB ad others, out of which the most acceptable one by the chemical structure and properties for filling is the floron F-2M (Russia). These materials have a relatively lower cost. Their use as part of the protective composition is possible under conditions of minimum content or total absence of organic solvents. Of interest is the study into the possibility of obtaining the paint and varnish coatings with floron powder filler with high protective properties and adhesion without the use of specialized primers or adhesives.

### 3. The aim and tasks of research

The aim of present work is to develop new ebonite compositions for protective coatings using the chemically resistant powder fluoropolymer F-2M.

To accomplish the set aim, the following tasks were to be solved:

– to establish the influence of floron powder on the rheological properties of compositions;
– to study the process of vulcanization of the compositions with a floron filler;
– to examine the ohmic-capacitive characteristics of ebonite vulcanizates and coatings in order to evaluate their chemical resistance.

### 4. Materials and methods for examining the ebonite compositions and vulcanized coatings

#### 4.1. Examined materials and equipment used in the experiment

We chose a binding base for the ebonite compositions considering the following requirements:

– low enough viscosity of a binding oligomer, which enables satisfactory technological characteristics of the compositions when applying them at the surfaces to be protected, taking into account complete absence or the minimal content of a solvent;
– the possibility of vulcanization of the compositions with available vulcanizing agents that provide for obtaining the coatings high physical and mechanical properties and adhesion.

In addition, when selecting the binding oligomers, we considered the existence of raw materials and industrial
Technology organic and inorganic substances

base, as well as the cost of components in order to ensure a wide practical application of the developed materials and their economic efficiency.

In this regard, in the present work we studied new types of 1.2-oligo-butadienes, which are manufactured under the trade mark “KRASOL-LB” (firm “Cray Valley”, France) with molecular weight $\overline{M}$ = 2100–3058 g/mol with a narrow molecular mass distribution. Characteristics of these materials are given in Table 1.

Properties of the examined oligo-butadienes KRASOL LB

<table>
<thead>
<tr>
<th>Properties</th>
<th>Measuring unit</th>
<th>KRASOL LB, trade name</th>
<th>Determining methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight, $\overline{M}$</td>
<td>g/mol</td>
<td>2100</td>
<td>3058</td>
</tr>
<tr>
<td>Polydispersity $\overline{M}_w/\overline{M}_n$</td>
<td>1.35</td>
<td>ISO CD 12</td>
<td></td>
</tr>
<tr>
<td>Viscosity at 25 °C</td>
<td>Pa·s</td>
<td>5.5</td>
<td>9.7</td>
</tr>
<tr>
<td>Link microstructure: 1.4-cis, 1.4-trans, 1.2-vinyl</td>
<td>%</td>
<td>15</td>
<td>25</td>
</tr>
</tbody>
</table>

At room temperature, “KRASOL-LB” is a clear, colorless, viscous liquid of honey-like consistency, not mixed with water and alcohols. It is well mixed with non-polar organic fluids, petroleum and bitumen. It is a non-toxic and non-flammable liquid. The chemical properties of “KRASOL-LB” are defined by the existence of dual bonds mainly in lateral vinyl groups.

We employed as a filler for oligo-butadienes the ftorlon powder F-2M made in Russia. Characteristics of the ftorlon powder are given in Table 2.

Characteristics of the ftorlon powder F-2M (TU 2213-012-13696708-2002)

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Dimensionality</th>
<th>Magnitude of indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>1750</td>
</tr>
<tr>
<td>Melting point</td>
<td>°C</td>
<td>157–164</td>
</tr>
<tr>
<td>Working temperature</td>
<td>°C</td>
<td>−40...+145</td>
</tr>
<tr>
<td>Tensile strength at break</td>
<td>MPa</td>
<td>44.1–52.9</td>
</tr>
<tr>
<td>Relative elongation</td>
<td>%</td>
<td>450</td>
</tr>
<tr>
<td>Flammability</td>
<td>–</td>
<td>self-extinguishes</td>
</tr>
</tbody>
</table>

To conduct the vulcanization, the compositions were introduced with powder sulfur (GOST 127-76) of density 2070 kg/m³ and melting point at 112.8 °C.

