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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Study of the Oxidation Process of Metallic Pigments in the Presence of Silicone Resin Under Heating

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Abstract—Oxidation of particles of Stapa 4 zinc paste and its composites with Stapa 1515 n. 1 aluminum paste, Silres MSE 100 silicone resin, and microtalc under heating in air was studied by differential-thermal and X-ray phase analyses and electron microscopy. The oxidation of zinc particles starts after a temperature of 330°C is reached, whereas in the presence of Silres MSE 100 resin, the process in which zinc particles are oxidized becomes substantially slower. The oxidation of aluminum particles in the Zn–Al–resin system begins at 560°C. Additional introduction of microtalc shifts the exothermic processes to higher temperatures. A composite was developed for a zinc-aluminum paint to be used to form heat-resistant coatings on metals.

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The most important criteria of heat-resistance of coatings are the stability in the temperature range 200–650°C without flaking-off the base, resistance to thermal shocks, and corrosion resistance. An essentially temperature-resistant coating system consists of at least two components: silicone resin serving as a binder and pigments and(or) fillers [1]. The choice of these latter depends on the expected working temperature of articles. It is known that scaly pigments (aluminum powder, zinc dust) and fillers (mica, talc, iron mica) improve the heat resistance of coatings by 50–100° and are also overlapping each other, with the oxidation resistance and corrosion protection thereby improved [2, 3].

Use of aluminum and zinc pastes makes it possible to diminish or completely eliminate dusting, raise the production safety, and improve the sanitary-hygienic working conditions and production ecology, obtain high-quality homogeneous paint, and take into account specific features of a technological process. In particular, of indubitable interest are aluminum- and zinc-containing pastes with lamellar structure of particles, manufactured by Eckart company.

Coatings with zinc pigments have excellent corrosion-protection properties. However, manufacturers of protective heat-resistant paints recommend forming a finishing aluminum-containing coating on zinc coating in order to preclude evaporation of melted zinc at their working temperatures exceeding 420°C.

The protective potential of organosilicon coatings can be only understood with an integrated approach to analysis of their physicomechanical properties and deep insight into, and consideration for all the physicochemical and mechanical phenomena occurring in the film-forming base both in the isolated state and during the service life of a coating. At high working temperatures, metals and nonmetals commonly lose their mechanical strength, and metals, in addition, have a poorer corrosion resistance. In this context, a question arises of protective coatings that should combine anticorrosion properties and thermal stability. A study of the oxidation process of metallic pigments in contact with atmospheric oxygen is of fundamental importance or solving the corrosion problems.

The goal of our study was to examine the oxidation of zinc particles heated in air and in the presence of an aluminum pigment, silicone resin, and a scaly filler by modern physical methods and to obtain on their basis and heat-resistant anticorrosion coating.

EXPERIMENTAL

As objects of study served 99% methyl silicone resin of Silres MSE 100 brand (manufactured by Wacker), cured at room temperature in the presence of a catalyst; metallic pigments: 65% aluminum paste of Stapa 1515 n. 1 brand and 90% zinc paste of Stapa 4 brand (both manufactured by Eckart), prepared using organic solvents (white spirit and solvent naphtha); and scaly filler, microtalc of Jetfine 1A brand (Imerys). The resin : Al : Zn ratio (in terms of the dry residue of the pigments) was 1 : 0.3 : 0.1. Microtalc was introduced into the composites in amount of 30 wt % relative to their content of the resin. The amount of the aluminum and zinc pigments in the composites remained constant.

Thermographic studies of the samples were carried out with a Netzsch STA 409 PC/PG instrument at a heating rate of 0.5 deg min^{-1} in air in the temperature range 30–90°C. X-ray diffraction patterns of the starting samples and those thermally treated at 600 and 700°C for 1 h were obtained on a D 8 ADVANCE diffractometer (Bruker, Germany).

The microstructure of the samples was determined by scanning electron microscopy on a LEO 1420 instrument. Gold layers were deposited onto the surface of the samples in a VUP-2K vacuum evaporation installation.

