PERIÓDICO TCHÊ QUÍMICA
ARTIGO ORIGINAL

ESTUDO DE REVESTIMENTOS ISOLANTES TÉRMICOS LÍQUIDOS PARA ECONOMIZAR ENERGIA COM BASE EM SISTEMAS LOCAIS FINAMENTE DISPERSOS

STUDY OF ENERGY-SAVING LIQUID THERMAL INSULATING COATINGS BASED ON LOCAL FINELY DISPERSED SYSTEMS

ИССЛЕДОВАНИЕ ЭНЕРГОСБЕРЕГАЮЩИХ ЖИДКИХ ТЕПЛОИЗОЛЯЦИОННЫХ ПОКРЫТИЙ НА ОСНОВЕ МЕСТНЫХ ТОНКОДИСПЕРСНЫХ ЗЕРНИСТЫХ СИСТЕМ

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RESUMO

Introdução: Nos últimos anos, na ciência dos materiais de construção, tem havido uma tendência para a introdução ativa de microesferas ocas de vários tipos para modificar as propriedades dos materiais de construção. As microesferas ocas são mais amplamente utilizadas na produção de revestimentos isolantes térmicos líquidos, que reduzem a perda de calor, protegem as estruturas da corrosão e superaquecimento, evitam a formação de condensação, reduzem os custos operacionais e aumentam o tempo entre reparos. **Objetivo**: Avaliar a influência das características estruturais de sistemas granulares nas propriedades de materiais isolantes térmicos. **Métodos**: Propõe-se determinar e avaliar as características estruturais de pós de carga pelo método de espalhamento de raios-X a baixo ângulo. A característica mais importante deste método é analisar a estrutura interna de sistemas desordenados - partículas, espaço de poros, interfaces entre heterogeneidades de substâncias heterogêneas. Ao avaliar a condutividade térmica e a resistência térmica, o método de fluxo de calor estacionário foi usado de acordo com GOST 30290-94. A essência do método é criar um fluxo de calor estacionário que passa por uma amostra plana de uma certa espessura e dirigido perpendicularmente às faces frontais (maiores) da amostra, medindo a densidade desse fluxo de calor, a temperatura das faces frontais opostas e a espessura da amostra. **Resultados e discussões**: O artigo discute os resultados de estudos experimentais que possibilitaram a criação de revestimentos isolantes térmicos líquidos (LTIC) à base de ligantes poliméricos, pós minerais finos e um complexo de aditivos modificadores. Estudos experimentais da estrutura e propriedades de revestimentos de isolamento térmico com base em ligantes de polímero preenchidos confirmam sua superioridade sobre análogos estrangeiros. **Conclusões**: Foi estabelecido que durante a produção de LTIC, suas propriedades de blindagem térmica podem ser reguladas alterando: a pressão, a viscosidade do peso molecular do gás; a porosidade da macroestrutura e aglomerados; a condutividade térmica da fase sólida e gasosa do sistema; o coeficiente de acomodação; número de coordenação; tamanho de partícula primária; dimensão fractal que caracteriza as características topológicas da estrutura das partículas, agregados, glóbulos, aglomerados e sua tendência para dissipar a energia das moléculas de gás.

Palavras-chave: *microssílica, condutividade térmica, diatomita, pós minerais, fuligem branca.*

ABSTRACT

Introduction: In recent years, in building materials science, there has been a tendency for the active introduction of hollow microspheres of various types for modifying the properties of building materials. Hollow microspheres are most widely used in the production of liquid thermal insulating coatings, which reduce heat loss, protect structures from corrosion and overheating, prevent condensation formation, reduce operating costs and increase the time between repairs. **Aim:** Assessment of the influence of the structural characteristics of granular systems on the properties of thermal insulating materials. **Methods:** It is proposed to determine and evaluate the structural characteristics of filler powders by the method of small-angle X-ray scattering. The most important feature of this method is analyzing the internal structure of disordered systems - particles, pore space, interfaces between heterogeneities of heterogeneous substances. When assessing thermal conductivity and thermal resistance, the stationary heat flux method was used following GOST 30290–94. The essence of the method is to create a stationary heat flux passing through a flat sample of a certain thickness and directed perpendicular to the front (largest) faces of the sample, measuring the density of this heat flux, the temperature of the opposite front faces and the thickness of the sample. **Results and Discussion**: The paper discusses the results of experimental studies that make it possible to create liquid thermal insulation coatings (LTIC) based on polymer binders, fine mineral powders, and a complex of modifying additives. Experimental studies of the structure and properties of heat-insulating coatings based on filled polymer binders confirm their superiority over foreign analogs. **Conclusions:** It has been established that during the production of LTIC, their heat-shielding properties can be regulated by changing: pressure, the viscosity of the molecular weight of the gas; porosity of macrostructure and clusters; the thermal conductivity of the solid and gas phase of the system; the coefficient of accommodation; coordination number; primary particle size; fractal dimension characterizing the topological features of the structure of particles, aggregates, globules, clusters and their tendency to dissipate the energy of gas molecules.

Keywords: *microsilica, thermal conductivity, diatomite, mineral powders, white soot.*

