PROPERTIES OF ED-8P RESIN-BASED POWDER COMPOSITIONS

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In producing compositions by the method of dry mixing of the components, the effect of the type and concentration of the hardener and the temperature regime of hardening on the process of formation of a three-dimensional polymer structure and the technological and electrical-insulation properties of powder compositions based on ED-8P solid epoxy oligomer is studied. A poorly combustible polymer compound for deposition of insulation by the method of fluidized-bed spraying that ensures hermetic sealing and IR-laser marking of mass-produced items is developed. A number of regularities that make it possible to control the technological properties of the compositions are established.

Improvement of the quality and service reliability of products for electronics and development of highly efficient methods for their hermetic sealing that eliminate releases into air and water basins are responsible for the topicality of creating new electrical-insulation polymer compositions [1]. Among them are epoxy powder materials [2] for hermetic sealing of products by the method of spraying that offer undeniable environmental and economic advantages over liquid polymer compositions. Owing to the wide range of epoxy resins, hardeners, polymerization accelerators, modifiers, and fillers and the possibility of variation by means of the methods and parameters of manufacture, powder compositions can have a combination of highly diverse technological and service properties. The absence of readily inflammable and toxic solvents in powder compositions contribute to improvement of working conditions and a decrease in the explosion and fire hazard of production.

Of special interest for this purpose are epoxy powder compositions that ensure, along with electrical-insulation properties, the possibility of marking the products with an IR laser, since the methods for applying marker symbols with dyes now in use are unacceptable for modern production because of low productivity and the impossibility of incorporating them into controlled automatic lines. In comparison with traditional methods, the use of laser marking in mass production makes it possible to significantly (by more than a factor of 40) increase the productivity of the process and the contrast of the symbols applied, to decrease the labor input, to decrease the energy expenditure, and to mark small-sized, fine, and fragile or intricately shaped products [3].

With allowance for special properties of the production of the products and their operating conditions, certain requirements for technological properties are imposed on powder compositions that specify the temperature of film formation, the spreading of the melt, and the gelation time in the selected temperature regime.

Given below are results of investigating the effect of the nature of the hardener, its content, and the temperature regime of hardening on the process of formation of a three-dimensional polymer structure and the technological and electrical-insulation properties of ED-8P resin-based powder compositions sensitive to IR laser radiation.

To produce the compositions, we used the method of dry mixing of powdered components as the most profitable and economic method under the production conditions that ensures production of compositions that are stable in storage. The production of epoxy powders by dry mixing included: 1) grinding of the components to the dimensions of particles with a diameter of ~1 mm, 2) mixing of the hardener with the epoxy resin, 3) mixing of all the components of the composition.

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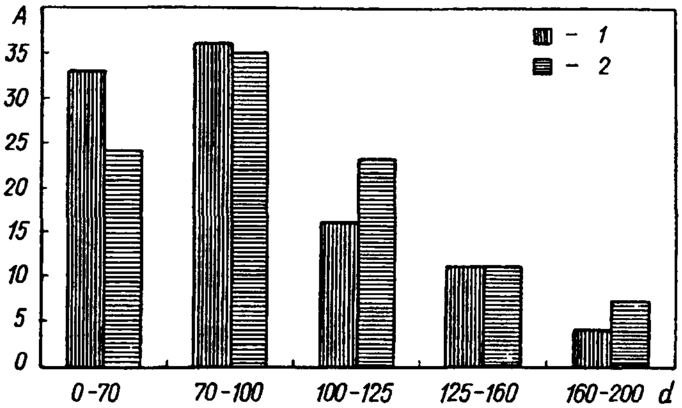

Fig. 1. Change in the granulometric composition of a powder composition in accelerated aging: 1) initial specimen, 2) after aging at 40°C for 10 h.

Since simple mechanical mixing fails to ensure the required quality of the compositions (the necessary granulometric composition and the absence of separation in transportation and coating deposition), we used a SAND-1 planetary ball mill to prepare the compositions. The compositions were crushed and homogenized at a rotational speed of the tool of 160 rpm for 15 min, since preliminary investigations showed that an increase in the speed and duration of the process leads to significant overgrinding of the material, which is undesirable in hermetic sealing of products by spraying in a fluidized bed due to removal of material and separation of the particles by composition. The granulometric composition of the powder in grinding under the above conditions is presented in Fig. 1 (histogram 1). As the data of the figure show, in spite of heterodispersion, the bulk of the powder (85%), from data of a sieve analysis, is composed of particles with a size of 2–125 μm. An evaluation of powder caking under accelerated conditions of aging (40°C, 10 h) showed that insignificant aggregation of the particles is observed (Fig. 1, histogram 2): the content of the 2–70 μm fraction decreases while the content of the 100–125 μm fraction increases.