The DTA curve of the zinc paste shows an endothermic peak at a temperature of 106°C, which is associated with an up to 10% loss of mass by a sample and is due to the evaporation of the organic solvents contained in the paste (Fig. 1a). At 419°C the DTA curve shows an endothermic peak corresponding to the melting of zinc [4]. The oxidation of the zinc pigment starts at 330°C, which is confirmed by the TG and TGA data. For example, an exothermic peak with maximum at 359°C is observed in the temperature range 330–400°C. In this case, the oxidation of metal particles is presumably limited by the diffusion of the oxidizing agent (atmospheric oxygen) across the oxide film of zinc particles, which is poorly permeable to the oxidizing agent [5]. The poor permeability of the oxide film on zinc pigment particles is confirmed by the small fragment of the metal oxidized on heating a sample to 400°C. About 6% of the metal is oxidized in the given temperature interval.

An exothermic peak with a maximum at 628°C is observed in the temperature range 513–730°C (Fig. 1a). Presumably, the oxide film cracks in this temperature interval due to the melting of the metal within particles

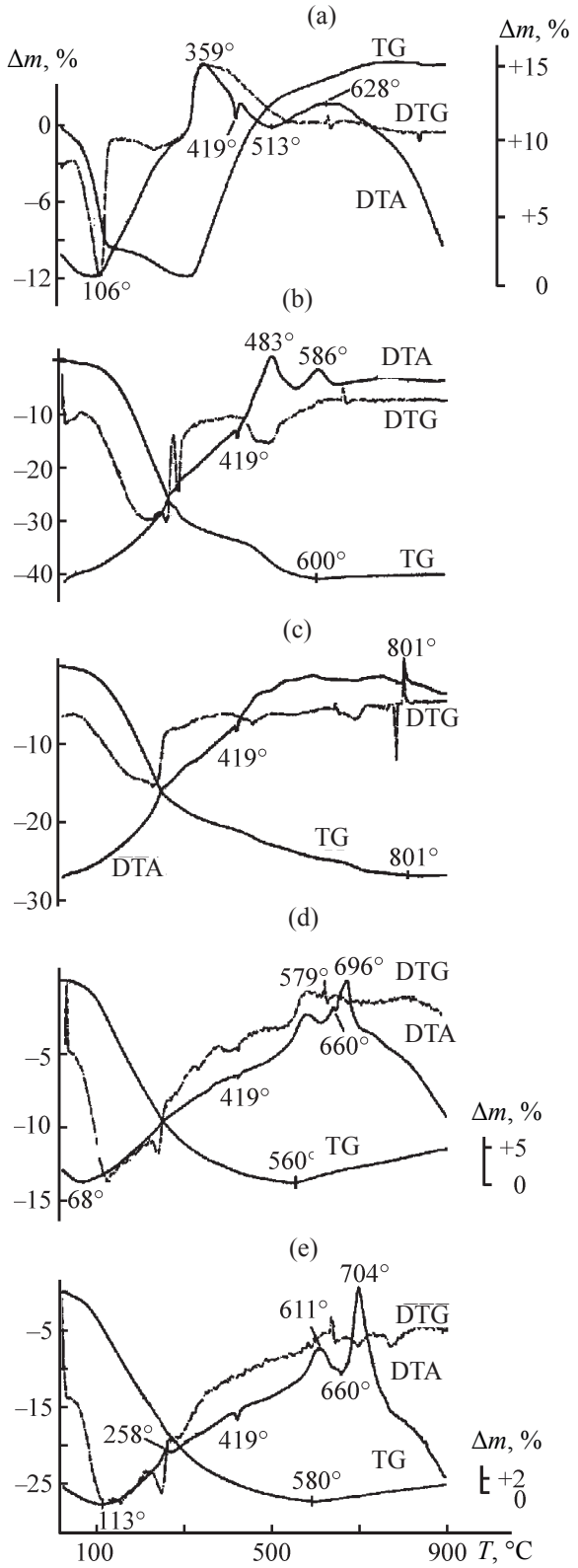

Fig. 1. Derivatograms of experimental samples: (a) zinc paste and composites of the systems (b) Zn–resin, (c) Zn–talc–resin, (d) Zn–Al–resin, and (e) Zn–Al–talc–resin. (Δ*m*) Loss of mass and (*T*) temperature.