АБСТРАКТ

Введение. В последние годы в области строительного материаловедения намечается тенденция активного внедрения полых микросфер различного вида для модификации свойств строительных материалов. Наиболее широкое применение полые микросферы находят при производстве жидких теплоизоляционных покрытий, которые снижают теплопотери, защищают конструкции от коррозии и перегревов, препятствуют образованию конденсата, позволяют снизить эксплуатационные затраты и увеличить срок межремонтной службы. **Цель.** Оценка влияния структурных характеристик зернистых систем на свойства теплоизоляционных материалов. **Методы.** Определение и оценку структурных характеристик порошков наполнителей предлагается выполнять методом малоуглового рентгеновского рассеяния. Важнейшей особенностью данного метода является возможность анализа внутренней структуры разупорядоченных систем – частиц, порового пространства, поверхностей раздела между неоднородностями гетерогенных веществ. При оценке теплопроводности и теплового сопротивления применяли метод стационарного теплового потока в соответствии с ГОСТам. Сущность метода заключается в создании стационарного теплового потока, проходящего через плоский образец определенной толщины и направленного перпендикулярно к лицевым (наибольшим) граням образца, измерении плотности этого теплового потока, температуры противоположных лицевых граней и толщины образца. **Результаты и обсуждение.** В статье рассмотрены результаты экспериментальных исследований, которые позволяют создавать жидких теплоизоляционных покрытий (ЖТП) на основе полимерных связующих, тонкодисперсных минеральных порошков и комплекса модифицирующих добавок. Проведенные экспериментальные исследования структуры и свойств теплоизоляционных покрытий, на основе наполненных полимерных связующих, подтверждают их превосходство над зарубежными аналогами. **Заключение.** Установлено, что при производстве ЖТП их теплозащитные свойства можно регулировать путем изменения: давления, вязкости молекулярного веса газа; пористости макроструктуры и кластеров; теплопроводности твердой и газовой фазы системы; коэффициента аккомодации; координационного числа; размера первичных частиц; фрактальной размерности, характеризующей топологические особенности строения частиц, агрегатов, глобул, кластеров и их склонность к диссипации энергии молекул газа.

Ключевые слова: *микрокремнезем, коэффициент теплопроводности, диатомит, минеральные порошки, белая сажа.*

1. INTRODUCTION:

There is a wide selection of various thermal insulation materials on the construction market. To the already existing and well-proven polystyrene foam, mineral wool heaters, more and more new materials are added, which manufacturers offer to use to consumers in various climatic and building conditions (Danilov V. I., 2014; Selyaev V. P., 2012; Golovanova L. A., 2014).

Relatively recently, some companies began to offer modern ultra-thin liquid composite heat-insulating coatings for insulating house facades, as well as engineering communications. According to the manufacturers themselves, the use of such heat-insulating materials can lead to significant energy savings (Komkov V. A., 2010; Beregovoy A. M., 2008). However, the thermal and physical properties of the presented heat-insulating coatings have not yet been fully studied. Available studies by various authors (Shirinyan V. T., 2007; Golovach Yu. Yu., 2008; Maneshev I. O., 2013; Loginova N. A., 2010) on the determination of the thermal conductivity coefficient of the same types of liquid thermal insulation coatings (LTIC) often show a significant difference.

One of the most important parameters determining the thermal insulation properties of materials based on microstructured mineral powders (silica, diatomite) is thermal conductivity. Knowing some characteristics of dispersed systems, such as the size, thermal conductivity of the material of primary particles, the filling method, and some others, it is possible to theoretically calculate the thermal conductivity of granular systems based on the polystructural theory of Solomatov V.I. (Solomatov V. I., 1991) and the model of. Dulnev G. N. (Dulnev G. N., Zarichnyak Yu. P., 1974).

In this regard, it was decided to conduct experimental studies of the thermal conductivity of liquid heat-insulating coatings to identify their true values and dependence on the composition and properties of the main components.

2. MATERIALS AND METHODS:

2.1.1. Materials and methods for determining the thermal conductivity of LTIC

To study the properties (distribution of inhomogeneities in size, particle size, topography, and shape of nanoobjects) of microdispersed materials were used the small-angle X-ray diffractometer Hecus S3 MICRO.

In the analysis of the internal structure of disordered systems - particles, pore space, interfaces between inhomogeneities of heterogeneous substances, small-angle X-ray scattering was used based on the diffraction method, which is widely used to study highly dispersed powders.

As the scattering coordinate, were used the magnitude of the scattering vector modulus s = 4π sinθ/λ, where 2θ was the scattering angle, λ = 1.5418 Å is the wavelength of the radiation used. The scattering intensities were recorded in the range of s values from 0.0094 to 0.40 Å-1, which made it possible to study inhomogeneities with linear dimensions L ~ (2 π)/S, in the range of 2 to 60 nm.

The methods for determining the coefficient of thermal conductivity of thin-layer heat-insulating coatings given in (Anisimov M. V., 2015; Selyaev V. P. *et al.*, 2018; Khabibullin Yu. Kh., 2015; Pavlov M. V., 2014) in accordance with the following methods based on the following GOSTs for determining the thermal conductivity coefficient. Undoubtedly, when conducting research, it is advisable to use GOST test tools (test tools with methods for each GOST are given below) (GOST 30290–94, 1996; GOST 7076-99, 2000; GOST 28574-90, 1991; GOST 52487-2005 (ISO 3251:2003), 2007) which allows obtaining a reliable, reproducible assessment of the studied characteristics. When assessing thermal conductivity and thermal resistance, the method of stationary heat flux was used accordingly to (GOST 30290–94, 1996; GOST 7076-99, 2000; GOST 28574-90, 1991; GOST 52487-2005 (ISO 3251:2003); 2007).

According to the composition (formulation) of liquid thermal insulation coatings, the following methods were used:

- Determination of thermal conductivity and thermal resistance in the stationary thermal regime of the LTIC following GOST 7076-99.

The essence of the method is to create a stationary heat flux passing through a flat sample of a certain thickness and directed perpendicularly to the front (largest) faces of the LTIC, measuring the density of this heat flux, the temperature of opposite front faces, and the thickness of the sample.

Thermal conductivity was determined on an ITS-1 device after preparing a sample of a rectangular parallelepiped.

The following devices are used to test LTIC:

- for measuring effective thermal conductivity and thermal resistance - ITS-1;
- device for determining the thickness - vernier caliper;
- drying electrical cabinet, - ShS-80-01-SPU up to 200 °C;

- laboratory scales for general purpose - maximum load no more than 1 g, actual scale division from 1 to 0.01 mkg.

Determination of thermal conductivity:

- preliminarily prepared liquid composite heat-insulating coatings were applied to glass with a size of 150×150 and a thickness of 3 mm. The thickness of the applied layers was from 1 to 2-6 mm, ± 0.02-0.03 mm, and drying was carried out within 24 hours to constant weight. On each sample, presetting the thickness from 1 to 6 mm, the heat flux density, thermal resistance, and thermal conductivity coefficient were determined for the ITS-1 devices. According to the ITS-1 device, the surface of the heater and refrigerator plates are made of metal. The deviation from the flatness of the working surfaces should be no more than 0.025% of their maximum linear size.

