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OBTAINING HOLLOW GLASS MICROSPHERES AND THEIR USE IN THE PRODUCTION OF WATER-DISPERSION COATINGS

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The results of obtaining hollow glass microspheres and their effect on the properties of water-dispersion facade coatings when the titanium oxide and calcium carbonate in the formula are replaced by an equivalent volumetric number of spheres are presented.

Key words: hollow glass microspheres, lacquers, paints, titanium oxide, calcium carbonate.

Hollow glass microspheres (HGM) are fine free-flowing powders consisting of thin-walled (0.5 – 2.0 μm) spherical glass particles with diameter 10 – 200 μm or more. In most cases the most important characteristics are the weight characteristics of HGM — the actual and apparent (bulk) density, which vary as a function of the HGM brand in the range 80 – 700 and 70 – 400 kg/m^3 , respectively. The moisture content of the powders, as a rule, does not exceed 0.5%. The basic characteristics of HGM produced by the leading manufacturers are presented in Table 1.

The unique combination of the spherical shape, controlled parameters, low density, relatively high strength under uniform compression, sound insulation, and dielectric properties make HGM some of the most important technogenic fillers for polymer materials [1 – 6]. By using HGM it is possible not only to greatly modify the thermophysical properties of composites but also to improve the technological conditions of processing polymers — reduce shrinkage and viscosity of filled polymer composites, guarantee dimensional stability of molded parts, and reduce the wear of molding equipment.

Hollow glass microspheres have proven to be highly effective fillers for lacquers and paints, making it possible to improve the physico-mechanical properties of coatings on account of their capacity to scatter light in different media

because of the refractive index difference between the air in the microspheres and the medium in which the microspheres are distributed [7, 8]. So, most ordinary fillers in the coating industry (talc, calcium carbonate, and others) are characterized by a high thermal conductivity compared with HGM. For example, the thermal conductivity of S22 microspheres is equal to 0.07 $\text{W}/(\text{m} \cdot \text{K})$, which is 55 times lower than the thermal conductivity of CaCO_3 (3.89 $\text{W}/(\text{m} \cdot \text{K})$). On the other hand the replacement of a small amount of titanium oxide as a light-reflecting high-coverage pigment by HGM reduces its amount, which in turn lowers the production cost of the article. It is also necessary to take account of the fact that the density of HGM is 15 – 20 times lower than that of TiO_2 — 0.22 versus 4.1 g/cm^3 .

Even though the cost of HGM is relatively high compared with other types of fillers, the use of HGM nevertheless is economically beneficial, since even small additions (5 – 20% by volume) into the composite material result not only in savings of an expensive raw material but also impart new properties to the fabricated materials. The steady growth in the use of HGM in different industries and forecast data clearly demonstrate the indisputable promise of hollow glass microspheres in the coating industry [7, 8].

The choice of glass composition for obtaining HGM is determined by the method used to obtain glass microspheres as well as by the conditions of the subsequent processing of the spheres and the properties of the articles fabricated on their basis. The main condition is that during synthesis of the glass a definite amount of compounds capable of undergoing

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TABLE 1. Basic Characteristics of HGM from Leading Manufacturers

Manufacturer, trademark	HGM properties			
	Average size, μm	Apparent density, g/cm^3	Real density, g/cm^3	Thermal conductivity, $\text{W}/(\text{m} \cdot \text{K})$
Emerson and Cuming (USA) Minnesota, Mining and Manufacturing Company (3M Company) (USA)	30 – 80	0.14 – 0.19	0.22 – 0.38	0.08 – 0.10
Graverbel (Belgium)	30 – 60	0.09 – 0.37	0.15 – 0.38	0.029 – 0.115
PQ Corp., Q-Cel (USA)	45 – 60	0.14 – 0.19	0.23 – 0.35	–
PA Industries (USA)	65 – 75	0.11	0.20 – 0.21	0.04
Fillite Ltd (Great Britain)	90	–	0.31 – 0.40	0.04
	150	0.18 – 0.45	0.7	0.09