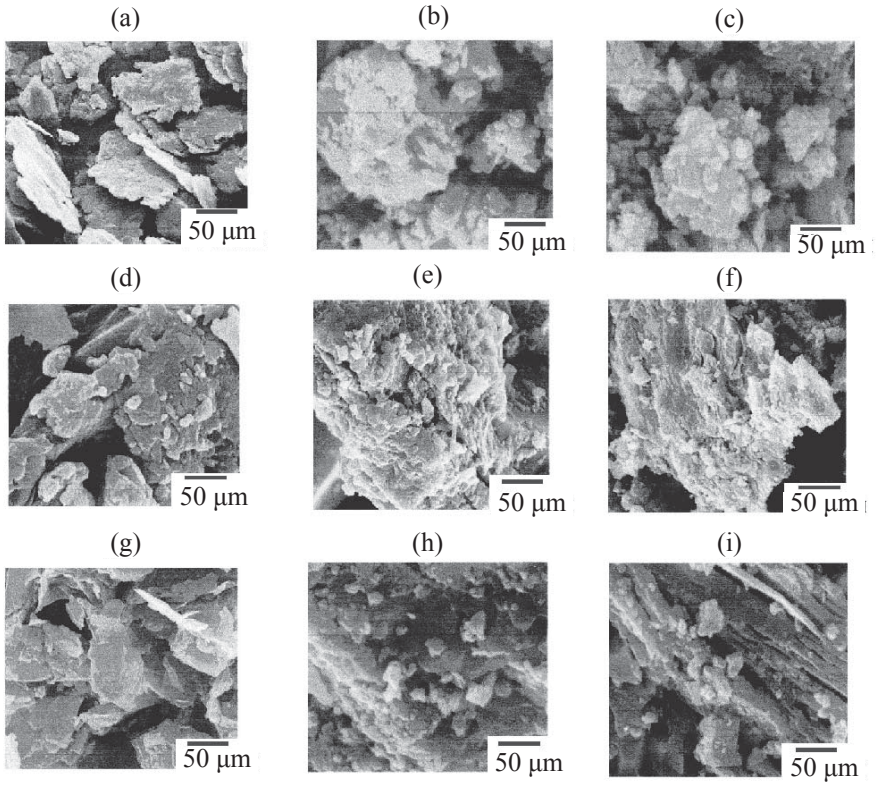

Fig. 2. Micrographs of samples of (a–c) zinc paste, (d–f) paste-based composites with resin, and (g–i) those with talc and resin. Samples (a, d, g) were dried at 20°C for five days and thermally treated at (b, e, h) 600 and (c, f, i) 700°C for 1 h.

and to the volume expansion of the melt, with the zinc melt coming into direct contact with atmospheric oxygen [5]. The gain in mass on reaching 730°C is 14%. As the temperature is raised further, the oxidation rate decreases. According to TG data, about 1% of the metal is oxidized when a sample is heated in the temperature range 730–900°C. The total gain in mass on reaching 900°C is 15%.

According to the results of an electron-microscopic study, the starting zinc paste particles have a flaky shape (Fig. 2a). The micrographs of the zinc pigment thermally treated at 600 and 700°C show ruptures of the oxide film on the surface of zinc particles (Figs. 2b and 2c).

An X-ray phase analysis of the starting zinc paste demonstrated the presence of a single phase, zinc (Fig. 3, curve *1*). The zinc oxide phase is manifested in a zinc sample after its thermal treatment at 600 and 700°C (Fig. 3, curves *2* and *3*). No metallic zinc was found in a sample thermally treated at 700°C.

DTA data for a composite containing zinc paste and Silres MSE 100 resin demonstrated that intense release of components formed in thermal destruction of the resin is observed up to 600°C (Fig. 1b). According to the TG data, the loss of mass by a sample is 40% in the temperature range 20–600°C. AS the temperature increases further, the decomposition process becomes slower and oxidation of zinc in accordance with the DTA data cannot be visually determined. In our opinion, two processes occur in the temperature range 600–900°C: further decomposition of the resin and slight oxidation of zinc, which is confirmed by the XPA data (Fig. 4, curve *1*). The endothermic peak at 419°C corresponds to the melting of zinc.

The electron micrographs of a composite containing a zinc pigment and the resin, dried at 20°C, show that zinc particles are glued together by the binder at places of its accumulation (Fig. 2d). The micrograph of samples thermally treated at 600 and 700°C shows that the surface of the particles is covered by a crust-like coating (Figs. 2e and 2f).

Two phases, Zn and ZnO, were found by XPA in the composite with the zinc paste and resin, thermally treated at both 600 and 700°C (Fig. 4, curves *1* and *2*). It was shown in [6] that Silres MSE 100 resin thermally treated at these temperatures is X-ray-amorphous.

