

Protective coating based on liquid ebonite and water dispersion CSPE

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Annotation: Compositions and their properties for protective coatings based on liquid ebonite and water dispersion of CSPE were described. The experimental data of different testing are confirmed their high effectivity for corrosion protection.

Key words: corrosion protection, liquid ebonite mixtures, oligobutadiene, water dispersion CSPE, service properties.

Progress in protective coatings send for more effective polymeric materials such as liquid ebonite compositions or waner dispercion of chlorsulfinated polyethylene [1,2].

Liquid ebonite compositions (LEC) are intended for anticorrosion protection of equipment operating in chemically aggressive environments in cases where rubber and ebonite mixtures lining by lining with rubber sheets is technologically difficult or cannot be used at al [3.4]. Especially effective is the use of LEC in the technology of protecting complex-shaped and perforated equipment, for example, filter centrifuge rotors, pump and fan impellers, valve bodies, small diameter pipes, and the like (Fig. 1).

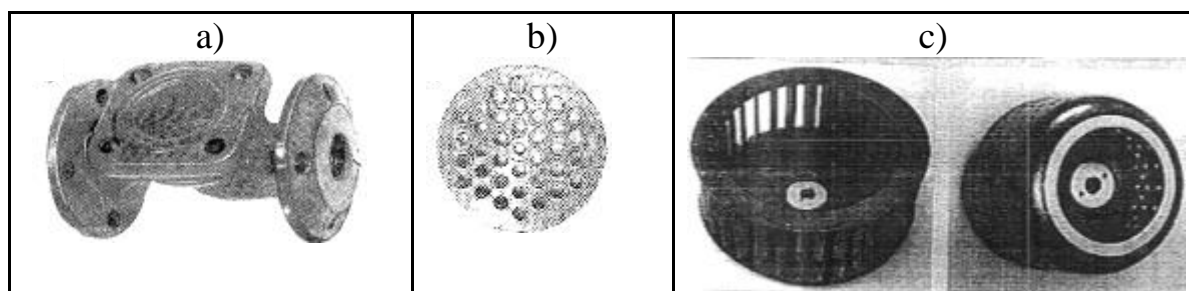
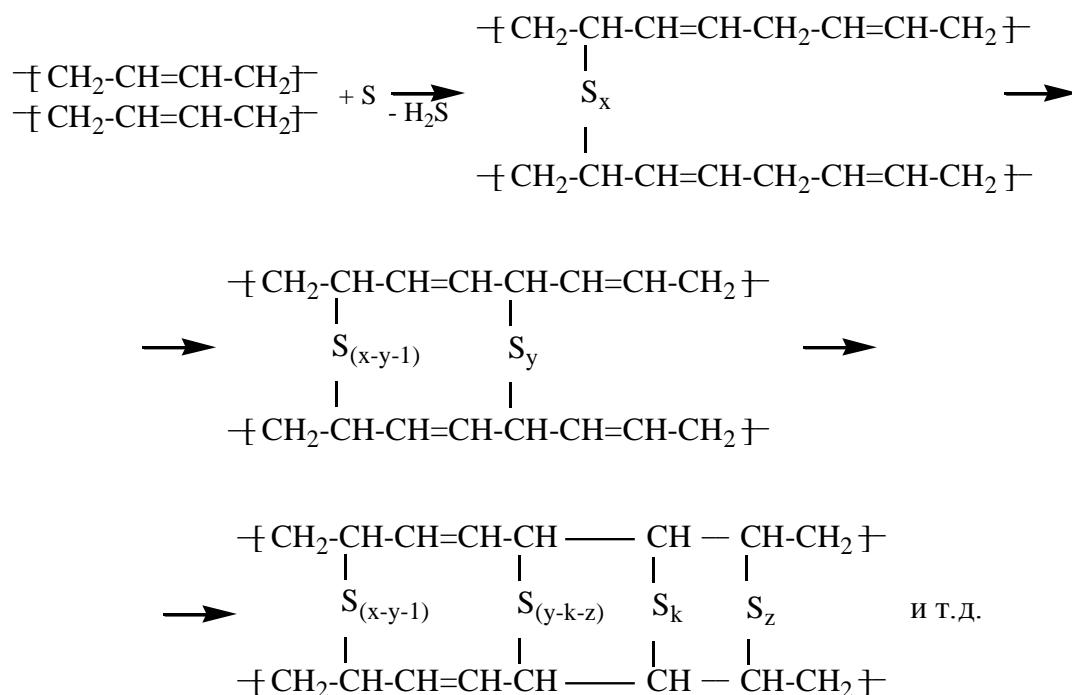


Fig. 1 - Examples of equipment elements, rubberized ZhEK: valve body (a), tube sheet (b), fan wheel and centrifuge rotor (c).

Obtaining ebonite coatings from LEC is based on the chemical vulcanization of highly unsaturated diene oligomers with sulfur (23-33% wt.) and accelerators at a temperature of 130-150 °C: Increasing the temperature above 150°C accelerates the vulcanization process, but can lead to swelling and porosity coatings.



LEC traditionally uses various grades of carbon black, as well as kaolin and aerosil, as structure-forming fillers. The viscosity of the filled compositions increases by 1-3 decimal orders compared with the viscosity of the binder oligobutadiene.

