

Polystyrene Paint for Protecting Concrete Structures from Corrosion

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ABSTRACT

The purpose of this work is development and study the properties of varnish paint materials based on a foam polystyrene solution, intended for corrosion protection of concrete and reinforced concrete building structures. This goal determined the formulation of the following tasks:

- Select solvents and determine the optimum polymer concentration
- To develop optimal compositions of varnish paint materials
- Determine the durability of the developed varnish paint materials under various operating conditions.

Information about the possibility of using foam polystyrene waste in the development of paint formulations is given. The optimal types of solvents have been determined. The optimum concentration of the polymer in the solvent has been selected. The long-term strength of polymer coatings has been investigated. The fragile mechanism of destruction for films based on expanded polystyrene solution has been established. It was revealed that in the process of thermal aging of plasticized polymer films based on expanded polystyrene solutions, the nature of the destruction of the coating changes from forced elastic to brittle. The change in the value of the structure-sensitive factor was revealed depending on the content of the plasticizer. In the course of aging, a change in the ratio between the short-term and long-term strength of plasticized coatings is observed.

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Introduction

The issues of combating corrosion do not lose their relevance at the present time. One of the ways to increase the durability of concrete and reinforced concrete structures is the use of varnish paint coatings. For building structures operating in low, medium, and highly corrosive vapor-gas environments and not exposed to mechanical stress, paint coatings are the main means of protection. Their advantages are relatively high chemical resistance, the ability to apply complex configurations on the surface, ease of resumption and repair.

Currently, one of the important problems is the creation of a sufficiently effective anti-corrosion protection of building structures for glass production.

The peculiarity of the operation of building structures at enterprises for glass production consists in a strong aggressive effect of the used technological media on traditional cement concrete and solution containing siliceous fillers.

The most aggressive component for the atmosphere of the chemical glass polishing workshop is hydrogen fluoride, possibly

an increased content of vapors in the air HF during unloading and loading of products, as well as under the roof; possibly splash penetration HF on building structures, accidental splashing with solutions HF .

It is known that hydrogen fluoride with calcium hydroxide forms practically insoluble calcium fluoride, the volume of which is 25.7% less than the volume of calcium hydroxide [1]. Under the action of hydrogen fluoride on the cement stone, the destruction of crystalline hydrates and the loss of water occur, which additionally increases the porosity.

When low concentrations of hydrogen fluoride act on concrete, the neutralized layer has increased strength; however, its permeability seems to increase, because the resulting solid products have a smaller volume than the original ones. After the neutralized layer reaches a certain thickness, the process proceeds with internal diffusion inhibition.

Based on the results obtained, the authors conclude that hydrogen fluoride in high concentrations is more aggressive to concrete than hydrogen chloride and sulfur dioxide.

In this regard, it becomes necessary to protect concrete and reinforced concrete building structures at enterprises for glass

production from the action of hydrofluoric acid vapors. One of the effective ways of scientific and technological progress in the production of building materials is the use of various polymer wastes as the main raw material.

Steelpaint (Germany) produces polyurethane varnish paint materials (PU-stelpaint) for anti-corrosion protection of equipment, tanks, pipelines. The range includes materials filled with zinc (PU-Zink) and aluminum (PU-ALU) powder, iron mica (PU-Mica), mineral pigments (PU-Tar). Polymer coatings are characterized by high resistance to atmospheric factors, excellent elasticity, exceeding the elasticity of epoxy coatings and chemical resistance [2].

In anti-corrosion technology, one of the first places among the most famous synthetic materials is occupied by epoxy resins. Coatings based on them have high adhesion properties, strength, waterproofness, chemical resistance [3].

To obtain varnish paint coatings, polystyrene and its copolymers can be used. Of interest is the use of polystyrene (PS) waste as one of the components for varnish paint materials.

Materials and Research Methods

For the preparation of polymer composites as a film former material, we used waste heat-insulating polystyrene foam grade polystyrene blocky (PSB) with density = 20 kg/m³ (GOST 15588-86) [4].

O-xylene, solvent, and a mixture of acetone with A-76 gasoline in a 1: 1 ratio (AB solvent) were used as solvents for the polymer. The main physical and chemical properties of the solvents used are given in Table 1 [5,6].

Table 1: Basic Physical and Chemical Properties of Solvents.