Introduction of microtalc into a composite containing the zinc paste and the resin shifts the exothermic processes to higher temperatures (Fig. 1c). The DTA curve of this

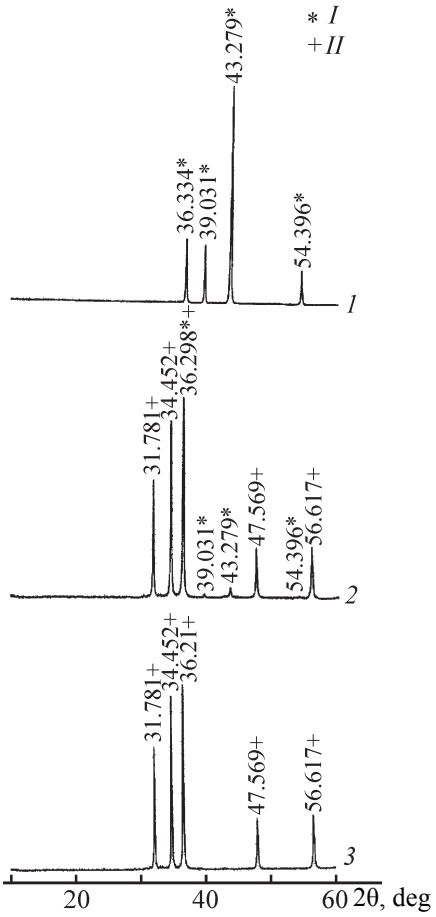

Fig. 3. X-ray diffraction patterns of zinc paste: (*1*) starting and that treated at (*2*) 600 and (*3*) 700°C. (2θ) Bragg angle; the same for Figs. 4 and 5. (*I*) Zn and (*II*) ZnO.

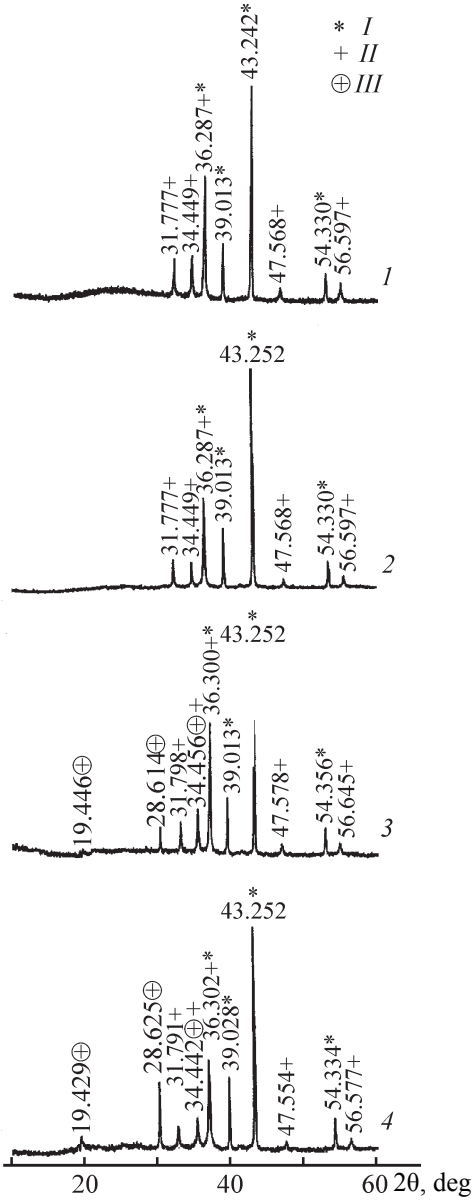

Fig. 4. X-ray diffraction patterns of composites of the systems (*1, 2*) Zn–resin and (*3, 4*) Zn–talc–resin thermally treated at (*1, 3*) 600 and (*2, 4*) 700°C. Treatment duration of samples 1 h; the same for Fig. 5. (*I*) Zn, (*II*) ZnO, and (*III*) $Mg_3Si_4O_{10}(OH)_2$.

composite shows an exothermic peak with a maximum at 801°C. The loss of mass is 27% on reaching 801°C and 28% on reaching 28%.