The main advantages of the LEC are:

- Absence of organic solvents in the compositions, which ensures fire and explosion safety, and also improves the environmental performance of gumming works;
- Long, and for some compositions, unlimited shelf life of compositions;
- Possibility of application to the protected surfaces by simple and affordable methods used in the technology of paint and varnish coatings (brush, paint roller, spraying).

Among the advantages of LEC, one should also include the possibility of curing the applied coating layers without the use of curing in boilers under steam pressure. Vulcanization of LEC coatings can be carried out with heated air in unpressurized circulating ovens. The possibility of such vulcanization makes it possible to obtain ebonite coatings based on oligobutadienes with high physical, mechanical and operational properties:

- Strength of the vulcanizate at break 30 - 50 MPa;
- Impact strength not less than 5 N*m;
- Hardness on a needle hardness tester not less than 96 units;
- Own adhesion without the use of adhesives, provided in the process of vulcanization (8 -12 MPa, when detached);
- Homogeneity and solidity of coatings due to the absence of adhesive joints;
- Chemical resistance at the level of linings made of sheet ebonites.

One-pack and two-pack LECs can be used to produce ebonite coatings.

Single-package low-viscosity LECs with viscosity up to 10^2 Pa·s are designed to produce single-layer or multi-layer coatings with each layer thickness up to 0.2 mm (Table 1). As a binder base of one-pack LEC, low-viscosity, highly unsaturated 1.4 cis oligo-oligobutadienes (iodine number 420-480) with a molecular weight of $2-3 \cdot 10^3$ and a viscosity of 1-3 Pa·s at 20°C, such as "Polioil Huls" (Germany), SKDNN (Russia), etc. Oligobutadienes with a mixed microstructure (30-35% 1.4-cis, 1.4-trans and 1.2 units) of the "Lithene" type, PBN, etc. are characterized by delayed vulcanization, therefore, it is necessary to introduce a larger amount of sulfur and vulcanization accelerators into compositions based on them. Butadiene-piperylene copolymers can also be used as the LEC binder.

Table 1 - Properties of one-pack LECs and coatings based on them

The basis of the composition	1.4-cis oligobutadiene	Oligobutadiene with a mixed microstructure of units	Copolymer of butadiene with piperylene
Technological properties of the compositions			
Appearance	Homogeneous viscous liquids of black color		
1	2	3	4
Conditional viscosity of the composition according to VZ-4 at 20 °C, sec	50 (75% solution in toluene) at 20°C, sec	45 (75% solution in toluene) at 20°C, sec	27% at 20°C, sec
Sulfur content, % mass	23 (33)	33	33

1	2	3	4
Duration of vulcanization, hour	2x150 °C	2x150 °C	2x150 °C
intermediate layers	8 (4)x150 °C	5 x150 °C	6 x150 °C
Consumption when applying one layer, kg/m ²	0.2		
Mechanical properties of vulcanizates and coatings			
Tensile strength, MPa (not less than)	26.0 (50)	27	28
Strength of bond with steel at separation, MPa (not less than)	8.0	8.0	10.0

A feature of one-package LEC is that all ingredients are in one heterogeneous system and do not contain solvents and any toxic ingredients. To ensure that such compositions do not undergo self-vulcanization during storage, oligomers and vulcanizing agents are used in their formulation that do not react with each other during storage under normal conditions, but effectively interact at the vulcanization temperature. Sulfur with accelerators of moderate activity satisfies such requirements most fully: captax (2-mercaptobenzothiazole), guanide-F (diphenylguanidine), etc. Single-pack formulations, due to the absence of solvents in their formulation, can be stored in open containers. They are made with the viscosity required for application by brush or roller. The shelf life of one-pack compositions is practically unlimited, since they do not contain curing agents that enter into chemical interaction with oligobutadiene binders at room temperature.

The two-pack compositions consist of a bonding base (component "A") and a low-temperature curing system (component "B"), supplied and stored separately.

The introduction of low-temperature vulcanization agents into the oligobutadiene binder is unacceptable due to the self-vulcanization of the compositions during storage and the loss of their technological properties. As a consequence, it is necessary to separate such compositions into two component parts, each of which could be preserved without scorching under normal conditions for the longest possible time.

Ingredients that are inert with respect to oligobutadiene at room temperature are introduced into the binder base of the composition (component "A"): sulfur, high-temperature vulcanization accelerators and fillers. Ingredients are introduced into the composition of component "B", which are also inert with respect to its binder base, on which it is made, in order to also prevent scorching during storage.

Thus, the problem of creating a two-pack ebonite composition is reduced mainly to the choice of an inert binder with respect to low-temperature vulcanizing agents. At the same time, it is desirable that the binder base of component "B" at the second stage of vulcanization at elevated temperature enter into chemical interaction with high-temperature vulcanization agents introduced into the base of the composition, actively participating in the construction of the vulcanization network of the ebonite coating.

Two-pack compositions are made operational by mixing components "A" and "B" just prior to use. After mixing components "A" and "B", the prepared composition should, on the one hand, ensure its self-vulcanization in the layer of the applied coating at a temperature of 20-25 ° C for a technologically acceptable time, and, on the other hand, maintain the necessary viability for the time required for use in the work of a sufficiently large amount of the composition.