The base formulation of the epoxy powder composition was developed on the basis of ÉD-8P epoxy oligomer with allowance for the flow temperature, the tendency of powders based on this resin toward fluidization, the hardening rate, and the capacity for mechanical grinding.

To endow the polymer coatings with a certain color and hiding power, we selected pigments. The suitability of one or another pigment is known to be governed by its heat resistance, chemical activity, hiding power, particle size, dielectric properties, atmospheric durability, and light fastness. The enumerated properties are rather general for all pigments and do not establish specific characteristics that would make it possible to evaluate the suitability of the pigments for one or another formulation of the powder composition, and therefore, in selecting the pigments, we used the following criteria as the basic criteria: the heat resistance evaluated by the maximum temperature at which holding the pigment for one hour did not result in a change in the color characteristics (a temperature of 100–160°C) and the light fastness evaluated by the decrease in the reflection coefficient after irradiation with a DRT-400 mercury-quartz lamp for 8 h.

Results of experimental data on the study of the effect of different pigments on the light fastness and heat resistance of coatings produced on the basis of ÉD-8P resin showed that it is appropriate to use green phthalocyanine pigment in the formulation of the compound since it ensures high light fastness (the decrease in the reflection coefficient after irradiation for 8 h is zero), heat resistance (the color characteristics in the indicated temperature range do not change), good dispersivity, and sufficient hiding power.

As is known, the degree of hardening of an epoxy oligomer largely determines the strength and dielectric properties of coatings based on it. One of the important difficulties that occur in developing rapidly hardening compositions is the need to combine accelerated hardening at low temperatures with maintenance of rather high stability (viability) of the powder in time (up to 6 months). Therefore, we need to select the corresponding hardeners or hardeners with accelerators.

TABLE 1. Content of Insoluble Polymer (%) in Hardening of a Composition for 30 min as a Function of the Type of Hardener and the Hardening Temperature

Hardening temperature, °C	Type of hardener and its concentration, wt. parts/100 g of epoxy oligomer										
	UP-0632				UP-607		UP-605/3		adipic acid	2-methylbenzimidazole	
	2	4	6	8	5	10	5	10	10	5	10
140	20	60	65	70					95		
150	37	68	82	82					95	94	96
160					10	70	6	2	95	95	96
170					7	87	18.3	89	95	95	97
180					7	92	89	89	95	97	97

TABLE 2. Effect of the Content of Hardener on the Formation of a Polymer with a Three-Dimensional Structure, Technological Properties of the Powder, and Dielectric Indices of Coatings

No. of composition	Amount of hardener, wt. parts/100 g of epoxy oligomer		Content of insoluble polymer as a function of the hardening time (min) at 150°C, %			Spreadability of the melt at 150°C, mm	Gelation time at 150°C, sec	Electrophysical properties of coatings for $T = 150°C$, $t = 60$ min		
	UP-0632	MBI	30	60	120			ρ, Ω·m	tan δ	ε
1	2	0	37	54	90	210	720	$2 \cdot 10^{12}$	0.01	5.4
2	3	0	50	70	88	132	680	$6 \cdot 10^{12}$	0.01	5.4
3	4	0	68	82	97	100	620	$3.2 \cdot 10^{13}$	0.009	4.8
4	6	0	91	96	97	14	105	$2.6 \cdot 10^{14}$	0.004	4.7
5	4	0.3	75	90	94	16	175	$1 \cdot 10^{14}$	0.008	4.5
6	4	0.5	84	94	98	24	120	$2.0 \cdot 10^{14}$	0.008	3.8
7	4	1	86	96	98	32	77	$2.0 \cdot 10^{14}$	0.007	4.0
8	6	0.5	93	98	99	11	45	$1.1 \cdot 10^{13}$	0.008	5.0
9	6	1	95	99	99	7	40	$4.0 \cdot 10^{14}$	0.004	4.7

To harden the epoxy oligomer (ED-8P resin), we used different types of solid hardeners: 1) UP-0632 amine hardener – tris(dimethylaminomethyl)phenol trisdianate, 2) UP-607 polyanhydride hardener – sebacic acid polyanhydride, 3) UP-605/3 catalytic-action acidic hardener – a complex of BF_3 with benzylamine, 4) adipic acid, 5) 2-methylbenzimidazole.