- Thermal conductivity of LTIC in accordance with GOST 30290–94.

This method applies to building materials and products with thermal conductivity from 0.02 to 1 W/m·K and establishes a method for non-destructive accelerated determination of thermal conductivity in the temperature range 278-313 K (5-40 °C).

The method consists of creating a one-sided short-term heat pulse on the surface of the product and recording the temperature change on this surface.

The tests were carried out with a steady thermal equilibrium between the investigated LTIC, the body of the primary transducer, and the environment, for which the primary transducer was installed on the surface of the LTIC prepared for testing following this GOST 30290–94, and held until steady readings appeared on the display of the second measuring device.

The following devices are used to test LTIC:

- thermocouple;
- voltmeter;
- device for determining the thickness - vernier caliper;
- drying electrical cabinet, - ShS-80-01-SPU up to 200 ° C;
- laboratory scales for general purpose - maximum load no more than 1 g, actual scale division from 1 to 0.01 mkg.

Determination of thermal conductivity:

- preliminarily prepared liquid composite heat-insulating coatings, as in GOST 7076-99, were applied to glass with a size of 150 × 150 and a thickness of 3 mm (samples must have a flat surface to accommodate the primary converter and ensure thermal contact between them). The thickness of the applied layers was from 1 to 2-6 mm, ± 0.02-0.03 mm, and drying was carried out within 24 hours to constant weight.

For testing thermal conductivity, a measuring complex is used: a primary transducer designed to convert a pulse of electrical energy into thermal energy and create an electrical signal characterizing the change in the surface temperature of LTIC product under the influence of a thermal pulse and a secondary meter for recording an electrical signal.

The used GOST 30290–94 is not the main one, but rather auxiliary and comparative.

- Adhesion of protective coatings for LTIC following GOST 28574-90.

When testing the adhesion of coatings in laboratory conditions, on each type of element of the protected structure, five places were selected at a distance of at least 300 mm from one another, and metal disks were glued to the coating in accordance with GOST.

The essence of the method consists in measuring the force required to detach the coating from the protected concrete surface in the direction perpendicular to the plane of the coating using a glued metal disk and a dynamometer.

The following devices and apparatuses are used to test LTIC:

- press for testing materials in tension with a maximum force of 10000 N;
- a device for cutting paint and varnish coatings near glued metal discs;
- organic solvents according to the materials for the test coatings;
- drying electrical cabinet, - ShS-80-01-SPU up to 200 °C;
- laboratory scales for general use - maximum load no more than 1 g, actual scale division from 1 to 0.01 mkg;
- metal spatula;
- metal (wire) and hairbrush;
- sandpaper for dry sanding.

Determination of adhesion of LTIC:

Preliminarily prepared metal discs 25 mm high and 20 or 50.6 mm in diameter with a hinge for transferring tensile forces and plates with dimensions of 100x100 mm and a thickness of at least 40 mm, made of cement-sand mortar composition. On the surface of the slabs, a layer of LTIC from 1 to 2-6 mm, ± 0.02-0.03 mm is applied and dried within 24 hours to constant weight. At the end of the holding (drying) period, metal disks are glued to the LTIC coating of the samples. Determination of the adhesion of coatings to the surface of the structure is carried out at the end of the period of complete curing of the adhesive by tearing the metal discs from the plate.

- Mass fraction of non-volatile substances according to GOST 52487-2005.

The essence of the method consists in drying a cup with LTIC in an oven at a temperature of 80 °C, a heating time of 60 minutes, and determination of the mass of the dry residue on the cup according to GOST.

The following devices and apparatuses are used to test the LTIC:

- a flat-bottomed cup made of metal or glass with a diameter of (75 ± 5) mm and a side height of at least 5 mm;
- drying electrical cabinet ShS-80-01-SPU up to 200 °C;
- analytical balance with weighing accuracy up to 0.1 mg;
- a desiccator with a suitable desiccant such as dry silica gel.

Determination of the mass fraction of non-volatile substances of LTIC:

According to GOST 52487-2005, the dish was degreased and cleaned; the mass of a clean, dry dish (m_0) was determined with an accuracy of 1 mg. Then, the LTIC for testing was weighed to an accuracy of 1 mg in a dish (m_1) and evenly distributed over the bottom using a tared metal wire. After weighing, the cup (m_1) was placed in an oven preheated to a predetermined temperature, and the cup was kept in the cupboard for a predetermined heating time. At the end of the heating time, the dish was transferred to a desiccator and cooled to room temperature, and the (m_2) dish with the residue was determined to the nearest 1 mg. The mass fraction of non-volatile substances *NV*, %, was determined using the following Equation 1:

$$NV = \frac{(m_2 - m_0)}{(m_1 - m_0)}100 \quad \text{(Eq.1)}$$

2.1.2. Prediction of thermal conductivity and assessment of the influence of the structural characteristics of granular systems on the properties of thermal insulation materials

The features of structural heterogeneities of microsilica (Maneshev I. O., 2013; Dombrovsky L. A., 2005; Selyaev V. P., 2012) and natural diatomite of the Utesai deposit, as well as a powder-filler of a vacuum insulating panel, were investigated using the method of small-angle X-ray scattering.

The experimental material was obtained in the form of small-angle X-ray scattering indicatrices for all investigated dispersed powders. As the scattering coordinate, we used the magnitude of the scattering vector s = 4π sinθ/λ, where 2θ is the scattering angle, λ=1.5418 Å is the wavelength of the radiation used. Scattering intensities were recorded in the range of s values from 0,0094 till 0,40 $Å^{-1}$, which made it possible to study inhomogeneities with linear dimensions L ~ $\frac{2\pi}{s}$, within 2 ... 60 nm. In Figure 1 shows the experimental small-angle X-ray scattering curves of the natural diatomite of the Utesay field and the filler powder of the insulating panel. The scattering indicatrices of the other three microsilica are similar to the small-angle X-ray scattering curve.