Butadiene oligomers with terminal functional groups can be used as a binder base for two-pack compositions, allowing pre-vulcanization of coatings at room temperature. These oligomers include KRASOL-LBH, NISSO-PB, Hystle, and others with $M_n = 1000-3000$ and terminal hydroxyl or carboxyl functional groups.

Oligobutadiene diols (OBD) are capable of curing with diisocyanates to form pre-polymers. The curing of urethane pre-polymers with a molecular weight of 1200-2000 with a content of isocyanate groups of 4.5-7.5% and a viscosity of 20-50 Pa·s is carried out with polyols or diamines at room temperature. The viability of such compositions is determined by the time of loss of fluidity and can be adjusted in the range from 45-60 minutes to several seconds, depending on the type of cross-linking agent and the accelerator system. Compositions based on HBD with a pot life at 20°C of 1 - 1.5 hours are used for application with a brush or paint roller. When applying 2-4 layers, the total thickness of the coating is up to 2 mm. Fast curing compositions with a pot life of a few seconds are applied by spraying using special installations in which the mixing of the binder and produced directly in the mixing head of the spraying device.

The basis of two-pack compositions can also be butadiene or butadiene-nitrile oligomers with carboxyl groups. Interaction of carboxyl groups of rubbers in these compositions with a cross-linking agent (metal oxide), occurs at room temperature, which makes it possible to "cold" scorch compositions, providing the possibility of applying the second and subsequent layers.

Based on high-viscosity 1.4-cis oligobutadiene (viscosity = 1000 -1200 Pa·s), liquid two-pack compositions were developed using a redox system based on parabenzoindioxime with manganese dioxide and an ultraaccelerator - zinc diethyldithiocarbamate for pre-vulcanization at room temperature.

Two-pack LECs can be stored at room temperature for up to 6 months or more from date of manufacture. The viability of two-pack compositions after being introduced into the base of the vulcanizing system, depending on the brand, is at a temperature of 15-25 °C from 1 to 2 hours, therefore, it is necessary to prepare such compositions based on their full use over this period of time. After the introduction of the vulcanizing system into the base, the entire composition is thoroughly mixed until a homogeneous consistency is obtained.

Vulcanization of coatings from two-pack compositions is carried out in two stages. At the first stage, pre-vulcanization is carried out at room temperature with the formation of a weakly cross-linked rubber-like vulcanizate, and at the second stage, pre-vulcanization is carried out to the state of ebonite.

The type of gumming composition (one- or two-pack) is determined, on the one hand, by the type of oligomer used as a binder base (first of all, by its main molecular parameters and viscosity), and, on the other hand, by the technology of gumming and the purpose of the coating.

The technological process of gumming with liquid ebonite compositions (Fig. 2) includes the following operations:

- preparation of composition and product for carrying out gumming works;
- application of the gumming composition to the surface to be protected;
- vulcanization and quality control of the coating.

Before use, liquid ebonite compositions and vulcanizing pastes for them (in the case of using two-pack compositions) are thoroughly mixed in a packaging container. Mixing is carried out manually or using mechanical mixer (Fig. 3) until a homogeneous consistency is obtained, since during long-term storage, solid particles of some ingredients (sulfur, vulcanizatr accelerators and fillers) may settle.

A schematic flow diagram of the LEC gumming process is shown in fig. 2.