Name of the solvent	Density at 20°C, ρ_m (kg/m ³)	Vapor pressure at 20°C,(kPa)	Molecular mass	Surface tension at 20°C,(N/m)	Maximum permissible concentration,(mgm ³)
1	2	3	4	5	7
O-xylene, GOST 9949-76	880	1,34	106,16	30,03	50
Solvent, GOST 10214-78	860	-	-	-	100
Acetone, GOST 2768-84	790	23,99	58,087	23,32	200
Gasoline, A-76 GOST 2084-77	730	66,7	100	20	100

Powders of calcium fluoride, calcium oxide, calcium hydroxide, and waste of chemical glass polishing (WCGP) were used as fillers.

Fillers were selected based on the following conditions: they must be chemically inert to aggressive gases (calcium fluoride) or capable of binding corrosive gases as a result of a chemical reaction (calcium oxide, etc.). Silicon oxide was used as control filler.

Waste of chemical glass polishing (WCGP) is formed when used polishing solutions (a mixture of hydrofluoric and sulfuric acids) are neutralized calcareous solution. WCGP- is a mechanical mixture of calcium fluoride (46%), calcium sulfate (42%), silicon dioxide (5%), and other oxides (7%). Chromium oxide was used as a pigment Cr_2O_3 .

The main properties of the fillers and pigment used, as well as the mixture of the filler (calcium fluoride) with the pigment, are given in Table 2.

Table 2: Basic Properties of Fillers and Pigments.

Filler name	True density, ρ , (kg/m ³)	Bulk density, ρ_f , (kg/m ³)	Specific surface area, S_u , (m ² / kg)	Average particle size, $d_{\bar{r}0} \cdot 10^{-6}$
Calcium fluoride	2800	1080	517	4.14
Calcium oxide	2780	640	545	3.96
Calcium hydroxide	2240	390	1070	2.5
WCGP	2300	700	1466	1.78
Chromium oxide	5210	760	920	1.25
A mixture of calcium fluoride with chromium oxide (9:1)	2940	940	700	2.9
Silicon oxide	2610	920	430	5.57

Di-butyl phthalate (DBP) was used as a plasticizer. The parameter solubility of liquids was determined by the formula [5]

$$\delta = 4.1 \left[\frac{\gamma}{V^{1/3}} \right]^{0.43} \quad (1)$$

where γ - surface tension, N/ m;

V - molar volume.

To determine the solubility parameter of mixed solvents (acetone: gasoline mixture), the equation proposed by Small [5,6] was used:

$$\delta = \frac{\chi_1 V_1 \delta_1 + \chi_2 V_2 \delta_2}{V_1 + V_2}, \quad (2)$$

where χ_1, χ_2 - molar fractions of components;

V_1, V_2 - molar volumes of components;

δ_1, δ_2 - the solubility parameters of components.

The dynamic viscosity of the varnish paint compositions was determined by the Stokes method. The conditional viscosity of the varnish paint compositions was determined using a viscometer VZ-1 (GOST 8420-74. Varnish paint materials. Methods for determining the conditional viscosity).

The determination of the surface tension was carried out by the method of counting drops (stalagmometric method). The measurement of wetting ability of the polymer solution was carried out according to the contact angle (contact angle) [7,8].

The determination of the long-term strength was carried out at constant internal stress, under conditions of homogeneous uniaxial stretching, which was created by a suspended from the sample by the load of that or another magnitudes. The assessment of strength parameters and destruction of coatings were as follows.

According to the temperature-time dependence, the strength of polymer coatings can be described by the equation

$$\tau = \tau_0 e^{\frac{U_0 - \gamma \sigma}{RT}}, \quad (3)$$

where τ_0 - constant numerically equal to the period of vibrations of atoms;

U_0 - initial activation energy of destruction;

γ - structure-sensitive factor characterizing the internal overstress of bonds in a polymer;

σ - applied internal stress;

R - gas constant;

T - temperature, °K.

To assessment the parameters U_0, γ of the equation, a series of experiments was carried out to measure the durability at various internal stresses and temperatures. The values were determined U_0, γ, τ_0 by a graphical method. Taking as a basis a set of straight lines in coordinates $\lg \tau, \sigma$, we found the point of intersection of vertical lines with a graph $\lg \tau(\sigma)$ and used them to construct a second set of straight lines in coordinates $\lg \tau, 1/T$ at fixed values σ . By the slope of the obtained straight lines, the activation energy of the destruction process was calculated $U(\sigma)$ and a graph was built $U(\sigma) - \sigma$. Extrapolating to $\sigma=0$, the value was obtained U_0 and was determined from the slope of the straight line γ .