It was used the China city method (Selyaev V. P., 2012), the small-angle X-ray scattering curves were rearranged into the coordinates $\ln I(s) - s^2$ of the dependences shown in Figure 2. Pore size distribution curves for dispersed microsilica have pronounced maxima; a similar natural diatomite function is bimodal. Table 1 shows the results of the analysis of distribution curves - the maxima of the distribution functions d_B; average values of linear dimensions of scattering inhomogeneities <d>; variances of distribution functions Δd.

The fractal characteristics of all studied materials are shown in Table 2.

Dispersed microsilica obtained from natural diatomite, and natural diatomite, has three types of scattering inhomogeneities, two of which are mass fractals with dimensions D = 2.32 and D = 2.13. The scale of such objects is d = 4 ÷ 8 nm. Small-scale pores d = 8-40 nm have rather heavily indented interfaces with fractal dimensions (D_S = 6-α = 2.64). Condensed silica fume (production waste) does not have X-ray scattering inhomogeneities attributed to mass fractals. The surfaces of SiO_2 particles - pores have a fractal dimension D_S = 2.40. White soot contains fractal clusters of pore space with linear dimensions of 4 - 25 nm. The interface surfaces of larger scattering formations (25-40 nm) are strongly indented - their fractal dimension is D_S = 2.83. The scattering curve $\lg I(s)$ $\lg s$ of the filler powder has two crossover points: branched porous aggregates with dimensions of 20-40 nm have a fractal dimension D = 2.59, and irregularities on a scale of 12-20 nm have a highly irregular surface c D_S = 2.70. Also, the data of small-angle X-ray scattering allow us to suggest that on the surface of the smallest elements of the structure of the filler powder (4-12 nm), layers of scattering inhomogeneities with a lower electron density than that of silicon dioxide (parameter α=4.10) are possible.

2.1.3 A fractal model of heat transfer and the main parameters of a granular system affecting the thermal conductivity of a liquid thermal insulating coating (LTIC) product

The heat transfer mechanism in granular, porous systems is rather complicated since heat transfer occurs in a multiphase material.

Heat transfer in LTIC can be carried out from one solid particle to another (inductive component–λ_1). In this case, thermal conductivity will depend on: the chemical and elemental composition of the material; particle size distribution; surface topology - the presence of inhomogeneities, defects on the surface; the number of touches, and the area of contact between the particles.

It has been experimentally established that in the process of condensation in a colloidal solution from particles of silicon oxide, which have a size of 1/3 nm and are nuclei, particles with a size of 5/7 nm grow.

After that, the aggregation of particles begins, and the formation of globules with a size of 20-40 nm, from which clusters of a globular type with a size of 300/400 nm are formed. Depending on the conditions of synthesis and the process of cluster formation, the size of globules can reach sizes up to 1200 nm (Boldyrev, P.P., 1989). Then these globules form a macrostructure with a cubic or other type of packing.

The change in the particle size distribution of microsilica during the synthesis was recorded using a Shimadzu SALD 3101 particle size analyzer and an OLYMUSGX – 71 inverted microscope.

The obtained micrographs and granulometric histograms are shown in Figure 3 and Figure 4.

In the synthesis process, an opal microsilica structure is formed, which can be represented as a fractal model (Figure 5), which is represented as a fractal cluster with a coordination number *K* = 2.2 with a sticking probability *P* = 1 and if *P* = 0.2, then *K* = 2.514.

Equation 2 relates the cluster radius R and the number of particles in it n (Selyaev V.P., 2012):

$$n = (\frac{R}{r_0})^D \quad \text{(Eq.2)}$$

where r_0 - is the radius of an individual particle; *D* - fractal dimension of the cluster.

The mass of the formed cluster *m* is related to the radius R by Equation 3:

$$m = m_0(\frac{R}{r_0})^D \quad \text{(Eq.3)}$$

To determine the parameters of the fractal model using a diffractometer, we obtained the experimental dependences of the scattering intensity $I(S)$ on the scattering vector modulus *S* for amorphous silica synthesized from diatomite (Figure 6).

The character of the obtained experimental small-angle scattering curves $I(S)$ indicates two systems of relatively homogeneous scattering clusters in the synthesized microsilica. Clusters with a size d = 40.6 nm represent the first; the second – d = 7.5 ÷ 14.9 nm ≈ 10.1 nm. The size distribution of the scattering particles of the synthesized silica is shown in Figure 7. From the analysis of the graph, it follows that small-scale fractal formations make the main contribution to the scattering of radiation with a size d = 4/8 nm.

Consequently, the dispersed powder of amorphous silica of silicon dioxide contains three types of scattering objects of the nanoscale level with different fractal dimensions.

Fractal properties of porous systems made of amorphous silica are shown in Table 2.

The results obtained make it possible to calculate the maximum pore size R_{max} using Equation 4, which has the form:

$$R_{\max} = r_0(\frac{\rho_0}{\bar{\rho}})^{\frac{1}{(3-D)}} \quad \text{(Eq.4)}$$

where r_0- the size of the primary particle of silicon dioxide; ρ_0- true density SiO_2; $\bar{\rho}$ - density of matter in a cluster of size *r*; *D* - fractal dimension.

The density of the matter in a cluster of size *r* (Equation 5):

$$\overline{\rho}(r) = \rho_0 (\frac{r_0}{r})^{3-D} \quad \text{(Eq. 5)}$$

From Equation 5, one can obtain the relationship between the average density $\overline{\rho}(r)$ and the cluster size r.

The results of calculating the average density of clusters are shown in Table 3. Two cases were considered: 1 - primary particle size r_0=1; 2 - $r_0 = 2$. Particle density ρ_0=2.2 g/m^3, fractal dimension D = 2.5.

The ratio between the density *ρ* and the porosity *P*, the porosity of the granular system was determined by Equation 6:

$$P = 1 - \rho_i/\rho_0 \quad \text{(Eq.6)}$$

The calculated values of density and porosity are shown in Table 3.

The last row of Table 3 shows the values of the maximum pore sizes of clusters in the process of their growth, which are calculated by Equation 7:

$$R_{max} = r_0(\rho_0/\rho_i)^{1/(3-D)} \quad \text{(Eq.7)}$$

According to the literature data, the free path of a molecule in the air is $\ell = 1.1 \cdot 10^{-6}\text{cm} - 11\text{nm}$. Then the Knudsen criterion $K_n = \ell/d$ equal to the ratio of the mean free path of gas molecules *ℓк* to the distance *d* between the walls limiting the volume, in almost all cases will be less than 1, $K_n = \ell/2R < 1$. Consequently, a convective heat transfer mechanism is realized in the pores of the system.