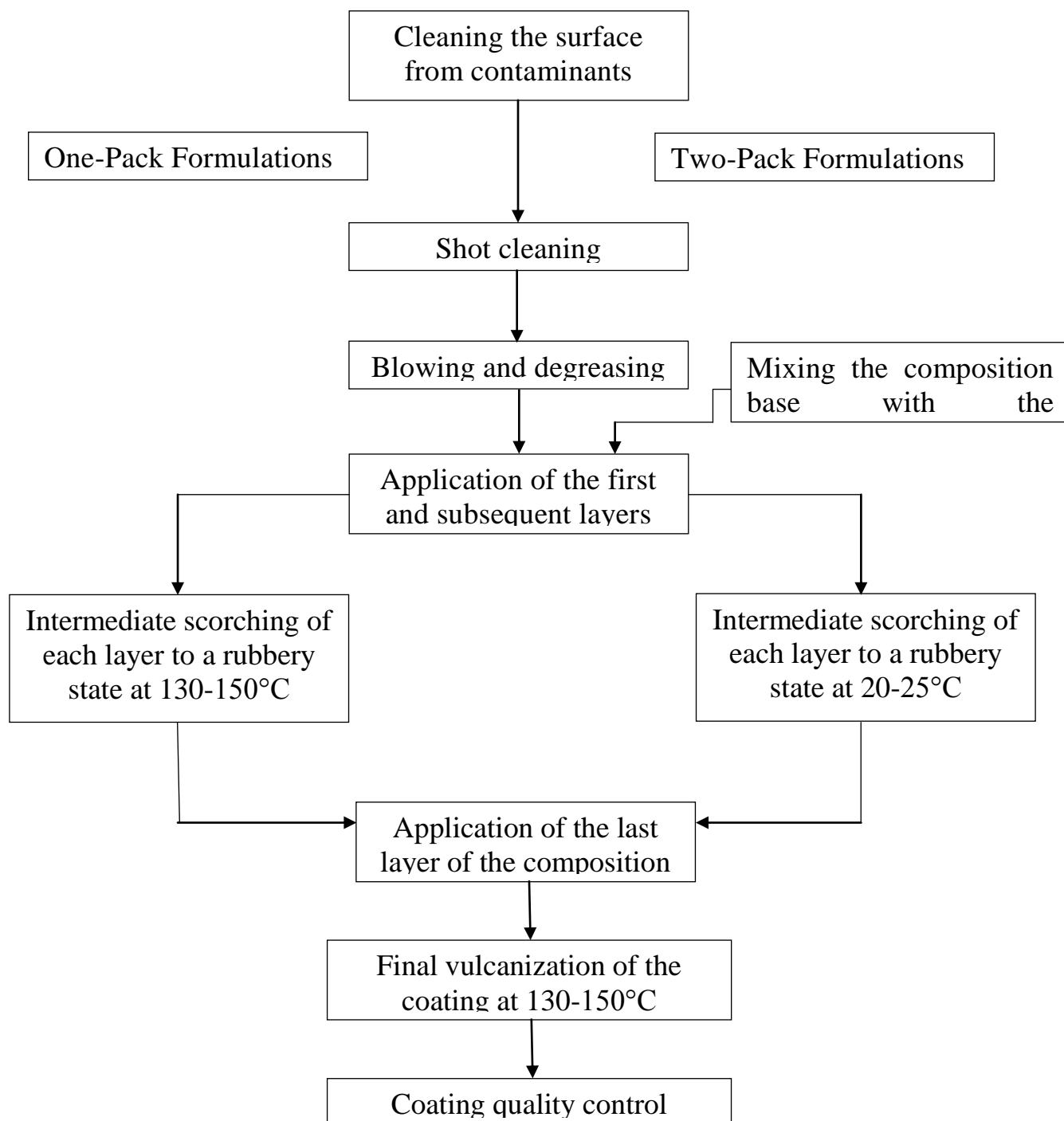


Fig. 2 - Schematic diagram of gumming with liquid ebonite compositions.

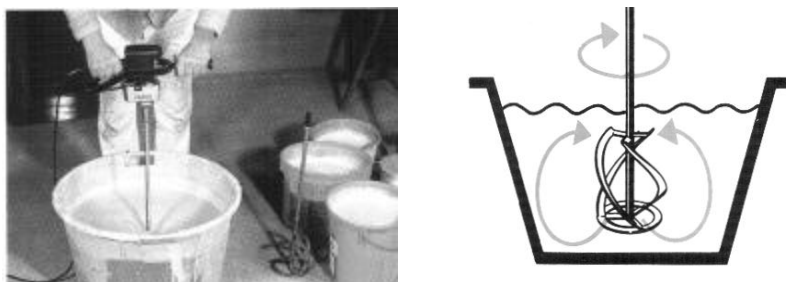


Fig. 3 – Mechanical mixer

Applying the compositions with a brush is used when gumming complex-profile and perforated products, for example, pump casings and impellers, valves, tees, bends, etc., as well as surfaces of small containers (measuring tanks, tanks, etc.). Application with a paint roller is used for gumming flat and even surfaces, such as electroplating baths, ventilation ducts, as well as cylindrical surfaces of a sufficiently large diameter. Spatula application is used for rubberizing small, flat surfaces with high-viscosity ebonite compounds. This method allows to obtain coatings with a thickness of 1-2 mm. Spray application allows maximum mechanization of the gumming process. This method is used to protect elements of equipment that have the form of bodies of revolution, such as rotors of filter centrifuges, impellers, pumps and fans. Application of the compositions by spraying is carried out on slowly rotating (5-30 min) products, which ensures uniform coatings in thickness. Spraying is carried out using installations of the HydroPress or 7000 N Wagner type, which allow applying compositions with a viscosity of 250-300 s according to the VZ-246 viscometer (nozzle No. 4).

The rubber-like coatings obtained as a result of "cold vulcanization" at 20-25°C do not have independent significance, but serve only to ensure the possibility of layer-by-layer application of compositions in order to obtain coatings of a given thickness at room temperature. Ebonite coatings are obtained at the second stage of vulcanization by a sulfur-accelerating vulcanizing system at a temperature of 130-150°C. Vulcanization of coatings from LEC is carried out in ventilated thermal chambers that provide a uniform temperature at all points of the volume. For vulcanization of coatings applied to parts such as bodies of revolution (rotors of centrifuges, impellers of pumps and fans, etc.), special devices are provided in the design of the heat chamber to ensure slow rotation of products during vulcanization, which makes it possible to obtain coatings of uniform thickness without sagging and streaks. Heat treatment at 130 - 150°C in a heat chamber leads to the formation of ebonite coatings characterized by high tensile strength (25 - 45 MPa), impact (5 N·m) and adhesion to carbon steels (up to 10 MPa at separation).

After vulcanization, in order to avoid the occurrence of significant internal stresses, leading to a decrease in the adhesion of coatings (both in the case of using one-pack and two-pack compositions), it is recommended to naturally slowly cool the product with a vulcanized coating in the heat chamber to a temperature of 20-25°C.