The compositions for conducting the research were prepared by thoroughly stirring the bulk ingredients with the binding base – oligo-butadiene.

4. 2. Method of determining the rheological properties

Rheological properties of oligomers and the filled compositions on their base were studied on the rotation viscometer “Rheotest-2” (Germany) with a system of coaxial cylinders at the ratio of radii of measuring cylinders 1:0.2 in the range of shear rates from 0.167 s⁻¹ to 16.2 s⁻¹.

When measuring the values of viscosity, ratios between the measured magnitudes and rheological parameters in the device are determined by the computational equations:

$$\tau = z \cdot \alpha$$  \hspace{1cm} (1)

where $z$ is the cylinder constant; $\alpha$ is the value defined by the scale of indicator device.

The value of viscosity magnitude ($\eta$) was determined by ratio:

$$\eta = \tau / D_v$$ \hspace{1cm} (2)

where $\tau$ is the shear stress, Pa; $D_v$ is the shear stress gradient on the cut, s⁻¹.

4. 3. Method of determining the strength when tearing the vulcanizates and adhesion of coatings

In order to study the properties of ebonite vulcanizates, we prepared samples of appropriate shape and dimensions according to the requirements of testing standard (GOST 269-66 Rubber. General requirements to conducting the physical-mechanical tests, Edition 1.09.2001). For this purpose, we applied a layer of the ebonit composition, thickness 0.2–0.3 mm, onto the substrate of fluoroplastic and carried out pre-vulcanization of the coating in a thermal box at temperature 150 °C for 2 hours. When the vulcanizate entered a rubber-like state, the received films were removed from the fluoroplastic substrate; we cut out samples out of them of standard dimensions for carrying out the relevant tests.

Next, we performed additional vulcanization of the samples under a given mode, and then we conducted their tests. Thickness of the samples was controlled by the thickness gauge MT-41NC (Russia) in line with GOST 270-75, indoors, at temperature 22±2 °C, on the tensile testing machine РМІ-250 (Russia) with a pendulum force-measuring device at deformation speed 50 mm/min. Determining the strength of connection between the coating and steel St3 was conducted by the tearing method in line with GOST 209-75.

The maximum error of indicators did not exceed 10 %, taking into account the Student criterion for the number of parallel measurements less than 20.

4. 4. Method of determining the chemical resistance and protective properties of coatings

We employed the ohmic-capacitive method in line with GOST 9.083-78 to study the chemical resistance and protective properties of coatings made of ebonite compositions.

The method is based on the change in frequency dependence of capacitance and resistance and makes it possible to objectively assess the protective properties of polymer coatings on a steel substrate. In the beginning of experiment, when a solid coating has no defects, the sample represents a capacitor. The capacitor plates are a metal and an electrolyte, ebonite is a dielectric, and the capacitance, measured, is the capacity of electric capacitor.

Under the influence of aggressive medium and when it enters the coating, the measured capacity is determined by the sum of electrical and electrochemical capacitance, while
the resistance, which was found experimentally, matches the actual values. We explored the protective properties of coatings in the 20% aqueous solution of H₂SO₄ and the 20% aqueous solution of HCl. In accordance with the methodology, the research is recommended to perform in the frequency range 10³–10⁵ Hz. However, given the high chemical resistance of ebonite coatings, the measurement range was expanded to 10⁶ Hz.

Thus, we employed the methods whose relative accuracy is from 1 to 3%, and the indicators whose coefficient of variation is not higher than 10%, which testifies to sufficient uniformity and stability of the values.