decomposition with gas evolution must be kept in the melt during heat-treatment. Of greatest interest from the standpoint of the possible solubility in the molten glass without decomposition are sulfates, specifically Na_2SO_4 , whose melting temperature without decomposition is equal to 884°C and which possesses the capability of mixing in definite quantities with the melt of silicate glass during its synthesis. The decomposition temperature of pure sodium sulfate is equal to $1200 - 1220^\circ\text{C}$, but in the high-viscosity medium of silicate melt (especially in the presence of oxidizer, for example, potassium nitrate) it can rise to $1400 - 1440^\circ\text{C}$ and higher. This feature of the behavior of sodium sulfate in silicate melts makes it possible to obtain melts of silicon borate glasses at temperatures below 1400°C and maintain non-decomposing fused sodium sulfate in the melt.

The behavior of Na_2SO_4 in silicate melts was examined in detail in our works [9, 10]. The silicate-glass compositions for obtaining HGM must be quite easily fusible with synthesis temperatures no higher than $1350 - 1380^\circ\text{C}$. Such low fusibility in silicate glasses guarantees high content of oxides of alkali and alkaline-earth metals as well as the presence of B_2O_3 in the makeup. For this reason glasses in the alkali-borosilicate systems are the first choice as a base for obtaining HGM. The range of glass compositions recommended in

the literature for obtaining HGM is ordinarily quite wide (Table 2).

We have developed and investigated glasses in the glass forming system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{ZnO}-\text{SiO}_2-\text{B}_2\text{O}_3$ [18, 19]. Finely ground powder of granulated glass with particle size not exceeding $50 \mu\text{m}$ was used to fabricate hollow glass microspheres. The hollow glass microspheres were formed using a plasma setup in the electric-arc plasma laboratory at the A. V. Lykov Institute of Heat and Mass Transfer. The hollow microspheres were separated from defective particles by means of flotation in water. Microspheres with sizes $20 - 100 \mu\text{m}$, average diameter $75 \mu\text{m}$, and wall thickness $1 - 2 \mu\text{m}$ were obtained (Fig. 1). The bulk density of the dried microspheres is equal to $0.107 - 0.252 \text{ g}/\text{cm}^3$ and the thermal conductivity $0.05 - 0.07 \text{ W}/(\text{m} \cdot \text{K})$. Hollow glass microspheres comprise light-reflecting high-coverage pigments that can be used in the fabrication of water-dispersion coating materials.

In the present work the formula for the facade water-dispersion paints was as follows (weight content, %): 24.91 water; 24.0 calcium carbonate; 15.0 fine chalk; 12.0 titanium dioxide; 20.0 dispersion; 1.5 ethylene glycol; 0.55 thickening agent; 1.06 including in sum an ammonia solution, dispers-

TABLE 2. Chemical Compositions of Glasses for Producing HGM

Manufacturer	Weight contents of glass composition, %								Source
	SiO_2	B_2O_3	Na_2O	CaO	ZnO	$\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3^*$	F	S	
3M Company (USA)	60 – 90	1 – 30	2 – 20	0 – 25	–	0 – 10	0 – 5	0.005	[11]
	72.2	–	$14.2 + 0.2 \text{ K}_2\text{O}$	$8.8 + 3.3 \text{ MgO}$	–	1.2*	–	–	[12]
Saint-Gobain Vitrage (France)	68	5.9	13.85	6.8	0.95	2.5	–	0.77	[13]
	55 – 80	5 – 15	11 – 16	0.1 – 3.0	1 – 5	3 – 8*	0 – 5	0.3 – 0.8	[14]
	72	7	18.8	–	–	1.0*	–	1.2	[15]
Nippon Sheet Glass Co (Japan)	68.4	10.3	19.4	–	0.94	–	–	0.82	[16]
Tokai Kogyo Co (Ja- pan)	60 – 80	6 – 15	2.0 – 12.5 0 – 3 K_2O	5 – 15 0 – 3 MgO	0 – 3	0 – 3 0 – 3*	–	0.05 – 1.00	[17]

* Content of Al_2O_3 .