The quality control of vulcanized ebonite coatings is carried out both visually and using special methods. During visual inspection, the coating must be even and monolithic, without visible pores, cracks, swellings, delaminations and other visible defects. A sign of undervulcanization of the ebonite coating is the so-called "fading of sulfur" on the cured surface, as evidenced by the formation of gray spots. The thickness of the coating is determined using magnetic or electromagnetic thickness gauges. The hardness of the coating is controlled using needle hardness testers. The continuity of coatings is determined using electrolytic or electrospark flaw detectors.

In terms of chemical resistance, ebonite coatings from liquid compositions are not inferior to facings made of sheet ebonite mixtures, and in terms of protective properties, due to the absence of adhesive seams, they surpass them.

Table 2 - Anticorrosive properties of coatings from liquid one-pack ebonite compositions

Aggressive environment	Concentration, % mass	Temperature, °C
Acids:		
1	2	3
Nitric	< 10	< 20
Sulfuric	< 50	< 80
Hydrochloric	< 35	< 20
	< 10	< 60
Acetic	< 50	< 20
Chemical bases		
Sodium hydroxide	< 20	< 20
Salt solutions		
Aluminum sulfate	< 20	< 80
Potassium bichromate	< 10	< 60
Calcium chloride	20	< 80
Potassium chloride	20	< 80
Zinc sulfate	20	< 60

1	2	3
Organic environment		
Acetone	-	< 20
Ethanol, butanol	-	< 60
Gasoline, white spirit	-	< 20
Transformer oil	-	< 60

Additionally we have studied LEM by using Studied 1.2-oligo-butadienes, which are manufactured under the trade mark “KRASOL-LB” (firm “Cray Valley”, France) with molecular weight $M_n=2100-3058$ g/mol with a narrow molecular mass distribution. Characteristics of these materials are given in Table 3.

Table 3 - Properties of the examined oligo-butadienes KRASOL LB

Properties	Measuring unit.	KRASOL LB trade name		Determining methods
		LB-2000	LB-3000	
Measuring unit	g/mol	2100	3058	ASTM D 3593 mod
Polydispersity		1,35		ASTM D 3593 mod
Viscosity at 25 °C	Pa·s	5,5	9,7	ISO 2555
Link microstructure: 1.4-cis 1.4-trans 1.2-viny	%	15 25 60		ISO CD 12

As a filler is using the ftorlon powder F-2M. Characteristics of the ftorlon powder are given in Table 4.

Table 4 - Characteristics of the ftorlon powder F-2M

Indicators	Dimensionality	Magnitude of indicator
Density	kg/m^3	1750
Melting point	°C	157–164
Working temperature	°C	–40....+145
Tensile strength at break	MPa	44,1–52,9
Relative elongation	%	450
Flammability	–	self-extinguishes

To conduct the vulcanization, the compositions were introduced with powder sulfur 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.

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 1.02 in the range of shear rates from 0.167 s⁻¹ to 16.2 s⁻¹.

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 5.

Table 5 - Formulation of ebonite compositions

Component	Amount			
	Composition № 1		Composition № 2	
	mass fractions	s % by weight	mass fractions	s % by weight
KRASOL–LB 3000	100	58,82	100	62,5
Sulfur	50	29,41	30	18,75
F-2M	20	11,77	30	18,75

Dependence of viscosity of the compositions filled with F-2M is shown in Fig. 4.

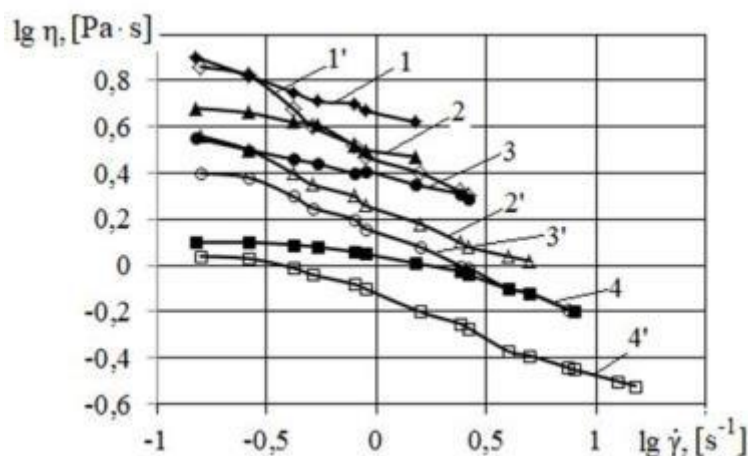


Fig. 4. Dependence of viscosity (η) of compositions No. 1 (1–4) and No. 2 (1'–4'), filled with the ftorlon F-2M, on the shear rate (γ).
 Temperature, °C: 1 – 50; 2 – 60; 3 – 70; 4 – 90

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. 5). 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.