At low pressures, *P* and temperatures *T*, heat transfer by gas molecules in the pores will occur when they collide with the pore walls.

Consequently, the thermal conductivity of granular fillers LTIC will depend on the accommodation coefficient, which characterizes the degree of completeness of energy exchange when a gas molecule collides with a surface. It is always less than one.

The value of the coefficient α depends on the surface topography. The more irregularities, defects on the surface, the greater the values α. This conclusion has been established experimentally.

The topography of the solid phase surface of the pore structure is estimated by fractal dimension *D*.

2.1.4 Experimental studies of the structure and properties of LTIC

In the course of the experimental study, the following were evaluated: density in the liquid and dry state, thermal conductivity (GOST 7076-99, 2000; GOST 30290–94, 1996. GOST – Government standard), adhesive strength to concrete bases (GOST 28574-90; 1991) and the mass fraction of non-volatile substances (GOST 52487-2005; 2007). The thermal conductivity of LTIC was determined using an ITS-1 device based on the method of stationary flows. The equipment and methods of the experiment are described in the above section “Materials and methods” for determining the thermal conductivity of LTIC for each GOST.

The search for optimal solutions was carried out based on scalarization methods and experimental-statistical modeling based on the concept of material property fields. The optimization of the compositions was carried out to achieve 4 minimum characteristics in terms of thermal conductivity and density in dry and liquid states while ensuring sufficient adhesion characteristics.

3. RESULTS AND DISCUSSION:

1. Based on the data obtained, it has been experimentally proved (Figure 8) that the optimization of the compositions of LTIC makes it possible to reduce the thermal conductivity of the coatings to 0.05V/m·K, which is comparable to those for the Korund LTIC (0.0546 V/m·K) and lower than for the Isollat LTIC (0.0713 V/m·K). The study of the adhesion characteristics of LTIC showed that the highest adhesive strength is possessed by compositions containing: 24% acrylic dispersion, 5% diatomite, and 2÷6% white soot.

2. Based on the experimental study, the compositions of LTIC have been developed that have high-performance characteristics that are not inferior, and sometimes even surpass the compositions adopted in comparative tests as standards (Gladkov S. O., 2008; Inin A. E. *et al.*, 2013; Druzhinina T. Ya., 2013; Vasilyeva I. L., 2018; Abramyan S. G. *et al.*, 2018). The technological scheme of the production process has been developed.

3. Sequentially applied 6 layers of thermal insulation coating with a thickness of about each layer 1 mm with intermediate drying for 24 hours. The number of layers and the thickness of the coating by the coefficient of thermal conductivity on glass with dimensions of 150 × 150 mm and a thickness of 3 mm. Using the ITS-1 device at each stage, equivalent indicators were determined: heat flux density, thermal resistance, and thermal conductivity coefficient of three-layer samples. The results obtained are presented in Table 4.

4. It has been experimentally established that the effective thermal conductivity of LTIC based on heterogeneous finely dispersed granular systems even at atmospheric pressure may be lower than the thermal conductivity of the gas filling the pores (Table 4).

5. From the analysis of the data obtained, it was established that the equivalent heat flux density of three-layer flat samples, depending on the thickness of the heat-insulating layer, is described by a logarithmic dependence by Equation 8:

$$q_{eq.} = 141.94 - 21.36 \cdot l_n(\delta_{LTIC}) \quad \text{(Eq. 8)}$$

Equivalent indicators of thermal resistance and thermal conductivity coefficient - linear Equations 9 and 10 of the form (Maneshev I. O., 2013):

$$R_{eq.} = 0.0292 + 0.0109 \cdot (\delta_{LTIC}) \quad \text{(Eq. 9)}$$

$$\lambda_{eq.} = 0.1747 - 0.0085 \cdot (\delta_{LTIC}) \quad \text{(Eq. 10)}$$

The calculated data (Equations 9 and 10) on the change in the coefficient of thermal conductivity of LTIC from the number of coating layers are presented in Table 4 and Figure 9.

It has been established that with an increase in the thickness of the coating in the range from 1 to 6 mm, an increase in λ_{LTIC} from 0.0358 till 0.0739 W/m·K is observed. The largest change in δ_{LTIC} with an increase in the coating thickness was recorded in the interval 1÷2 mm with the stabilization of the indicator for coatings with a thickness of 4÷6 mm. The coefficient of variation of this indicator over the entire investigated interval is 22.9%; narrowing of the investigated range of coating thicknesses leads to its significant decrease: 9.43% - for 2÷6 mm; 5.363% - for 3÷6 mm; 2.01% - for 4÷6 mm; 2.37% - for 5÷6 mm.

The results obtained indicate that this technique is promising, based on using the ITS-1 thermal conductivity meter for evaluating the thermal-physical indicators of thin thermal insulating coatings. For stable performance, it is advisable to research thermal insulating coatings with a thickness of 3/6 mm.

6. To predict the thermal conductivity of LTIC, topological models can be used that take into account the fractality of the structure of granular fillers and coating material.

7. It has been found that dispersed microsilica obtained from natural diatomite has three types of scattering inhomogeneities mass fractals with dimensions 2.32 and 2.13. The scale of such objects is 8-40 nm. Small-scale pores 4-8 nm have rather heavily indented interfaces (D_S = 2.64).

The results obtained confirm the presence of developed pore space of particles and agglomerates of dispersed silicon dioxide of nanometer sizes, which can be used to reduce the effective thermal conductivity of heterogeneous systems, for example, mineral silica powders of various origins. The investigated dispersed materials have similar parameters of the pore system at the nanometer level.

Analysis based on obtained gives grounds to believe that dispersed microsilica obtained from diatomite is most suitable: for creating a new generation of thermal insulation materials; as fillers for LTIC, VIP (VIP-vacuum insulation panel).