5. Results of examining the ebonite compositions and vulcanized coatings

For the study we selected ebonite compositions with the content of sulfur at 30–50 mass fractions and the ftorlon F-2M (20 and 30 mass fractions per 100 mass fractions of OB). Formulation of the compositions is given in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>Components</th>
<th>Composition No. 1</th>
<th>Composition No. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amount</td>
<td>% by weight</td>
</tr>
<tr>
<td>KRASOL-LB 3000</td>
<td>100</td>
<td>58.82</td>
</tr>
<tr>
<td>Sulfur</td>
<td>50</td>
<td>29.41</td>
</tr>
<tr>
<td>F-2M</td>
<td>20</td>
<td>11.77</td>
</tr>
</tbody>
</table>

Dependence of viscosity of the compositions filled with F-2M is shown in Fig. 1.

The values of activation energy of viscous flow of compositions No. 1 and No. 2, filled with ftorlon powder F-2M, calculated based on experimental data, are equal to 14.9 and 13.6 kJ/mol, respectively. It is significantly less than the values of activation energy of the non-filled OB. This phenomenon may be predetermined by a decrease in the forces of intermolecular interactions in OB with the introduction to it the inert F-2M in the absence of adhesive bonds between OB and the fluorine filler.

The study of vulcanization of the compositions based on the oligo-butadiene “KRASOL-LB”, filled with the ftorlon powder F-2M, demonstrated the possibility of obtaining the ebonite vulcanizates with high indicators of strength (Fig. 2). Increasing the dosage of sulfur in a composition to 50 mass fractions per 100 mass fractions of oligo-butadiene (33% by weight) enables conducting the vulcanization at 150 °C in 6–8 hours and obtaining the vulcanizates with strength to 27 MPa at tearing.

The process of vulcanization is characterized by a wide plateau of vulcanization, which ensures stable indicators when obtaining coatings. At maximum values of strength of the vulcanize, high adhesion of coatings is provided (9.8–10.2 MPa at tearing).

Results of the ohmic-capacitive research into a vulcanized coating based on the oligo-butadiene LB-2000 (vulcanization for 8 hours at 150 °C) in the 20% aqueous solution of H₂SO₄ revealed that the magnitude of resistance at frequencies 10³–10⁵ Hz does not practically change (Fig. 3) for longer than 300 hours. This testifies to the lack of penetration of the electrolyte into a coating.

![Dependence of strength of the vulcanizates (σ) based on "KRASOL" LB-2000 on the duration of vulcanization (τ). Sulfur content (% by weight): 1 – 23; 2 – 33](image)

![Dependence of resistance of the vulcanized coating (R) on time (τ) in the 20% aqueous solution of H₂SO₄; 1 – at frequency 1000 Hz; 2 – 10000 Hz; 3 – 20000 Hz; 4 – 100000 Hz](image)
A logarithmic dependence of the decrease in resistance on the frequency within a range is of the character close to linear (Fig. 4).

\[ \log R = a \log f + b \]

where \( R \) is the capacitance over time, \( t \), pF/cm\(^2\); \( C_0 \) is the initial capacitance, pF/cm\(^2\); 80 is the relative dielectric water permeability.

The values of water absorption, calculated by equation (3) and experimental data, are given in Table 4.

<table>
<thead>
<tr>
<th>Frequency, ( f \times 10^{-3} ) Hz</th>
<th>( X ) (%) over the time of experiment, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>164</td>
</tr>
<tr>
<td>10</td>
<td>258</td>
</tr>
<tr>
<td>100</td>
<td>330</td>
</tr>
</tbody>
</table>

Changes in the resistance of coatings on the duration of tests in the 20 % aqueous solution of HCl at frequencies \( 10^3 \)–\( 10^5 \) Hz are somewhat larger than in the 20 % aqueous solution of \( H_2SO_4 \) (Fig. 7).

<table>
<thead>
<tr>
<th>Frequency, ( f \times 10^3 ) Hz</th>
<th>( X ) (%) over the time of experiment, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.525</td>
</tr>
<tr>
<td>10</td>
<td>0.315</td>
</tr>
<tr>
<td>20</td>
<td>0.368</td>
</tr>
<tr>
<td>100</td>
<td>0.263</td>
</tr>
</tbody>
</table>

There are also somewhat larger changes in the dependences of coatings capacitance on the time of exposure in 20 % HCl (Fig. 8).

\[ x = \frac{100 \cdot \log(C_t/C_0)}{\log 80} \]
The calculated values of change in the mass of coatings in the 20 % solution of HCl, based on dependences of capacitance on the duration of testing, are given in Table 5.