Research Results

Polystyrene foam is soluble in any solvent with weak hydrogen bonds (xylene, solvent, gasoline), if the solubility parameter of these substances is in the range of 8-10.6 (cal/cm³)^{1/2}. Among solvents with medium strength hydrogen bonds (acetone), those with a solubility parameter in the range of 8.1-9.9 (cal/cm³)^{1/2} are most suitable. In substances with a strong hydrogen bond, the polymer is insoluble, because $\delta=0$.

It was found that solvents o-xylene, solvent and AB solvent will dissolve polystyrene foam well. The critical concentration of a solution of polystyrene foam in xylene is 16%, in a solvent - 24%, in a mixed solvent AB - 30%. From a rheological point of view, the best solvent among the investigated is a mixture of acetone with gasoline (1: 1).

Research has been done on the wetting ability of polystyrene foam solutions in AB solvent. The contact angles of wetting of the used fillers with solutions of polystyrene foam and the surface tension with solutions of polystyrene foam of various concentrations were determined. Based on the experimental data obtained, the value for the free energy of wetting was calculated. The results of experimental research are shown in Table 3.

Table 3: Wetting Ability of Foam Polystyrene (Fps) Solutions

Concentration of FPS, (%)	Surface tension (N/m)	Fillers							
		Calcium fluoride		Silicon oxide		Calcium hydroxide		WCGP	
		$\cos \theta$	U	$\cos \theta$	U	$\cos \theta$	U	$\cos \theta$	U
15	23.78	0.906	-21.54	0.875	-20.81	0.857	-20.38	0.866	-20.59
20	24.62	0.743	-18.29	0.731	-17.99	0.719	-17.7	0.695	-17.11
30	26.38	0.390	-10.29	0.375	-9.89	0.358	-9.44	0.375	-9.89

As the research results show, the free energy of wetting of a 15% FPS solution is higher than that of a 30% solution; therefore, a 15% FPS solution has a better wetting ability. The calculated consumption of fillers is presented in Table 4.

Table 4: Basic Properties of Fillers and Pigments

Filler type	Specific surface of the filler, (m ² /kg)	Average particle size of filler, 10 ⁻⁶ (m)	Bulk density, (kg/m ³)	Filler density, (kg/m ³)	Filler particle volume, unit volume	Volume of monolithic filler particles, unit volume	Film-former material solution volume, unit volume
1	2	3	4	5	6	7	8
Calcium fluoride	517	4,14	1080	2800	0,38	0,15	0,85
WCGP	1466	1,78	700	2300	0,17	0,05	0,95
Calcium oxide	545	3,96	640	2780	0,4	0,09	0,91
Silicon oxide	4307	5,57	920	2610	0,51	0,19	0,81
Calcium hydroxide	1070	2,5	390	2240	0,26	0,05	0,95
Mixture: calcium fluoride and pigment	700	2,9	940	2940	0,3	0,1	0,9

The Research of the long-term strength of polymer coatings was carried out on films based on a 15% FPS solution in AB solvent, filled with a mixture of calcium fluoride and pigment, without plasticizer and with optimum plasticizer content. Free films with dimensions 10x30 mm were tested.

In Figure 1 shows the time dependences of the strength of polymer films, obtained at different temperatures. Within the research time interval, the experimental data are fairly well described by a linear dependence

$$\tau = Ae^{\alpha\sigma}$$

where τ - time to destruction of the sample;
 σ - applied internal stress;
 A and α - constants, depending on the properties of the material.

There is a relationship between the time to fracture of the material, stretching internal stress and temperature, which is expressed by the equation (3) [9-12]. Equation (3) reflects the total temperature-time dependence of the strength of solid bodies. Equation (3) is a mathematical expression of the kinetic concept of the strength of solid bodies. According to this concept, mechanical destruction of materials is considered as some kind of kinetic process, while the strength index is not a limiting value, which has the character of a material constant. The process of destruction of polymers, according to Zhurkov, is not a purely mechanical phenomenon; it is the process of disintegration of intermolecular and interatomic bonds under the influence of thermal fluctuations caused by internal stress from the outside. Destruction wears local character; it occurs at weak points, where thermal fluctuations become commensurate with the energy of chemical bonds.