4. CONCLUSIONS:

1. As a result of the analysis of the influence of the structural parameters of the granular system formed from the synthesized particles of silicon dioxide, it was found that during the production of iron and steel products, their heat-shielding properties can be controlled by changing: pressure, viscosity, the molecular weight of gas; porosity of macrostructure and clusters; the thermal conductivity of the solid and gas phase of the system; the coefficient of accommodation; coordination number; primary particle size; fractal dimension characterizing the topological features of the structure of particles, aggregates, globules, clusters and their tendency to dissipate the energy of gas molecules.

2. Based on the research work carried out, it has been established that an additional decrease in thermal conductivity is possible due

to the optimization of the compositions of binders and the use of mineral fillers with low density. The performed analysis showed that the most promising fillers from this point of view are white soot and powders with an opal structure synthesized from diatomite's.

5. ACKNOWLEDGMENTS:

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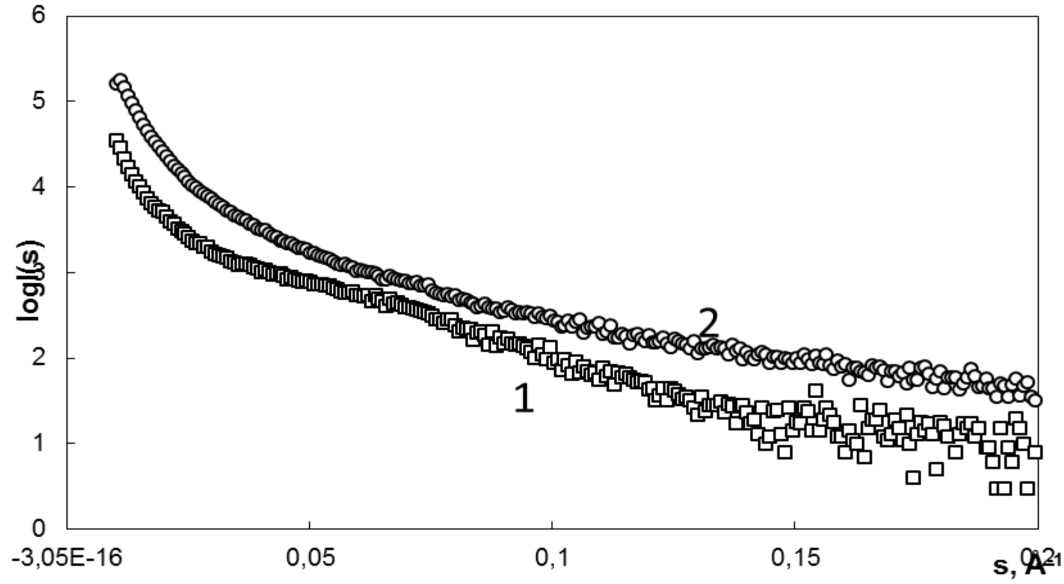

Figure 1. *Small-angle X-ray scattering curves of dispersed powders: 1 - natural diatomite; 2 - filler powder.*

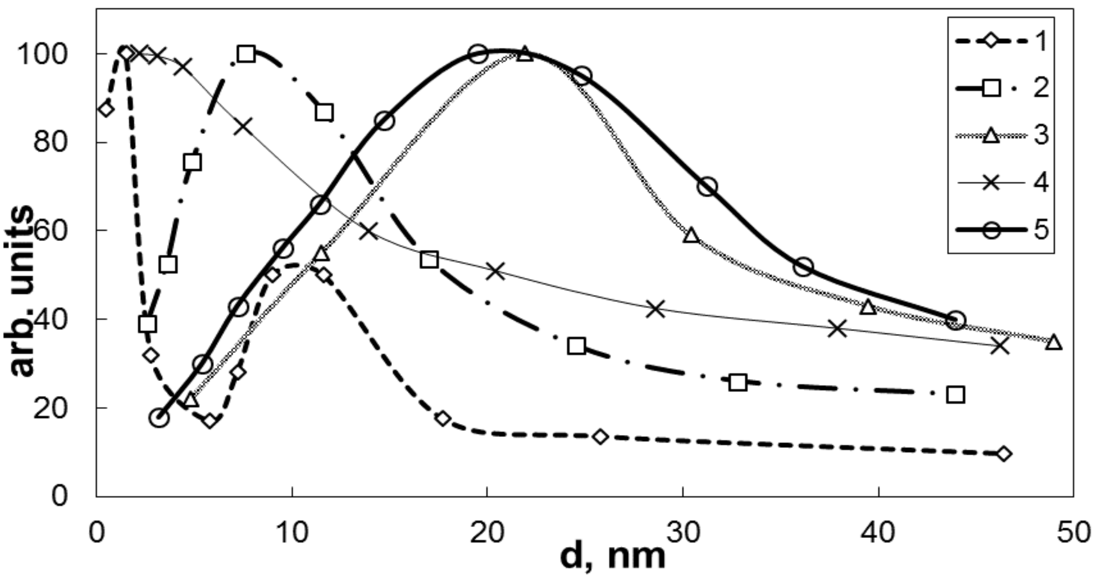

Figure 2. *Size distribution of scattering inhomogeneities: 1 - natural diatomite; 2 - dispersed microsilica obtained from diatomite; 3 - condensed microsilica; 4 - white soot; 5 - filler powder.*

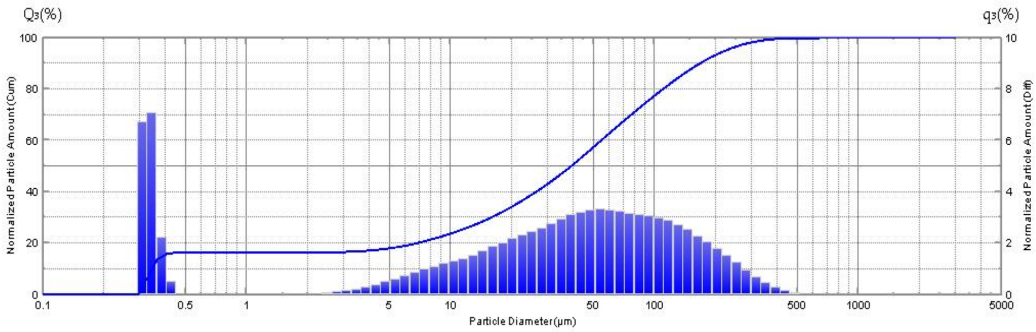

Figure 3. *Particle size distribution of synthesized silicon dioxide determined experimentally using a Shimadzu SALD 3101 analyzer*