### Table 5

<table>
<thead>
<tr>
<th>Frequency, ( f \times 10^3 \text{ Hz} )</th>
<th>( x ), over the time of experiment, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>164</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

Thus, based on the ohmic-capacitive characteristics of ebonite vulcanizates from the compositions filled with the ftorlon powder F-2M, it is possible to draw a conclusion about the chemical resistance of coatings in the 20 % solutions of sulfuric and hydrochloric acids. The values of change in the mass of ebonite samples, calculated based on experimental data, in 20 % sulfuric acid are 0.263–0.683 %, and in 20 % hydrochloric acid are 1.36–1.68 %. In other words, the coatings demonstrate a larger resistance to the action of sulfuric acid than hydrochloric.

### 6. Discussion of results of examining the ebonite compositions and vulcanized coatings

An analysis of rheological dependences of viscosity of the compositions filled with the ftorlon powder F-2M on the shear rate in the temperature range of 50–90 °C demonstrates that the ftorlon powder behaves as an inert filler, similar to such mineral fillers as kaolin, bentonite, etc. The value of activation energy of viscous flow of the compositions, filled with a ftorlon powder, is less than the activation energy of the oligo-butadiene “KRASOL-LB”, filled with kaolin as well as non-filled.

The data we obtained reveal that the compositions, filled with a ftorlon powder, at increasing the temperature up to 150 °C, required for conducting the vulcanization, will flow down the vertical surfaces, unable to provide for the assigned thickness of a coating. Therefore, in order to ensure the structural viscosity, the compositions must be introduced with thixotropic additives, such as aerosil, as was previously done by the authors to the compositions filled with kaolin [18].

Kinetic curves of dependences of vulcanization strength on the duration of vulcanization for the compositions, filled with the ftorlon powder F-2M, are similar to the dependences, characteristic for OB with predominant content of 1,2-links, filled with kaolin or other inactive fillers. The value of maximum strength and adhesion of vulcanized coatings to steel is at the level of indicators for already known similar ebonite vulcanizates [19].

Ebonite vulcanizates and coatings from the compositions filled with the ftorlon powder F-2M, demonstrated a higher chemical resistance in the 20 % solutions of sulfuric and hydrochloric acids in comparison with the vulcanizates and coatings from the known compositions HES-2, HES-3, HES-6 [19].

### 7. Conclusions

1. The compositions based on the oligo-butadiene “KRASOL-LB”, filled with the ftorlon powder F-2M, are the weakly structured systems with a pseudoplastic character of the flow and thus require the introduction of structure-forming additives up to 5 % by weight. Fluctuation grids of the compositions filled with ftorlon are easily destroyed under the action of uniform shear and temperature. At temperatures 50 °C and 90 °C, at an increase in the shear rate, there occurs approximately the same viscosity reduction by 1.9 Pa·s and 3.6 Pa·s, respectively, for compositions No. 1 and No. 2.

2. A study of the ohmic-capacitive characteristics of ebonite vulcanizates from the compositions filled with the ftorlon powder F-2M revealed their chemical resistance in the 20 % solutions of sulfuric and hydrochloric acids. The values of change in the mass of ebonite samples in the 20 % sulfuric acid, calculated based on experimental data, are 0.263–0.683 %, and in the 20 % hydrochloric acid – 1.36–1.68 %.

3. We determined that, based on the compositions of the oligo-butadiene “KRASOL-LB”, it is possible to receive ebonite vulcanizates and anticorrosive coatings with high strength (up to 27 MPa at tearing), adhesion (9.8–10.2 MPa at tearing) and chemical resistance.

### References

13. PCTFE/Kel-F®/Neoflon® [Electronic resource]. – Aetna Plastics Corp. – Available at: http://www.aetnaplastics.com/products/d/pctfe