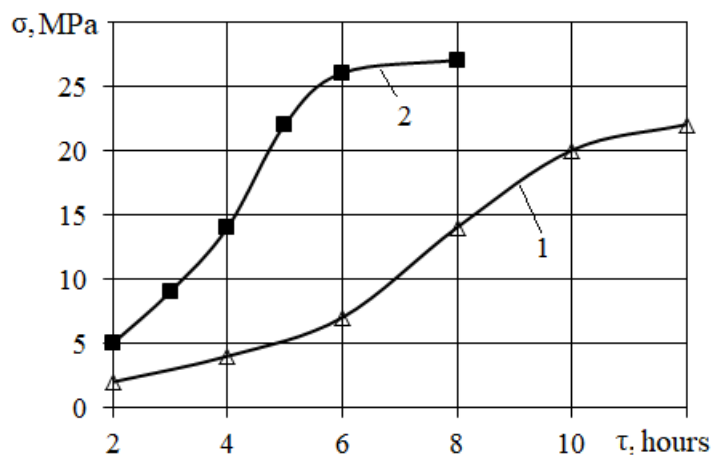


Fig. 5. Dependence of strength of the vulcanizates (σ) based on “KRASOL” LB-2000 on the duration of vulcanization (τ). Sulfur content (% by weight): 1 – 23; 2 – 33

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 vulcanizate, high adhesion of coatings is provided (9.8–10.2 MPa at tearing).

Elastomeric coatings based on vulcanizable chlorosulfonated polyethylene (CSPE) are widely used as crack-resistant coatings for the protection of concrete and reinforced concrete building structures. However, conventional protective compositions contain more than 80% toxic organic solvents, which requires the application of 5-7 layers with layer-by-layer drying, which is very laborious. O. Figovsky (1) showed that it is possible to use 40-60% aqueous dispersion of CSPE cured with Mannich bases (2-5% of CSPE). Mannich bases are formed by the reaction of amines with formaldehyde and (alkyl)phenols, as shown in Fig. 4.

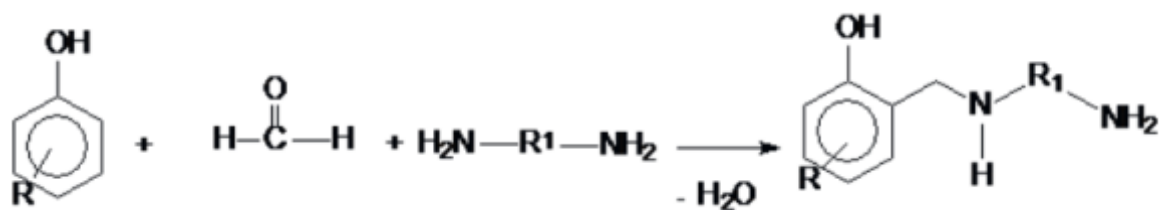


Fig. 4 - Mannich bases

Mannich Bases - Commercial EPI-CURE 185, EPI-CURE 195 and EPI-CURE 197 are low viscosity, phenol free products with the following specifications and typical properties:

Properties	Test methods	Units	EPI-CURE 185	EPI-CURE 195	EPI-CURE 197
Basic nitrogen content	ASTM D2896	% (m/m)	7.2-8.0	5.4-6.2	9.8-10.6
Viscosity at 25°C	ASTM D445	Pa.*s	0.3-0.7	0.5-0.9	0.15-0.25

The properties of CSPE coatings cured with 2.5% 2,4,6-tris-(dimethylaminomethyl)-phenol are given below:

- equilibrium swelling in water	6%
- equilibrium swelling in benzene	480%
- tensile strength	44.6 MPa
- elongation at break	580%
- residual elongation	1.2

The chemical resistance of CSPE coatings cured with 2.5% 2,4,6-tris-(dimethylaminomethyl)-phenol is very high (see table):

Aggressive environment :	Weight change after 250 hours, % :	Coef. resistance to strength :	Coef. elongation strength:
H ₂ SO ₄ , 60%	+ 4,6	0,91	0,93
HCl, 20%	+ 5,2	0,86	0,97
KOH, 40%	+ 3,7	0,95	0,96

Concrete structures, on which CSPE-based compositions are applied, are operated in various conditions, including in the shops of a number of chemical enterprises containing chlorine, hydrogen chloride, and sulfur dioxide in the indoor air. The coating applied to the supporting reinforced concrete structure has a high resistance to the formation of cracks in concrete (crack resistance). It withstands crack opening up to 3.5 mm, and, unlike per-vinyl chloride coatings, the protective properties of a coating based on CSPE are preserved both with a significant single crack opening and with periodically repeated deformation.

Application of CSPE coating for forming concrete and reinforced concrete structures.

Film coating are widely applied in forming concrete and reinforced concrete structures to accelerate concrete hardening and reduce appearance at setting. The film prevents evaporation of the water contained in the concrete, promotes hydration of cement, and thus provides reliable contact of the the cement stone and filler, It promotes an increase in concrete strength up of up to 30%, reduces damage and time of processing, and restricts moisture absorption.

The developed composition of a high-adhesion CSPE coating cured by a water solution of MA was applied as a covering in the formation of concrete articles. It was investigated with respect to its setting and hardening process by evaluating the concrete under loading.

According to the theory, shrinkage stresses in a concrete create the compressive stress s_{con} in contact layer of a concrete substratum. Therefore, the value of the moment M_{crack} is possible to find by formula:

$$M_{crack} = R_{con} W_{crack} + M_{cor}$$

where R_{con} is the ultimate tensile strength of concrete.

