

Effect of Adding Phosphorus-Containing Surfactants on the Properties of Organosilicon Compositions

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Abstract—We report the results of studying the effect of phosphorus-containing compounds, tetraethyl-diamino-*tert*-butyl phosphite and diethyl phosphite, on organosilicon compositions based on polyphenylsiloxane resin. The addition of these compounds in the composition improves the dispersion of aluminum dust, wettability of the aluminum/steel substrates by the organosilicon composition, and the gloss and surface roughness of the coatings. In the compositions with the maximum disaggregation factor of the pigment particles, the gloss is enhanced by 5% and the coating roughness is decreased by 40%.

Keywords: organosilicon enamels, polyphenylsiloxane, organic coatings, phosphorus-containing additives, surfactants, dispersion, wetting, coating gloss, and roughness

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INTRODUCTION

Organosilicon coating materials share the positive properties of both organic and inorganic compounds and thus are promising for designing novel coatings. One of the most economically sound methods to improve the quality of coating materials is to add surfactants to them [1]. Polyester, alkyd, and nitrogen-containing compounds are the substances conventionally used as surfactants in organosilicon enamels [2]. The effects of various phosphorus-containing organic compounds (PCOCs) on the properties of organosilicon materials, and phosphorus-containing bismaleimide [3], tris(trimethylsilyl) phosphite [4], and biphenyl phosphate [5] in particular, have recently been studied. In this respect, it was reasonable to evaluate the potential effect of PCOC as a surfactant in organosilicon coating materials.

EXPERIMENTAL

Materials used. KO-85 polyphenylsiloxane lacquer, further referred to as PPS (GOST (State Standard) 11066-74), was employed as a film-forming agent (Fig. 1a). Toluene (GOST 14710-78) was used as a solvent. Aluminum dust of PAP-2 grade (GOST 5494-71) was employed as a pigment. Two varieties of PCOC, tetraethyl-diamino-*tert*-butyl phosphite (TABP) and diethyl phosphite (DEP), were used as surfactants; their structural formulas are shown in Figs. 1a, 1b, and 1c.

These PCOCs were selected to be applied as surfactants because their molecules are diphilic. In addition, these compounds were first synthesized at the

Organic Chemistry Department of Karaganda State University; thus, we have made an attempt to find practical applications for them.

Experimental procedure. The effects of PCOCs on organosilicon compositions were evaluated according to the wettability and dispersing ability (in suspensions) and their influence on coating gloss and roughness.

Computer-controlled optical microscopy was the method employed to quantify the dispersing effect as it allows us to directly measure the changes in the linear size of the dispersions. Computer-controlled optical microscopy was carried out using a COM1 instrument. The specimen preparation procedure was tested using the reference samples. Calibration of the COM1 instrument using the standardized samples showed that the relative measurement error was $\leq 1.3\%$.

The PCOC content was varied from 0 to 2 g/dm³. Suspensions of coating materials were prepared at $(20 \pm 2)^\circ\text{C}$ in an airtight reactor (volume, 0.2 ± 0.01 dm³; packing factor, 0.60) equipped with a propeller agitator (rotational frequency, 300 min⁻¹). KO-85 lacquer (8.65 g) was diluted with toluene (1 g); preset amounts of PCOC and aluminum dust (0.35 g) were subsequently added. The mixture was thoroughly agitated for 30 min and the samples were collected using a pneumodosimeter (droplet volume, 0.02 mL). The samples, lying between the microscope slide and the cover slip, were exposed to static load ($P = 15$ g/cm²) during 1 min and then subjected to computer-assisted micro-optical scanning. The development of disaggregation processes was controlled according to the