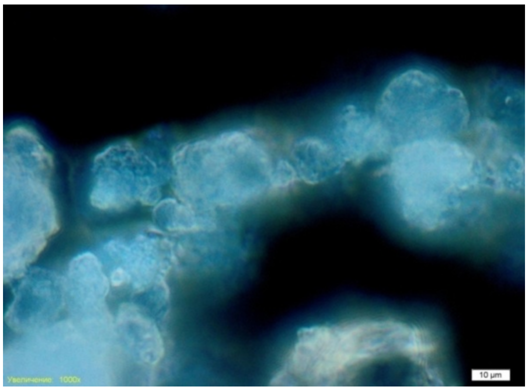

Figure 4. *Image of particles of amorphous silicon dioxide synthesized from diatomite, obtained using an OLYMUSGX - 71 invented microscope*

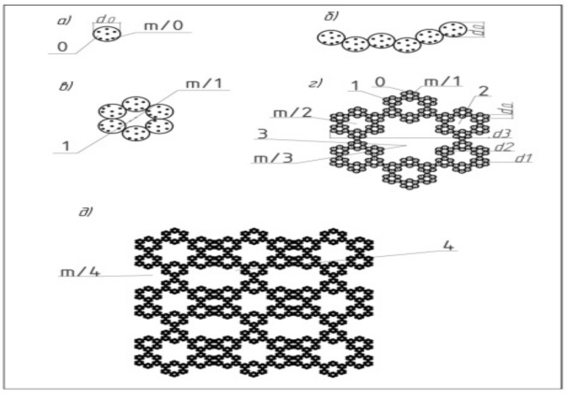

Figure 5. *Fractal model of the structure of dispersed microsilica: a) primary particle; b) fibrillar (chain) cluster; c) globular (spherical) cluster; d) associated cluster (CCA); e) the spatial framework of the macrostructure made of CCA clusters.*

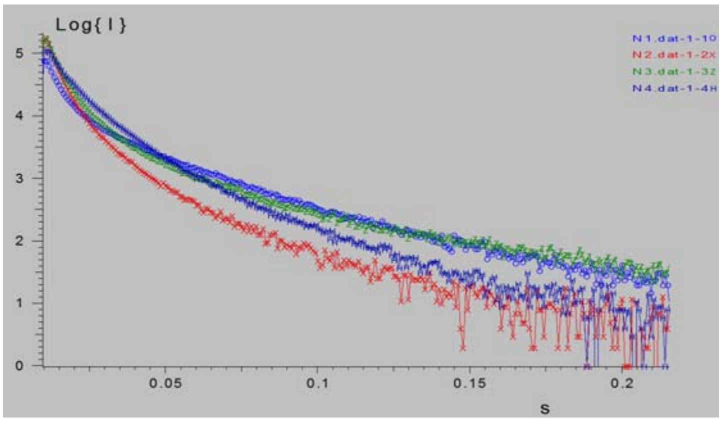

Figure 6. *Scattering intensity $I(S)$ versus the scattering vector modulus S for amorphous silica synthesized from diatomite*

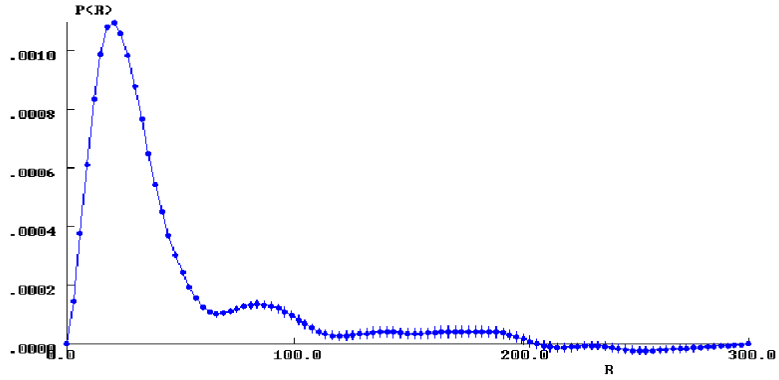

Figure 7. *Size distribution R (in angstroms A) of synthesized silica scattering particles*

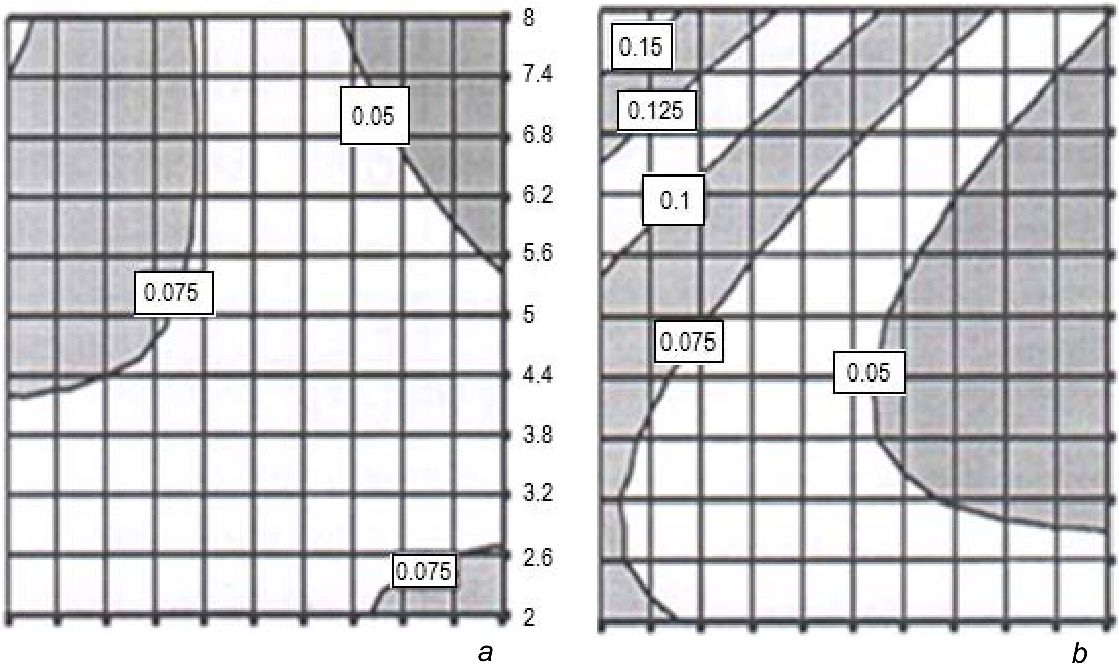

Figure 8. *Isolines of changes in the thermal conductivity of LTIC depending on the content of diatomite, silica, and acrylic dispersion: a - 16%; b - 20% (White soot content in% of binder mass)*