The forces arising from shrinkage strains are transmitted on the concrete in a plane of contact coating-substratum for an element.

$$M_{cor} = N_{shr} (e_0 + r_{cor}) ; e_0 = 0.5 h_{con} ; r_{cor} = h_{cor}/6 \Rightarrow M_{cor} = 2/3 (N_{shr} h_{con})$$

where $N_{shr} = s_{shr} d_c b$ $W_{crack} = (0.292 + nm) b h_{con}^2$
 and $n = 2 E_{rft} E_{con}$

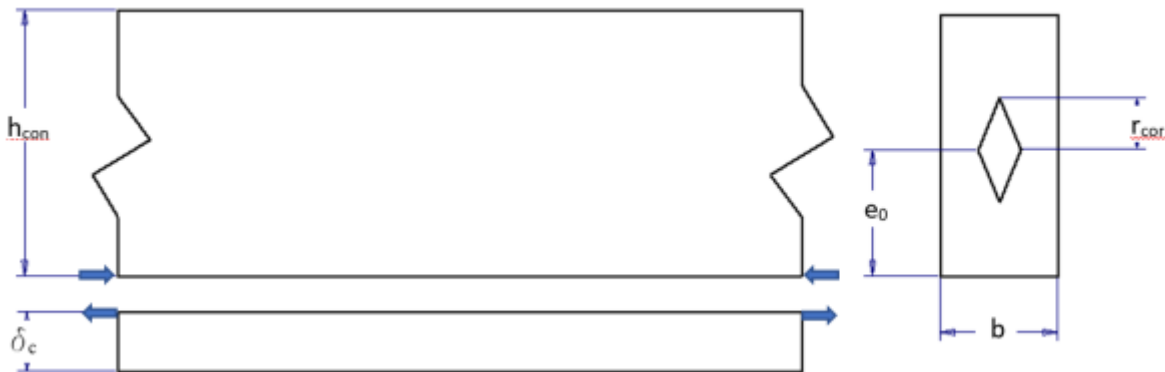


Fig. 5 – Calculation of polymer coating shrinkage strains.

From equation and from tests results, it follows that with an increase of shrinkage stresses and thickness of a polymeric coating, the moment of crack formation for reinforced concrete beams increases.

At Fig. 6 shown concrete samples for testing.

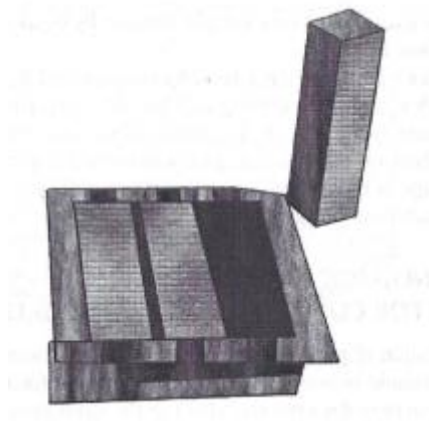


Fig. 6 – Concrete samples with a coating during natural hardening (concrete beams measuring 160x40x40 mm, reinforced by one bar D6 mm).

In order to estimate the efficiency of a protective crack-resisted coating during the formation and and development of cracks in a concrete substrate, an experimental investigation and numerical analysis (finite elements method) of the stress-strain state of a concrete sample with coating at a tension load was carried out.

Three stages of the model under loading were considered.

- Before formation of crack
- Formation of the crack
- With the given crack width

At first stage the tension load was corresponding to ultimate tensile stress 2.7 (for concrete B-30). The external load was 0.355t and crack width was 0.056 mm.

At second stage crack width was 0.0603 mm.

At third stage the tension load at reinforced bar was 340 MPa, by external force 1.71t and crack width was 1.77 mm.

Some of results are shown at Fig. 9.

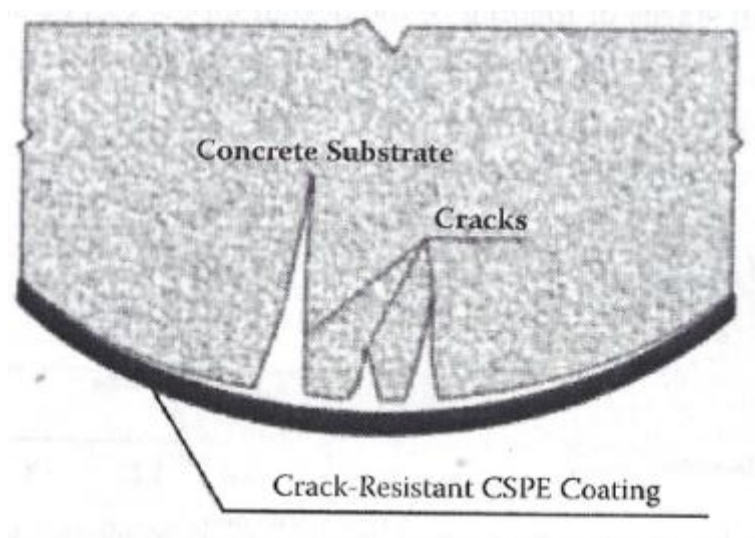


Fig. 7 – Stretched CSPE coating overlaps in a concrete substrate.