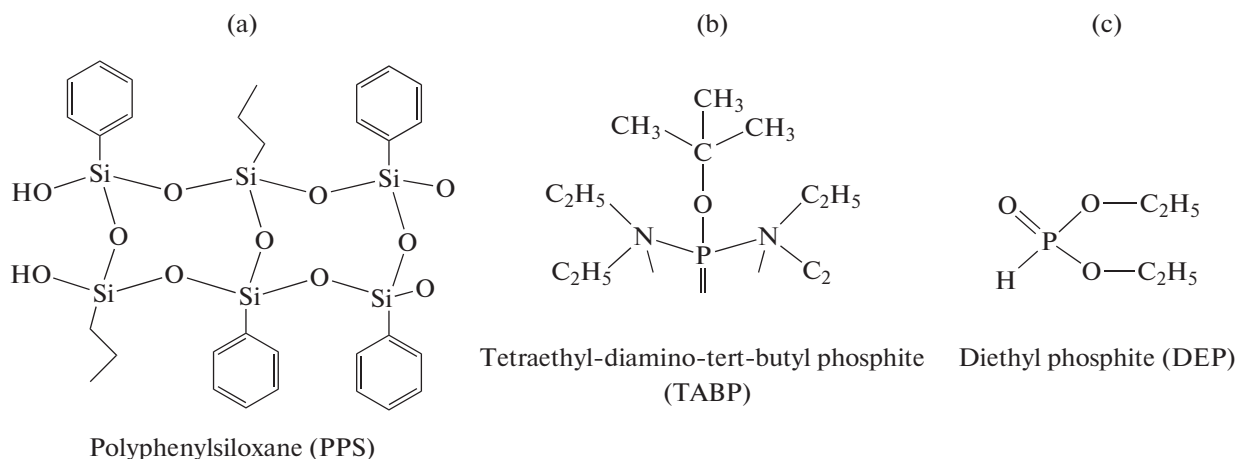


Fig. 1. Chemical formulas of compounds used.

changes in the average diameter of the particles' pigment (d_{av}).

The wettability of PCOCs was studied on aluminum (aluminum alloy of A85 grade, GOST 11069) or steel (steel plates of 08 kp grade, GOST 1050) substrates. The surface tension was measured at the polyphenylsiloxane/water solution ($\delta_{liq-liq}$, mJ/m²) and polyphenylsiloxane/air solution ($\delta_{liq-gas}$, mJ/m²) interfaces on an apparatus designed by Rebinder in the static mode using the maximum bubble pressure method [6]. The contact angles at the polyphenylsiloxane solution/aluminum/water interface (θ , °) and the polyphenylsiloxane solution/steel/water interface (θ , °) were determined using the method of selective wetting with a droplet projection under isothermal conditions at 298°K (on a classroom projector) [6]. No wetting hysteresis was observed as a droplet was kept for 30 min prior to measurements. The droplet

volume was the same (0.02 mL). The procedure for measuring the contact angles was tested using the reference objects. The contact angles for wetting the PTFE/steel/aluminum with water and toluene were measured; the resulting values were consistent with the published data; the relative measurement error was $\leq 1\%$.

The coating gloss was determined according to the ISO Standards 2813:1994 on an FB-2 gloss meter. The roughness of the coating materials was measured on a MIS-11 microscope according to the standardized procedure. The coating materials were applied and tested according to GOST 11066-74 for the following parameters: film appearance, dry-to-touch time (τ , h), hardness (x , arb. units), gloss (%), and roughness of the coatings (R_z).

RESULTS AND DISCUSSION

Studying the dispersing activity of PCOCs. Addition of PCOCs in the compositions improves pigment dispersion. The most significant pigment disaggregation is observed when the PCOC content is 0.25 g/dm³ (Fig. 2).

Aggregation of the particles' pigment was observed at the PCOC content in the composition being higher than 0.25 g/dm³ (Fig. 2). As the exposure duration of the suspensions and solvent content in them were increased, the aggregation of the particles developed further.

Studying the surface and wetting activities of PCOCs. Addition of PCOCs to the compositions reduces the surface tension at the PPS solution/air and PPS solution/water interfaces. Solutions with the PCOC content of 0.25–0.5 g/dm³ typically have the minimal surface tension.

The addition of PCOC to polyphenylsiloxane compositions enhances their wettability on aluminum/steel substrates. At TABP content of 2 g/dm³ in a 30% solution of PPS (commercial lacquer), the contact angles for wetting the aluminum and steel sub-

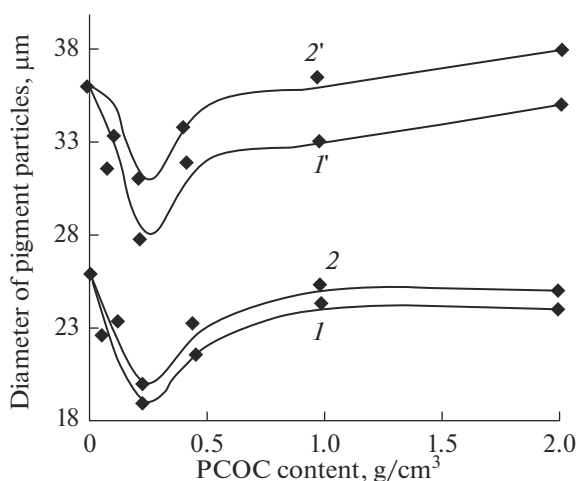


Fig. 2. Effect of PCOCs on diameter of pigment particles: (1) TABP; (2) DEP (at 10% solvent content); (1') TABP; (2') DEP (at 50% solvent content).

strates with water decreased by 16° and 31°, respectively. The interphase layer that was formed in the presence of PCOC allegedly possesses a much lower hydrophobicity.