A sample of the composite composed of the zinc paste, resin, and microtalc, thermally treated at 600 and 700°C, contains Zn, ZnO, and $Mg_3S_4O_{10}(OH)_2$ (Fig. 4, curves *3* and *4*). The micrograph of the given sample dried at 20°C shows scaly particles covered with a film of the binder, and no texture of the particles is seen (Fig. 2g). After this composite is treated at 600 and 700°C, its particles become rather closely conjugated with each other (Figs. 2h and 2i).

The DTA curve of the composite containing the zinc and aluminum pigments and the resin shows three endothermic peaks at 68, 419, and 660°C, the last two of which are associated with the melting of, respectively, zinc and aluminum, and also two exothermic peaks at 579 and 696°C (Fig. 1d). According to the TG data, the gain in sample mass in the temperature range 560–900°C was 5%, which is mainly due to the oxidation of aluminum particles. It has been shown previously [6] that, in the presence of Silres MSE 100 resin, the oxidation of aluminum particles starts after the temperature of 560°C is reached, with the gain in sample mass also being 5%.

Introduction of microtalc into a sample of the Zn–Al–resin system leads to a certain visually observed slowing down of the aluminum oxidation process (Fig. 1e), as also in the case of the Al–resin system [6]. For these

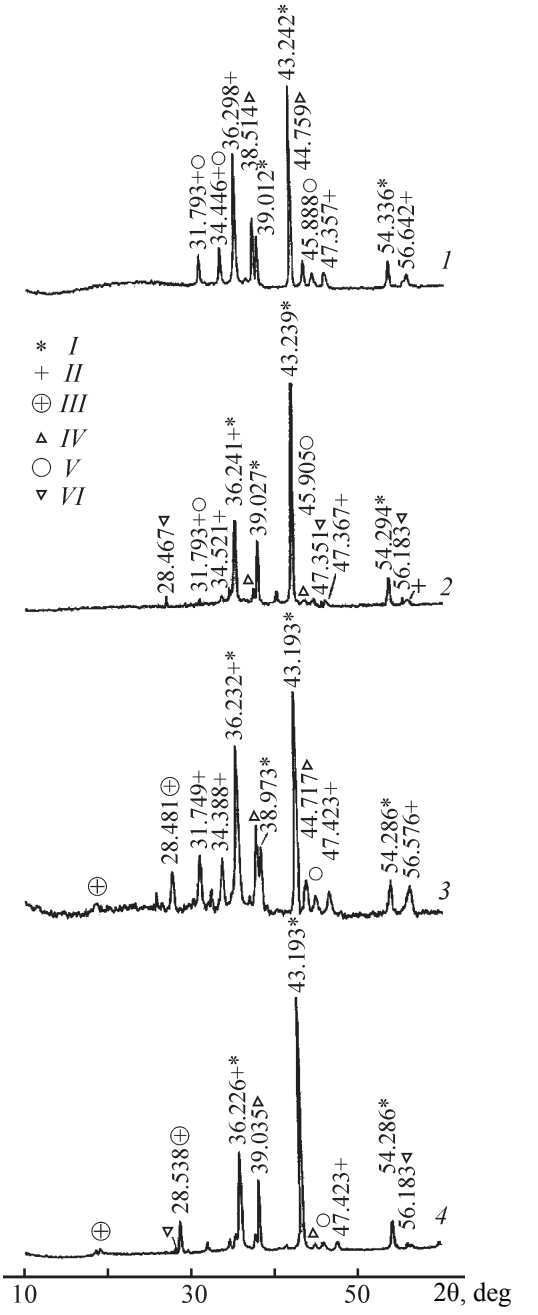

Fig. 5. X-ray diffraction patterns of the systems (*1, 2*) Zn–Al–resin and (*3, 4*) Zn–Al–talc–resin thermally treated at (*1, 3*) 600 and (*2, 4*) 700°C. (*I*) Zn, (*II*) ZnO, (*III*) $Mg_3Si_4O_{10}(OH)_2$, (*IV*) Al, (*V*) Al_2O_3, and (*VI*) Si.

two systems, an increase in the mass of the samples is observed around the temperature of 580°C, with this increase being 2% in both cases on reaching 900°C.

