Thin-layer thermal insulation coatings based on high-filled spheroplastics with polyorganosiloxane binder

V Yu Chukhlanov¹, O G Selivanov¹, T A Trifonova¹, M E Ilina¹ and N V Chukhlanova¹

¹Vladimir State University named after A.G. and N.G. Stoletovs Vladimir, 600000, Russia

E-mail: chukhlanov11@gmail.com

Abstract. Thermal insulation coatings, based on polyorganosiloxane as a binder and hollow glass microspheres, have been studied in this research. The developed materials are widely applied in various branches of science and engineering basically in construction. Components interaction processes are comprehensively studied. Spraying production methods of thin layer thermal insulation coatings have been researched. Ideal technological parameters for polyorganosiloxane coatings hardening depending on components ratio, ambient temperature, solvent and curative concentration have been determined. Stress related characteristics of constructional energy saving materials containing polyorganosiloxane have been researched. Components structure and ratio concerning compound extension strength properties have been revealed. Substantiation of Danneberg model application for the strength characteristics enhancing, when hollow microspheres are introduced, has been suggested. Thermal properties of coating thermal insulation have been studied. To research these characteristics standard methods applying devices IT-S-400 and IT-λ-400 have been chosen. Filler concentration increase was stated to decrease the composition heat conductivity coefficient and to the reduction of temperature dependence of this index. The authors suggested to employ the developed thermal insulation materials for construction and power engineering facilities operating under high temperature and other unfavorable environment.

1. Introduction
Spheroplastics are widely applied in various branches of science and technology including construction, aviation, cosmonautics, engineering, shipbuilding. The compounds filled with microspheric additive are of special interest nowadays. The main advantages of this material are its high physical and mechanical qualities combined with the little weight [1-4]. However polymer matrix application as binder makes the polymer limit materials functionality, due to low thermal stability and tendency to UV radiation decomposition. Thus silicon binders, characterized by high stability towards temperature and negative atmospheric factors, are considerably important [5-9]. However silicon binders are characterized by insufficiently high mechanical properties. The research objective is to determine optimal technological conditions for producing thin-layer thermal insulation coatings based on syntactic foam with polyorganosiloxane binder with terminal OH-group and to study stress related and thermal properties of the produced materials.
2. Materials and Methods
1. Low-molecular heat resistant polydimethylsiloxane rubber - linear polydimethylsiloxane with terminal OH - group with molecular mass range from 20000 to75000. The material called SKTN-A (B) (heat resistant low-molecular polydimethylsiloxane rubber) is produced at Synthetic Rubber Plant (Kazan city) in compliance with Standard GOST 13835-73;
2. Tetraethoxysilane [TEOS] TU 6-09-3687-74 (Angarsk city);
3. 50% diethylidicaprylate solution of tin tetraethoxysilane (activator K-18) produced in compliance with Standards TU 6-02-805-78;
4. Sodium boron silicate microspheres.

Analysis methods
1. Extension test method in compliance with GOST 15873-70;
2. Elastic modulus determination method in compliance with GOST 9550-81;
3. Destructive abruption stress method using adhesion meter «Constant A» in compliance with GOST 15140-78 «Adhesion determination method»;
4. Thermal conductivity coefficient determination method was defined under dynamic conditions in compliance with GOST 23630.2-79 using device IT - λ-400;
5. Thermal capacity determination method in compliance with GOST 23630.1-79 using device IT -C-400.

3. Results

3.1 Experimental research
The conversion of linear low-molecular modified organosiloxanes with terminal OH-group into three-dimensional structure occurs under the impact of tetraethoxysilane, partial hydrolysis residues (ethyl silicate 40) and other organic-silicon molecular compounds. In the course of three-dimensional polycondensation reaction gel formation is observed [10,11].

Formation and increase of gel amount is accompanied with drastic augument of system viscosity. Thus functional group reaction slows down and polycondensation process seldom finishes ate this stage.

The glass filler impact on polycondensation process of polydimethylsiloxane and tetraethoxysilane might occur as a consequence of OH- group presence on glass surface. Thus the research highlights [12,13] that colloid aerosil particles (size - 3-10 nm) can interact with OH - group and block the access of curing agent to them.

3.2 Curing optimal parameters choice
To produce thin-layer modified organopolysiloxane coating the method of compound spraying of on the surface to be protected is considered to be advanced. The index of filled compounds density is rather accurately calculated using the following formula:

\[ \rho_c = \rho_{f}(1-\Theta_b) + \rho_b \Theta_b \]

where \( \rho_{f} \), \( \rho_b \) - average microspheres and binder density correspondingly; \( \Theta_b \) - binder volume ratio.

The composition with density (p) maximally approaching the calculated value was considered optimal.

Comparative characteristics of thin-layer SP, received from composition with different viscosity, demonstrate that system viscosity is the principle parameter for reaching the SP calculated density. Consequently it is necessary to control compound density throughout the entire spraying process.

Solvent removal rate from the coating is basically defined by the hollow glass microsphere amount in the compound. It can be explained by the solvent adsorption on the microspheres surface. This process can be considerably accelerated by using high temperature drying.