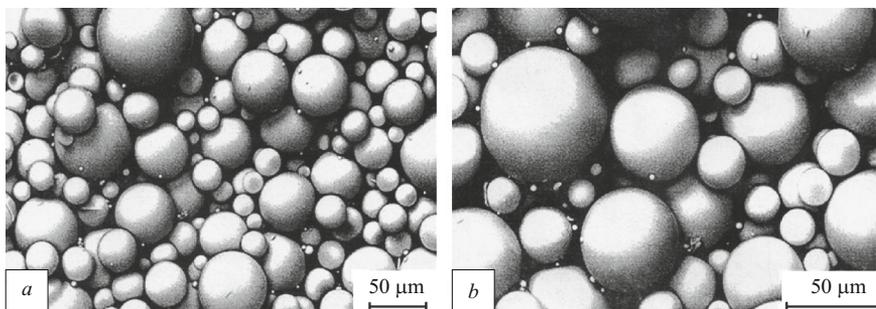


Fig. 1. Electron microscopic photographs of experimentally obtained hollow glass microspheres: $\times 300$ (a) and $\times 500$ (b).

ing agent, foam suppressor, coalescent, and preservative; components such as TiO_2 (1st series) and CaCO_3 (2nd series) in amounts 3.0, 6.0, 9.0% were replaced by an equivalent volume of the obtained hollow glass microspheres.

The amount of HGM introduced into the paint composition was determined using the following formulas:

$$\begin{aligned}\varphi(\text{TiO}_2) &= \omega(\text{TiO}_2)/\rho(\text{TiO}_2); \\ \varphi(\text{CaCO}_3) &= \omega(\text{CaCO}_3)/\rho(\text{CaCO}_3); \\ \omega(\text{HGM}) &= \varphi(\text{TiO}_2)/\rho(\text{TiO}_2); \\ \omega(\text{HGM}) &= \varphi(\text{CaCO}_3)/\rho(\text{CaCO}_3),\end{aligned}$$

where φ is the volume fraction of the components; ω is the mass fraction of the components; and, ρ is the density of the corresponding substance, g/cm^3 .

The water-dispersion coating material was fabricated by means of the standard procedure. Adherence to the rate regimes of the work, time intervals, and introduction sequence of the components is strictly mandatory in order to avoid the production of rejected coating product and destruction of the hollow glass microspheres. The properties of the coatings obtained by substituting HGM for titanium dioxide and calcium carbonate (the measurements were performed according to GOST specifications for each index) are presented in Table 3.

It was determined that indicators such as adhesion and resistance to standing water are not degraded upon replacement of titanium dioxide and calcium carbonate by HGM. In addition, the dry residue and density of the coating decrease (Fig. 2a), which has a positive impact on the consumption and cost of the coating material. Coatings containing microspheres are more hydrophobic than the corresponding standard coating. The addition of microspheres results in a reduction of water absorption (Fig. 2b) and thereby slows down the rate of destruction of the coating. However, the use of hollow glass microspheres makes it impossible to replace TiO_2 in large amounts. So, the coverage of the dried film increases by 35% upon replacement of 3 wt.% TiO_2 by microspheres and by 8% with 6% replacement of TiO_2 . For TiO_2 weight content $< 3\%$ in the water-dispersion coating the coating coverage sharply decreases, but it increases upon replacement CaCO_3 by HGM, irrespective of the amount.

Most pigments and fillers used in the coating materials possess high thermal conductivity compared with HGM. So,

the thermal conductivity is $6.7 \text{ W}/(\text{m} \cdot \text{K})$ in titanium dioxide and $3.8 \text{ W}/(\text{m} \cdot \text{K})$ in calcium carbonate. The data obtained in thermal conductivity tests of the coatings varied within the range of measurement error $0.207 - 0.225 \text{ W}/(\text{m} \cdot \text{K})$. This is due to the fact that in the case of hand the substrate thickness is 100 times greater than the coating thickness, so that the contribution made by the coating and the measurement of the thermal conductivity of a coated sample was very small.