Work of wetting (W_{wet}) is the measure that can be used to quantify changes in the interaction between the solid surface and the wetting liquid as the surfactant is adsorbed. The work of wetting is defined as the difference $\delta_{\text{s-liq}_1} - \delta_{\text{s-liq}_2}$; in accordance with Young's equation it can be calculated as

$$W_{\text{wet}} = \delta_{\text{liq}_1\text{liq}_2} \cos\theta. \quad (1)$$

The roughness (Ra) of the surface of the steel/aluminum substrate was 0.01 μm ($R_z = 0.05 \mu\text{m}$) and was not taken into account when calculating the work of wetting using Eq. (1). The change in the work of wetting ΔW_{wet} was the measure quantitatively characterizing the effect of surfactant adsorption on the surface tension at the liquid/solid interface. This change in the work of wetting was determined using formula (2):

$$\Delta W_{\text{wet}} = W_{\text{wet, surfactant}} - W_{\text{wet}}. \quad (2)$$

Table 1 shows the changes in the work of wetting in a 30% PPS solution after PCOC was added.

Of the two PCOCs studied, the greatest change in the work of wetting was observed for TABP.

Studying the intermolecular interactions in the solution by dielectrometry and viscometry. In order to measure the dielectric characteristics and viscosity, the as-prepared PCOC solutions were kept at 298 K for 24 h. The dynamic viscosity of the solutions was measured with a VPZh-1 capillary viscometer ($d = 0.56 \text{ mm}$) upon thermostating at 298 K; the relative measurement inaccuracy was $\leq 1.5\%$ [6]. The orientation and deformation polarizations were recorded according to the periods of charging or discharging of the capacity sensor by stable current at a frequency of 10 kHz on a PDE-1-100 instrument. The experimental values of permittivity (ϵ') and the dielectric loss tangent ($\tan\delta$) were used to determine the coefficient of dipole-segmental losses ϵ'' ($\epsilon'' = \epsilon' \times \tan\delta$), which rises with the increasing molecular mobility of the polymers. The relative measurement error is $\leq 1.2\%$.

The addition of PCOCs to PPS solutions reduces the coefficient of dipole-segmental losses (ϵ'') from 22.5 to 10 (for 1 g/dm^3 TABP). The fact that the dynamic viscosity of the solutions increases from 17.3 to 17.6 (for 1 g/dm^3 TABP) also suggests that the molecular mobility of the chains of polyphenylsiloxanes was reduced.

Effect of PCOCs on the quality of the coating material. No effects of PCOC were revealed as the coating material was drying. The curing time of the coating in the presence of PCOC, according to GOST 19007-73, remained at the normal level (2 h, GOST 11066-74). The addition of PCOC reduced the hardness of the baked coating material (3 h at $350 \pm 5^\circ\text{C}$) with respect to the reference sample. For TABP, this decrease was 0.05 arb. units; for DEP, it was 0.1 arb. units. This

Table 1. Effect of PCOC content on changes in work of wetting of aluminum substrate with 30% PPS solution (ΔW_{wet} , mJ/m^2)

Surfactant type	PCOC content in composition, g/dm^3				
	0	0.25	0.5	1	2
DEP	—	0.7	4	6	6.4
TABP	—	6	6	6.1	7.4

effect was not revealed for the cold-setting coatings (24 h at $20 \pm 5^\circ\text{C}$). The addition of PCOC enhanced the gloss by 5% and reduced the surface roughness of the coating material by 40% (from 5 to 3 μm).

CONCLUSIONS

The studied PCOCs enhanced the pigment dispersion. TABP was the most efficient dispersing agent. The maximum dispersing activity of PCOC was achieved when its content in the composition was $\sim 0.25 \text{ g/dm}^3$.

PCOCs added to the composition reduced the hydrophobicity of aluminum and steel substrates. TABP was the most efficient wetting additive for commercial lacquer (a 30% solution of PPS).

The addition of PCOCs enhanced the gloss and surface roughness of the coating materials. In the compositions with the maximum disaggregation of the pigment's particles, the gloss increased by 5% and the surface roughness was reduced by 40%.

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