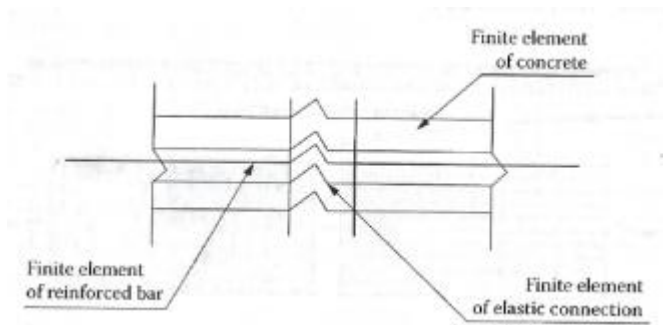


Fig. 8 – Finite element model.

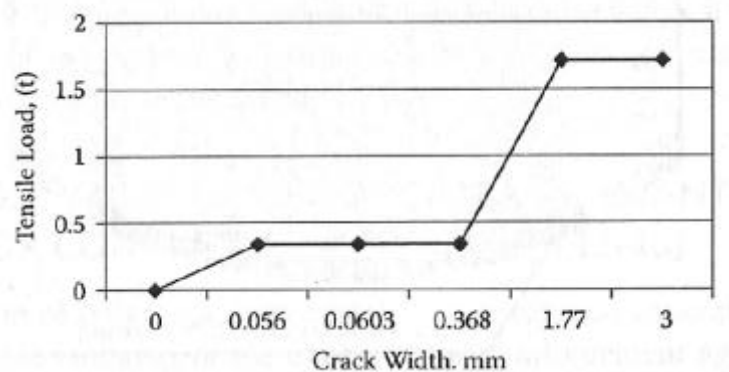


Fig. 9 – Displacement of finite elements of model at design tension stress in reinforced bar.

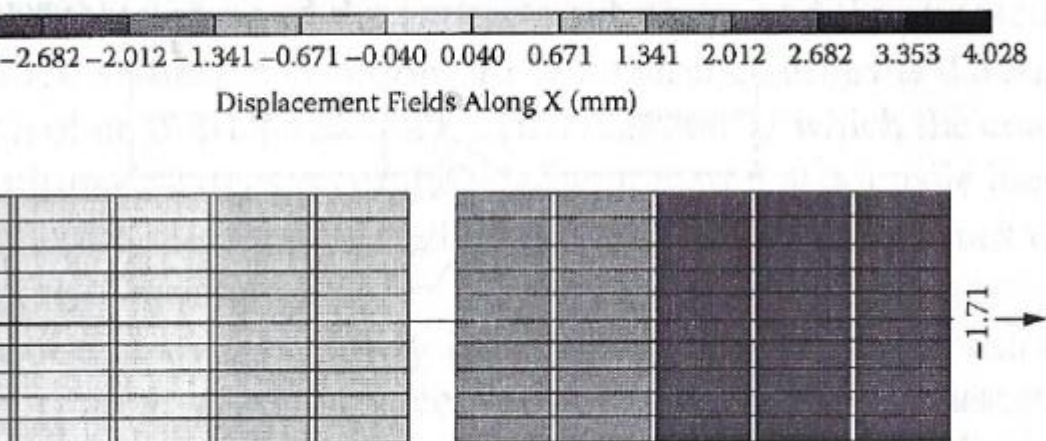


Fig. 10 – Development of crack formation in concrete substratum.

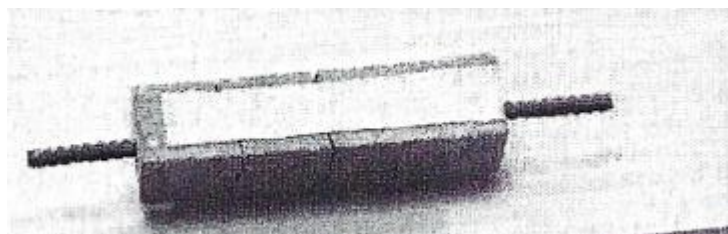


Fig. 11 – Test sample of crack-resistant coating on concrete substratum.

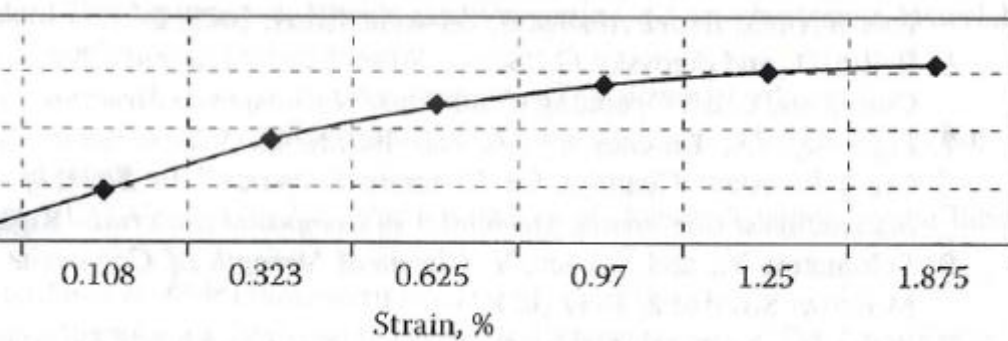


Fig. 12 – Stress-strain relationship of crack-resistant coating under tensile loading.

As a result of theory, numeric solution and testing, the optimum polymer coating width was found about 2.0-2.5 mm.

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