The probability of breaking the bonds is determined by a factor $(U_0 - \gamma\sigma)/RT$. Stretching internal stress lowers the initial barrier U_0 by an amount $\gamma\sigma$, thereby increasing the likelihood of breaking the bonds responsible for the strength of the polymer.

The pre-exponential factor τ_0 is independent of plasticization, orientation, molecular weight and chemical structure of the polymer. All of the above factors affecting the structure of the material affect the coefficient γ . The constant U_0 is the same for polymers with thermal destruction energy.

Based on the data obtained, the temperature dependences of the durability of films (Figure 1) are constructed, which are straight lines with different slopes, all straight lines intersect at one pole at $\tau_0 = 10^{-12}$ s.

Based on the experimental data obtained, the temperature dependences of the durability of films based on a solution of foam polystyrene were constructed (Figure 1). All straight lines intersect at one pole at $\tau_0 = 10^{-12}$ s.

Figure 2 shows the time dependence of the strength of films based on foam polystyrene solution obtained at temperatures of 273, 291, 295, 303°K.

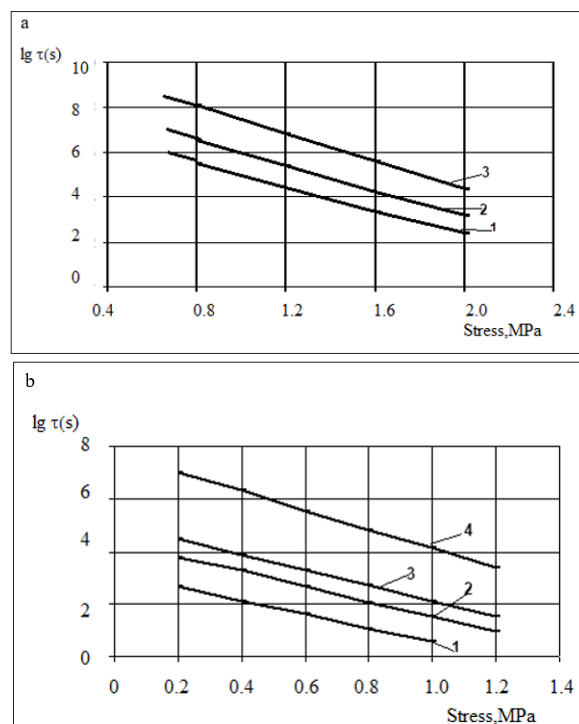


Figure 1: Time dependences of the strength of unplastized (a) and plastized (b) polymer films based on foam polystyrene solution at different temperatures: unplastized (a) 1 - 30°C; 2 - 18°C; 3 - 0°C; plastized (b) - 1 - 30°C; 2- 22°C; 3 - 18°C; 4 - 0°C

The data obtained for the films under researched were used to calculate the values of γ and U_0 . The data are presented in Table 5.

Table 5: The Values of the Coefficient γ And U_0 For Films Based on Foam Polystyrene Solution.

Film type	γ (J / mol.MPa)	U_0 , (kJ / mol)
Without plasticizer	24	81,5
With optimal dibutyl phthalate DBP content	25,5	81,5

An analysis of the results obtained allows us to conclude that the introduction of a plasticizer into films based on foam polystyrene solution changes the value of the structure-sensitive factor γ , characterizing the internal overstress of bonds in the polymer. So, the value γ for plasticized films was 25.5 kJ / mol.MPa, for unplasticized films - 24 kJ / mol.MPa.

The initial energy barrier U_0 , determined by extrapolating the dependences $U(\sigma)$ to the value $\sigma = 0$ is the same for both plasticized and unplasticized films and is 81.5 kJ/mol. Moreover, as can be seen from the data obtained, with the introduction of a plasticizer, the strength of films based on foam polystyrene solution decreases by about 1.5 times, and the value U_0 does not change.

Obviously, this indicates that in brittle and forced-elastic fracture, when the time τ_p is much less than the relaxation period τ , the destruction of polymers is determined by the breaking of chemical bonds and the temperature-time dependence of strength is described by the Zhurkov equation. The activation energy with a decrease in the destructive internal stress increases in accordance with the fluctuation theory of the strength of solid bodies $\sigma = 0$ and at is equal to the energy of bonds responsible for the destruction of the polymer.