Hollow glass microspheres are recommended for use in the production of heat-insulation paints and underpaint put-

TABLE 3. Properties of Water-Dispersion Coatings Containing Hollow Glass Microspheres

Index	Weight content of microspheres in coating makeup, %			
	0.00	0.14	0.28	0.43
Coating color and appearance	White film with even, uniform, mat surface			
Mass fraction of non-volatile substances, %, not less than, upon replacement of:				
TiO_2	61.12	56.14	54.95	51.89
CaCO_3		53.47	47.12	38.62
Density, g/cm^3 , upon replacement of:				
TiO_2	1.47	1.45	1.42	1.31
CaCO_3		1.34	1.15	1.13
Coating pH		8 – 9		
Drying time to degree 3 at temperature $(20 \pm 2)^\circ\text{C}$, h, not more than		1.0		
Degree of wear, mm, not more than		60.0		
Coverage of dried film, g/m^2 , not more than, upon replacement of:				
TiO_2	180	115	165	100
CaCO_3		134	105	104
Adhesion, MPa, not less than		1.0		
Film resistance to standing water $(20 \pm 2)^\circ\text{C}$, h, not less than		24.0		
Water absorption, %, upon replacement of:				
TiO_2	1.73	1.73	1.31	1.12
CaCO_3		1.34	1.25	1.01

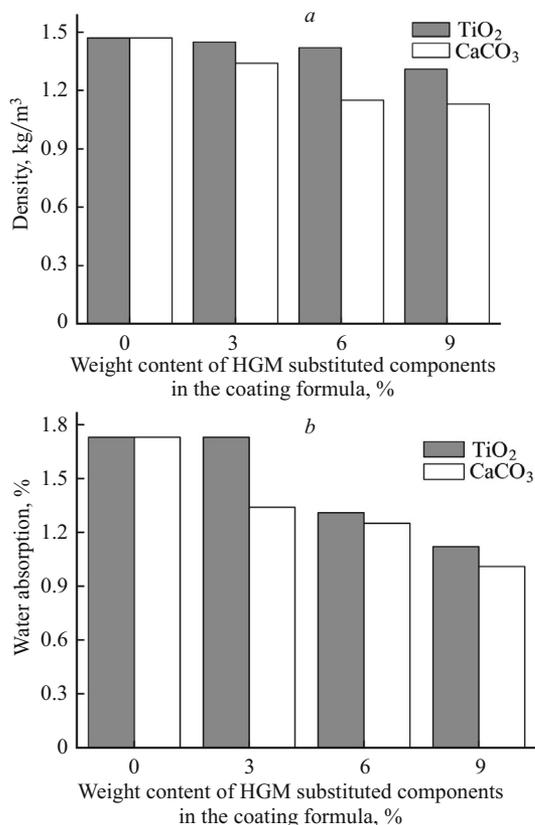


Fig. 2. Change of density (a) and water absorption (b) of lacquer-paint coatings upon replacement of titanium dioxide and calcium carbonate by hollow glass microspheres.

ties. The volume fraction of glass microspheres in the formula for heat-saving paints must be quite high, reaching 50% by volume.

Thus, it can be concluded on the basis of these studies that the use of hollow glass microspheres in the production of water-dispersion paints is of practical interest.

The partial replacement of TiO₂ by glass microspheres lowers the cost of lacquer paint materials and at the same time improves individual characteristics of coatings. Specifically, it increases the coating coverage and decreases the density of the paint.

The replacement of calcium carbonate by HGM significantly increases the coverage of lacquer-paint material and decreases density, which makes it possible to decrease paint consumption by 1 m².

The introduction of hollow glass microspheres into the formula for water-dispersion paints increases the hydrophobicity of the coating, which decreases water absorption and slows down the rate of destruction of the paint.

If calcium carbonate is used as the filler in heat-insulation coating materials, it is recommended that all of it (by volume) be replaced by glass microspheres, because most of the ordinary fillers used in coating materials have high thermal conductivity compared with hollow glass microspheres.

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