Based on an analysis of results of investigating the effect of different types of hardeners and their amount on the cross-linking of a powder composition (Table 1) it was established that the use of UP-0632 amine hardener (allowing for the need for a decrease in the hardening temperature) or 2-methylbenzimidazole is the most appropriate. The other hardeners used have certain drawbacks: to harden compositions with UP-607, a relatively high hardening temperature (170°C) is needed, UP-605/3 decreases the heat resistance of the polymers, although an undeniable advantage of it is the high hardening rate of the coatings, and adipic acid is distributed unsatisfactorily in melts with epoxy oligomers and forms patches in hardening that degrade the appearance of the coatings. In addition, to obtain a content of the gel fraction of more than 90% in hardening, we need to introduce into the formulation of the composition at least 10 wt. parts of the indicated hardeners per 100 wt. parts of the resin, which makes no sense economically.

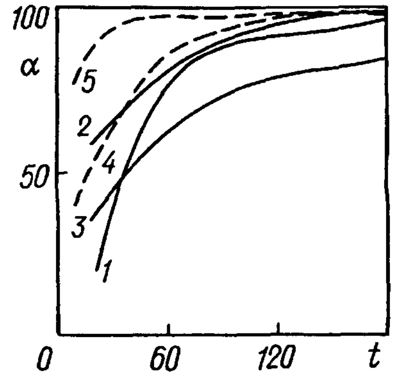

Fig. 2. Content of the gel fraction vs. concentration of a fire-retardant (1-3) and antimony oxide (4, 5) for different times of composition hardening at 150°C: 1) 0, 2) 2.4, 3) 3.4, 4) 2.0, 5) 4.0 wt.%.

The use of 2-methylbenzimidazole (MBI) ensures production of rapidly hardening powder compositions with a high content of insoluble polymer, good physicomechanical properties, improved stability in storage, but, allowing for its shortage and cost (as compared to UP-0632), we studied the possibility of using it as a hardening accelerator mixed with UP-0632 amine hardener.

Table 2 gives data on the effect of the formulation of the mixture hardener on the formation of a polymer with a three-dimensional structure and the electrical-insulation (the specific volumetric resistance ρ, the dielectric constant ε, the dielectric loss tangent $\tan\delta$) and technological (the spreading of the melt, the gelation time) characteristics of the compound.

As Table 2 shows, the introduction of small amounts of MBI (0.3–1.0 wt. % per 100 g of epoxy oligomer) into the formulation of UP-0632 hardener enables us to accelerate significantly the hardening of the compound (as compared to compositions without 2-methylbenzimidazole) and ensures production of coatings with a high content of insoluble polymer in 30 min of hardening at a temperature of 150°C. The degree of hardening increases insignificantly with the temperature (t = const) in the temperature interval of 120–150°C. Varying the formulation of the mixture hardener and the hardening time ensures the possibility of controlling the content of insoluble polymer.

It should be noted that a substantial effect of the concentration of intentional additions on the process of hardening is observed, and the content of insoluble polymer (the gel fraction) depends on the type of addition and its concentration. Figure 2 presents the content of insoluble polymer as a function of the concentration of an organic halogenous fire-retardant and antimony oxide. It can be seen that an increase in the concentration of the fire-retardant to 3.4 wt.% leads to a decrease in content of the insoluble polymer. And conversely, an increase in the content of antimony oxide to 4 wt.% increases the rate of the process of hardening (Fig. 2, curves 4 and 5).

It is known that the capacity of melted compositions for spreading (the spreadability of the melt) is important for hermetic sealing of vertical surfaces. In the investigation, we developed a number of formulations of powder compositions that ensure a spreadability of the melt in the interval of 5–70 mm and a gelation time of 40–130 sec at 150°C, which enables us to select the needed formulation of the composition in relation to the kind of technical product and the method for depositing the composition (Table 2).

For coatings produced based on the formulations developed, we evaluated the quality of marking. It was established that they ensure contrast marking of products under the action of one pulse of IR laser radiation with an energy density of 0.5 J/cm^2. The marker symbols are alcohol- and gasoline-resistant and are stable to mechanical actions and climatic factors.