For a more visual representation of the intensity of the decrease in long-term strength in comparison with short-term, the results of research of the long-term strength for films at a temperature of 20 ° C and a load of 0.5 N are presented in coordinates $\tau - \sigma \tau / \sigma_{sh}$ (Figure 4). The short-term strength σ_{sh} is taken as the strength at a loading time of 10 s, $\sigma \tau$ and is the film strength over time τ . From Figure 4 it follows that the most intense drop in long-term strength occurs in the first hours of exposure to the load. By 100-150 hours, the decrease in strength is significantly slowed down.

The introduction of plasticizers has a significant effect on the long-term strength of varnish paint films. So, by 150 h at room temperature, the long-term strength of films without a plasticizer was 66% of the short-term (curve 4, Figure 3) with a plasticizer - 32% of the short-term (curve 1, 4).

With heat aging, the hardness of the coatings increases and their long-term strength also increases. Thus, freshly prepared films have an established long-term strength of 32%; the long-term strength of these films after 150 hours of thermal aging is 42% of the short-term, and after 400 hours of thermal aging - 54% of the short-term (curves 2, 3, Figure 4).

The obtained experimental data make it possible to solve a number of important practical problems. For example, knowing the internal stress under the influence of which the coating works for a long time, it is possible to estimate its durability. Thus, the experimental data obtained make it possible to predict the durability of polymer coatings based on foam polystyrene solution under operating loads.

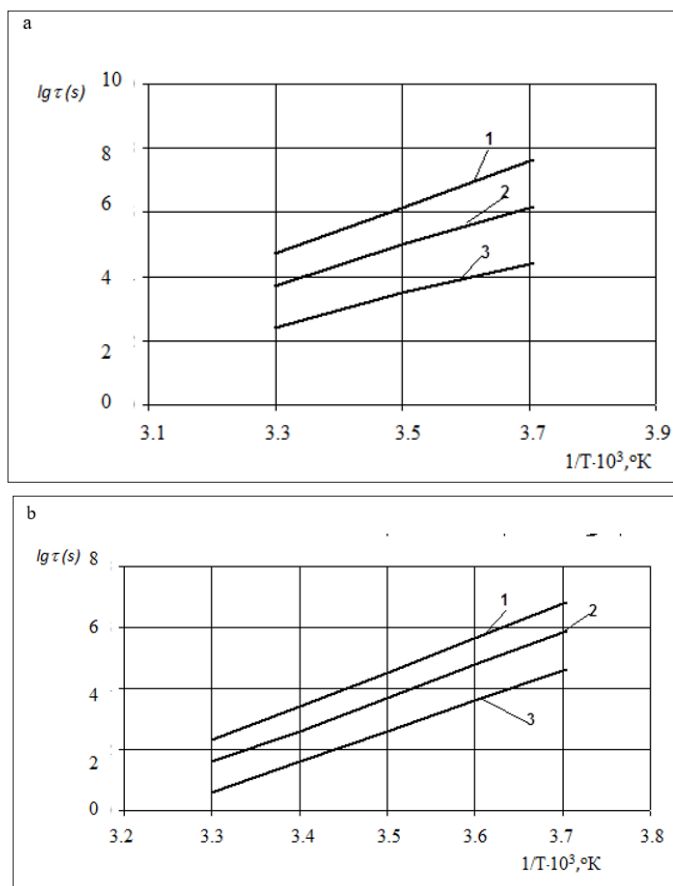


Figure 2: Temperature dependence of the durability of unplasticized (a) and plasticized (b) polymer films at various internal stresses: 1- $\sigma = 1$ MPa; 2 - $\sigma = 1.5$ MPa; 3 - $\sigma = 2$ MPa.