Stress-related characteristics of polydimethylsiloxane based materials
Coatings stress-related characteristics are defined by both the property of binder and filler, and their production technology. Particles size and filler fractional structure relatively influence the strength properties of the “filler – binder” system.
The increase of material strength limit is observed during the introduction of filler into elastomer. This hardening can be explained applying elastomer molecule sliding model on the filler surface (Danneberg model [14]). The lack of the filler causes firstly the short loaded chains cut but in its presence the number of loaded chains increases and load transfer occurs correspondingly. When polydimethylsiloxane volume ratio decreases by 30%, drastic decrease of the coating strength limit occurs, caused by the binders deficit in the interspheric space.

Besides the enhancement effect is possible due to the chemical bonds formation between binder and filler, i.e. non responding polydimethylsiloxane hydroxyl groups and silanol groups at the glass filler surface.

Abruption strength testing of the sprayed sphereplastics of the various structure bases revealed pronounced extreme nature of the elastic modulus dependence on the binder structure. Ideal bonding of coating with the base is achieved when binder content reaches 30 + 45% vol. When polydimethylsiloxane amount reaches 30%vol abruption strength characteristics improve due to the material strength limit increase.

Coating abruption strength properties largely depend on the base material. Thus coating adhesion on the steel base is higher than on the aluminium base. Apparently it is connected with the oxide film on aluminium surface and correspondingly the difference in the number of hydroxyl groups on the material surface.

In order to increase coating adhesion properties base surface was preliminary covered with 40-50 micron of sealant sublayer Viksint 28 – low-molecular silicone rubber SKTN-1 filled with ferrous oxide (red oxide). The sublayer was pneumatically sprayed with 40% sealant solution in toluene with addition of hardening agent and consequent hardening at ambient temperature during 72 hours. Adhesion sublayer greatly enhances coating abruption strength limit regardless base material.

Frequently impact resistance ranks high importance characterizing thin layer cover resistance towards mechanic stress impact. Testing revealed that samples impact resistance is extremely high and depends mainly on the binder type and volume in coating (Table 1).

| Kind of binder | Content of binder, % vol | Shock strength, sm/kg |
|---------------|-------------------------|-----------------------|
| SKTN -1       | 10                      | 21                    |
| SKTN -1       | 20                      | 37                    |
| SKTN -1       | 30                      | 42                    |
| SKTN -1 + red oxide (Viksint -28) | 10 | 32 |
| SKTN -1 + red oxide (Viksint -28) | 20 | 45 |
| SKTN-1 + red oxide (Viksint -28) | 30 | 54 |

3.3 Coatings heat transfer properties

Coatings heat transfer properties are defined by the ratio of binder and filler, as well as by their nature. Conductivity of composite materials made-up of several component can be estimated using the following function [15]:

\[ \lambda = \lambda_b (1 - \varphi) + \lambda_f \varphi \]

where \( \lambda \) - multicomponent material conductivity;
\( \lambda_b, \lambda_f \) - first and second component conductivity;
\( \varphi \) - filler volume ratio.

Table 2 presents the estimated and experimental values of coating heat conductivity coefficient with polydimethylsiloxane binder at 25 °C.

| Kind of binder | Content of binder, % vol | Shock strength, sm/kg |
|---------------|-------------------------|-----------------------|
| SKTN -1       | 10                      | 21                    |
| SKTN -1       | 20                      | 37                    |
| SKTN -1       | 30                      | 42                    |
| SKTN -1 + red oxide (Viksint -28) | 10 | 32 |
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| SKTN-1 + red oxide (Viksint -28) | 30 | 54 |
Polydimethylsiloxane amount, % (volume) | Coating density, kg/m³ | Coating heat conductivity coefficient, W/m K
---|---|---
30 | 482 | 0.104
50 | 573 | 0.156
70 | 805 | 0.228
100 | 1080 | 0.350

Generally estimated and experimental data are rather close. Figure 1 demonstrates temperature relations of syntactic foams with different binder amount.

When polydimethylsiloxane amounts 50%, heat conductivity coefficient does not depend on the temperature (Curve 3).

![Figure 1. Heat conductivity coefficient dependence on temperature](image)

Coating heat capacity with the polydimethylsiloxane binder, similar to the previous case, is largely defined by the components relation. High heat capacity of pure polydimethylsiloxane (Curve 1) is mostly determined by the flexibility of polymer macromolecule segments and minor intermolecular interaction. This also refers to the compounds with high polydimethylsiloxane content (Curves 2, 3).

When the temperature rises, molecule mobility is also rising and spheroplastics heat capacity is increasing correspondingly (figure 2) especially for the composition with high polyorganosiloxane content.
Due to high thermal stability up to 250 °C and resistance to the majority of external aggressive factors, the developed syntactic foams can be applied for the production of light weight sandwich panels, heat insulating materials and coatings for the construction industry, heat power engineering, nuclear energy industry and other branches of industry.

4. Conclusions
The carried out research has demonstrated a real possibility of developing polydimethylsiloxane binder based coatings possessing advanced heat-insulation properties. For obtaining coating with minimal subfrothing and correspondingly with the highest microspheres packing capacity and the best stress related properties the following conditions are to be observed:
- compound durability time is to be enough for complete air removal;
- cure temperature is to be much lower than the solvent boiling temperature as it may cause material subfrothing due to intensively release of vapor;
- thermal dependence of heat conductivity coefficient is minimal at high compound filling, moreover with temperature rise it becomes negative.

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Figure 2. Specific heat - temperature dependence
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