The sample of the composite in the Zn–Al–resin system, thermally treated at 600 and 700°C, contains Zn, Al, Al_2O_3, and ZnO phases (Fig. 5, curve *1*). The sample treated at 700°C contains Si in addition

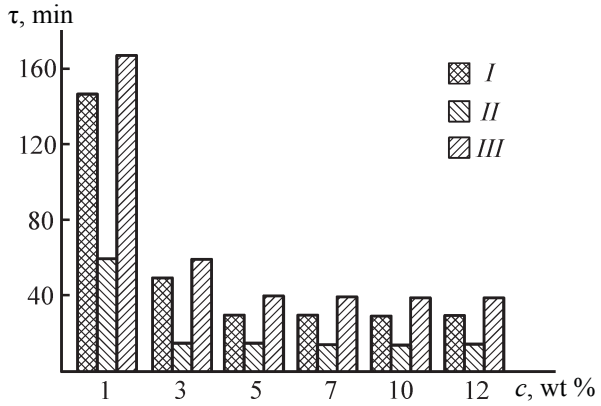

Fig. 6. Time τ of coating drying in relation to the type and amount *c* of a catalyst (20°C/50% rel. hum.). (*I*) Tyzor BTP, (*II*) Tyzor PITA, and (*III*) Tyzor AA-75.

to the above phases. According to the XPA data, the composite of the Zn–Al–talc–resin system thermally treated at 600°C contains Zn, Al, Al_2O_3, ZnO, and $Mg_3Si_4O_{10}(OH)_2$, and that treated at 700°C, Zn, Al, Al_2O_3, ZnO, $Mg_3Si_4O_{10}(OH)_2$, and Si.

The heat-resistance paint was prepared in a laboratory dissolver with fixed cutter rotation speed of 900 rpm in a metallic vessel. The paint composite contained, together with resin, zinc, aluminum, and microtalc, also a solvent (solvent naphtha), auxiliary additives (foam extinguisher, aerosol), and curing catalyst. As catalysts served organic titanate of Tyzor AA-75 brand (SuPont), tetra-*n*-butyl titanate of Tyzor BTP brand (DuPont), and a chelate complex of titanium ethyl acetoacetate of Tyzor PITA brand (DuPont), which can catalyze the hydrolysis and condensation of SiOR or SiOH groups to give Si–O–Si bonds. The catalysts were introduced into the paint in the final stage of its preparation.

A visual inspection of the behavior of paints in closed vessels demonstrated that single component compositions are stable during 6 months (the whole observation period).

Samples of 08 kp steel substrates were preliminarily degreased with *R*% solvent and cleaned by the blast method in conformity with the Swedish standard Sa 2.5. The roughness of the cleaned surface was within the range 25–75 μm. The paint was applied to a substrate by the air atomization method.

Our study demonstrated that the time of physical drying of the coatings to the unstuck extent (grade 3) at a temperature of 20 ± 2°C depends on the type and content of a catalyst (Fig. 6). It can be seen in Fig. 6 that, in the presence of Tyzor PITA catalyst, coatings dry up faster as compared with the presence of other catalysts.

Properties of test coatings

Parameter	Value
Coating color	Silvery
Coating adhesion, points, not more than	1
Thermal stress: from 20 to 600°C in 4 h and keeping at 60°C for 2 h	No damage
Coating adhesion after the thermal stress, points, not more than	1–2
Coating resistance to static treatment with fluids at 20°C, not less than:	
water	300
3% NaCl solution	100
industrial oil	150

For example, the time of coating drying to the unstuck state is 15 min at a Tyzor PITA content of 3 wt %, 30 min with 5 wt % Tyzor BTP, and 40 min with 7 wt % Tyzor AA-75. An excess amount of the catalyst results in that more brittle coatings with poorer adhesive properties are formed.

The physicomechanical properties of coatings in the presence of Tyzor PITA are listed in the table.

CONCLUSIONS

(1) The oxidation of zinc particles starts after the temperature of 330°C is reached, with their oxidation becoming substantially slower in the presence of Silres MSE 100 resin. At temperatures in the range 600–900°C, two processes are observed: decomposition of the resin and slight oxidation of zinc particles.

(2) The oxidation of aluminum particles begins at 560°C in the Zn–Al–resin system and at 580°C in the Zn–Al–talc–resin system.

(3) The drying rate of the coatings depends on the type and content of a catalyst, which makes it possible to obtain compositions optimally adapted for the desired drying duration.

(4) The composition of heat-resistant zinc-aluminum paint is suggested.

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