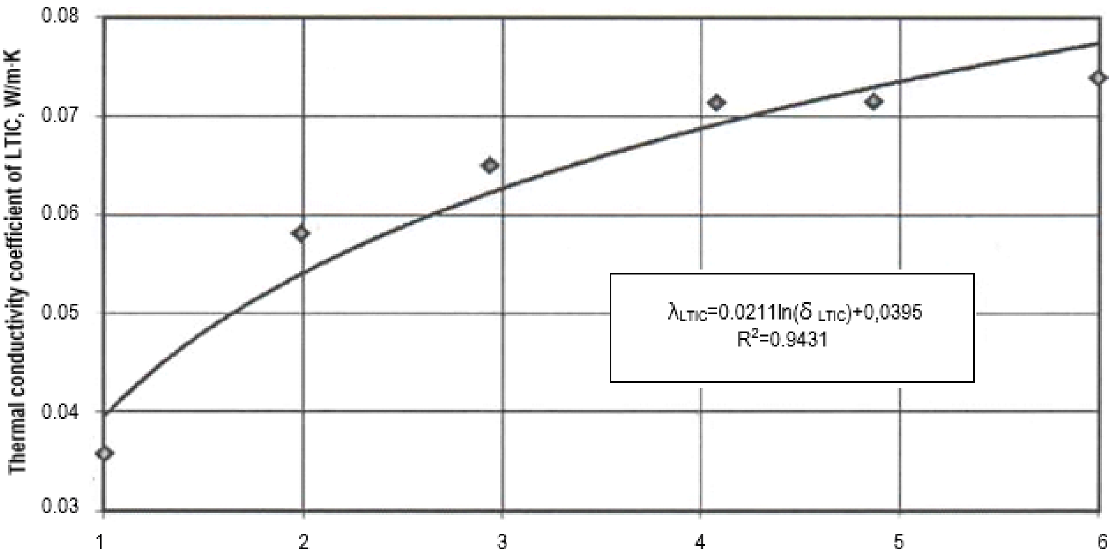

Figure 9. *Change in the coefficient of thermal conductivity of liquid thermal insulation* depending on the thickness of the coating

Table 1. *Pore size distribution of dispersed microsilica*

Powder type	**d_B, nm**	**< d >, nm**	**Δd, nm**
Natural diatomite	2 10	2 7	7 - 15
Dispersed microsilica obtained from diatomite	8	12	3 – 18
Condensed silica fume	22	26	10 – 34
White soot	2	13	2 - 21
Powder - filler	20	20	8 - 37

Table 2. *Fractal characteristics of the investigated materials*

No.	**Material**	**Δs, $Å^{-1}$**	**α**	**D**	**D_S**	**d, nm**
1	Natural diatomite	0.013 – 0.026	2.59	2.59		24 – 48
		0.031 – 0.061	1.56	1.56		10 – 20
		0.067 – 0.095	3.73		2.27	7 – 9
2	Dispersed microsilica obtained from diatomite	0.016 – 0.025	2.32	2.32		25 – 40
		0.025 – 0.080	2.13	2.13		8 – 25
		0.080 – 0.160	3.36		2.64	4 – 8
3	Condensed silica fume	0.016 – 0.160	3.60		2.40	4 – 40
4	White soot	0.016 – 0.025	3.17		2.83	25 – 40
		0.025 – 0.160	2.66	2.66		4 – 25
5	Powder - filler	0.016 – 0.032	2.59	2.59		20 – 40
		0.032 – 0.056	3.30		2.70	12 – 20
		0.056 – 0.160	4.10			4 – 12

Table 3. *Density and porosity of silica clusters synthesized from diatomite*

i	**0**	**1**	**2**	**3**	**4**	**5**	**6**
r_i, nm	1.0	5.0	10.0	40.0	100.0	300.0	1200.0
$r_0(1)/r_i$	1.0	0.2	0.1	0.025	0.01	0.003	0.00083
$\rho_1(r_i)$, g/	2.2	0.97	0.7	0.35	0.22	0.132	0.066
$P_1(r_i)$, %	0	56	68	84	90	94	97
$r_0(2)/r_i$	1	0.4	0.2	0.05	0.02	0.006	0.00166
$\rho_2(r_i)$, g/	2.2	1.39	0.98	0.49	0.311	0.18	0.089
$P_2(r_i)$, %	0	37	56	78	86	92	96
R_{max}, nm	4	9.98	20.2	80.6	201	595	2440

Table 4. *Measurement of thermal-physical parameters of three-layer samples depending on the number of layers and the thickness of the liquid thermal insulating coating*

Layer number	**Thickness of applied layers, mm**	**Equivalent heat flux density $q_{eq.}$, W/m^2**	**Equivalent thermal resistance $R_{eq.}$, m^{2}K/W**	**Equivalent thermal conductivity coefficient, $\lambda_{eq.}$, W/m·K**	**Thermal conductivity coefficient λ_{LTIC}, W/m·K**
1	1.01	0.043	142.4	0.163	0.0358
2	1.99	0.049	125.9	0.163	0.0581
3	2.94	0.060	118.7	0.149	0.0651
4	4.08	0.072	114.0	0.140	0.0713
5	4.87	0.083	106.6	0.131	0.0714
6	5.98	0.096	104.0	0.125	0.0739