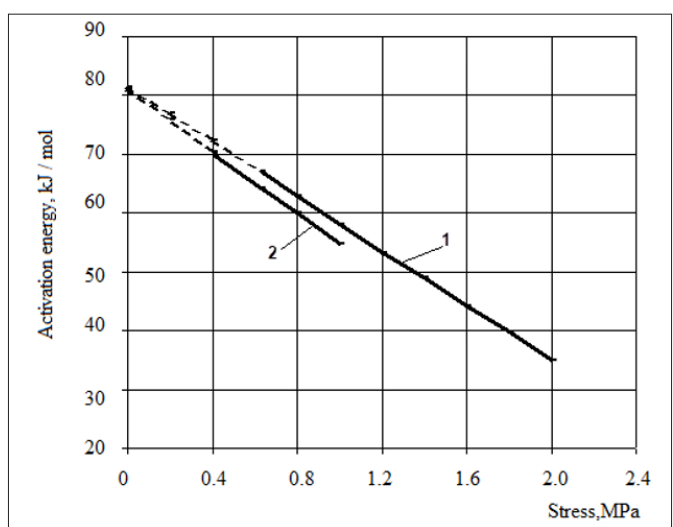


Figure 3: Dependence of activation energy of destruction of polymer films based on foam polystyrene solution: 1 - without plasticizer 2 - with a plasticizer content of 4%.

The short-term strength σ_{sh} is taken as the strength at a loading time of 10 s, σ_{τ} and is the film strength over time τ . Figure 4 it follows that the most intense drop in long-term strength occurs in the first hours of exposure to the load. By 100-150 hours, the decrease in strength is significantly slowed down.

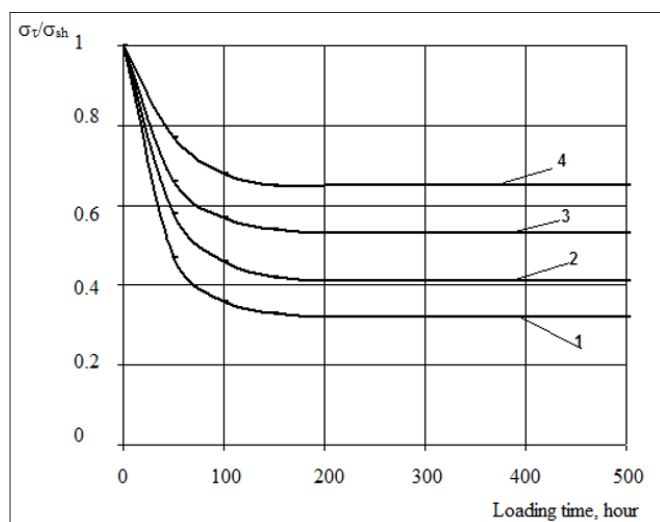


Figure 4: Dependence $\sigma_{\tau}/\sigma_{sh}$ of polymer films based on foam polystyrene solution on loading time:

- 1 With Optimal Plasticizer Content;
- 2,3 With an Optimal Plasticizer Content After 150 And 400 Hours of Heat Aging;
4. Without Plasticizer.

The short-term strength σ_{sh} is taken as the strength at a loading time of 10 s, σ_{τ} and is the film strength over time τ . Figure 4 it follows that the most intense drop in long-term strength occurs in the first hours of exposure to the load. By 100-150 hours, the decrease in strength is significantly slowed down.

The introduction of plasticizers has a significant effect on the long-term strength of varnish paint films. Thus, by 150 h at room temperature, the long-term strength of films without a plasticizer was 66% of the short-term strength (curve 4, Figure 6) with a plasticizer - 32% of the short-term strength (curve 1, Figure 4).

With heat aging, the hardness of the coatings increases and their long-term strength also increases. So, after curing, films have a steady long-term strength of 32% of the short-term; the long-term strength of these films after 150 h of thermal aging is 42% of the short-term, and after 400 h of thermal aging - 54% of the short-term (curves 2, 3, Figure 4).

Conclusion

Selected solvents for foam polystyrene. The regularities of changes in the viscosity of solutions of foam polystyrene depending on its concentration and type of solvent have been established. The value of the critical content of the polymer in the solution was determined. The value of the critical content of dispersed fillers in the varnish paint composition has been determined theoretically and experimentally. A model of changing the viscosity of varnish paint based on foam polystyrene solution depending on the volume fraction of fillers is proposed. It was found that the temperature-time dependence of the strength of polymer films based on foam polystyrene (FPS) solution obeys the Zhurkov dependence. The change in the value of the structure-sensitive factor γ was revealed depending on the content of the plasticizer. It has been established

that the steady-state long-term strength of plasticized coatings based on foam polystyrene (FPS) solution is 32% of the short-term one, and of non-plasticized coatings - 66% of the short-term one. In the course of aging, a change in the ratio between the short-term and long-term strength of plasticized coatings is observed.

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