By the method of differential thermal analysis we studied the relative heat resistance of coatings as a function of the type of hardener and the content of intentional inorganic additions. According to the degree of the effect on the heat resistance the hardeners investigated correspond to the following sequence: 2-methylbenzimidazole > sebacic acid polyanhydride (UP-607) > adipic acid > amine hardener (UP-0632). Figure 3 presents thermogravimetric curves for compositions that contain different amounts of aerosil and antimony oxide. It can be seen that an increase in the content of aerosil above 1.8 wt.% leads to a decrease in the relative heat resistance.

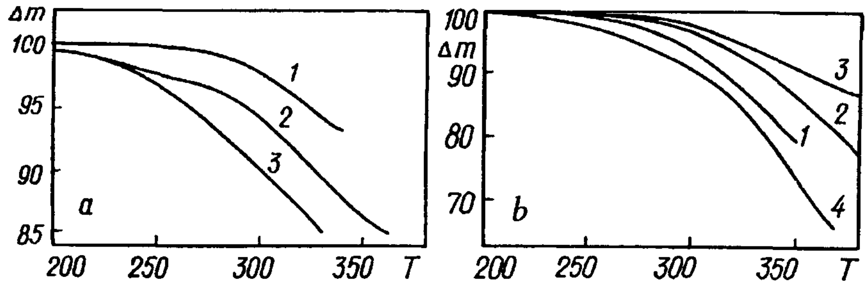

Fig. 3. Curves of mass loss by the compound vs. content of disperse silicon oxide (a) and antimony oxide (b): a: 1) $c = 1.2$, 2) 1.8, 3) 2.2; b: 1) $c = 2$, 2) 7, 3) 9, 4) 17.

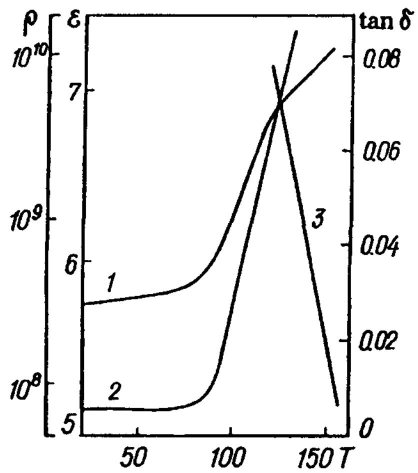

Fig. 4. Dielectric constant (1), loss tangent dielectric (2), and specific volumetric resistance (3) vs. temperature for coatings hardened at 150°C for 60 min.

The effect of the content of Sb_2O_3 on the relative heat resistance is extremal in character: an increase in it from 2 to 9 wt.% has a stabilizing action on the thermodestruction of the composition; when the amount of Sb_2O_3 is increased further to 17 wt.%, a decrease in the heat resistance is observed.

Dielectric characteristics of coatings produced based on the compound developed are presented in Table 2, and their variation as a function of the temperature is presented in Fig. 4. As follows from the given data, these indices correspond in magnitude to the All-Union State Standard (GOST) for electrical-insulation materials. When the temperature increases above 90°C the dielectric properties decrease. The dielectric loss tangent as a function of the temperature has no maximum of dipole-relaxation losses: a monotonic increase in the losses from 100 °C is observed, which indicates the predominance of ionic conduction in this case. The changes in the dielectric indices observed lie within the range of these quantities at elevated temperatures for similar powder compositions and are largely attributable to the properties of the epoxy binder.

Thus, as a result of the investigation performed we developed optimum variants of formulations of poorly combustible (the oxygen index is at least 35) powdered polymer compositions based on ED-8P epoxy oligomer that ensure IR laser marking of products. The compositions can be prepared by the simple and economic method of dry mixing of the components. However, it should be noted that this method of producing the compositions is suitable only for hermetic sealing of products that do not require high decorative properties of the surface. High sensitivity of the compositions to IR laser radiation makes it possible to mark products by radiation with an energy density of 0.5 J/cm^2, which permits a significant increase in the productivity of this process, a decrease in the labor input, and a decrease in the energy expenditure. We established a number of regularities for controlling the technological properties of the compositions: the spreadability of the melt, the gelation time, the hardening time and temperature, and the stability in storage as a function of the formulation.

NOTATION

ρ, specific volumetric resistance, $\Omega \cdot m$; tan δ, dielectric loss tangent; ε, dielectric constant; t, hardening time of the composition, min; T, hardening temperature of the composition, ^{o}C; Δm, mass loss, %; c, concentration, wt.%; A, fractional yield, %; d, particle size, μm; α, content of the gel fraction, %.

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