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DEVELOPMENT AND PROSPECTS OF THE APPLICATION OF SYNTACTIC FOAM PLASTICS AS HEAT-SHIELDING MATERIALS IN SPACE-ROCKET TECHNOLOGIES

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We present information on the development and operating properties of NTZP-U syntactic foam plastics based on polyurethane aqueous dispersions, glass, and polymeric microspheres and the data on the thermal properties and durability of the developed heat-shielding materials under the conditions modeling the in-flight temperature conditions formed on the surface of the coating of the nose cone of a "DNEPR" launch vehicle.

Keywords: heat-shielding materials, syntactic foam plastics, method of airstream spraying, physicomechanical characteristics.

To form external heat-shielding coatings (EHSC) on the spacecraft equipment (SE), it is customary to use liquid compositions sprayed by the methods of airstream or airless spraying. Among the great number of materials used for heat shielding, it is of interest to study the so-called syntactic foam plastics (SFP), i.e., gas-filled materials formed by a polymeric matrix with hollow microspheres of different nature (glass, ceramic, metallic, or polymeric) distributed in the matrix. The cellular structure of SFP is formed by introducing gas-containing microspheres in the polymeric matrix. In this case, the physical structure of SFP is similar to the structure of ordinary foam plastics obtained by the method of foaming. The ordinary foam plastics and SFP are heterophase systems of the "solid-body–gas" type. As a distinctive feature of the SFP, one can mention the presence of three and more phases because the chemical composition of the material of the walls of hollow microspheres often differs from the composition of the polymeric matrix. The SFP are sometimes attributed to filled plastics because the process of their manufacturing excludes the procedure of chemical foaming of the polymeric matrix and can be described as its mechanical filling by hollow microspheres. This is why they are often called physical foams [1]. The cellular structure of SFP depends on the amount, uniformity of distribution, and the sizes of filler particles. Since hollow microspheres introduced in the filler have, as a rule, continuous shells, the obtained materials contain isolated gas-structural elements and, hence, they can be called absolute foam plastics. This fact and the absence of anisotropy of the macrostructure due to the "perfect" spherical shapes of the microspheres and uniformity of their filling are responsible for the valuable properties of SFP. As compared with ordinary "chemical " foam plastics, they are characterized by higher strength-to-mass ratio and much lower water absorption; moreover, they can withstand high hydrostatic pressures. Their properties can be varied within sufficiently broad ranges by changing both the types of the binder and filler and their ratio and the technology of manufacturing and curing [1].

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In the spacecraft technology, the so-called TTP-FSU heat-shielding coatings with a density of 0.28–0.44 g/m^3 are used especially extensively. These are, in fact, chlorosulfonated SFP based on chlorosulfonated polyethylene with hollow phenol-formaldehyde microspheres. Parallel with microspheres, these materials also contain some other powder fillers, namely, polymethylmethacrylate, polypropylene, and wood flour [2]. Coatings of this kind are obtained from liquid compositions containing toluene, which is a toxic organic solvent that causes irritation of mucous membranes of the respiratory tracts and eyes and affects the nervous system [3]. In view of the harmfulness and hazard of using these organic solvents in sprayed heat-shielding compositions, various attempts are now made to develop SFP based on aqueous dispersions of polymers, such as butadiene-styrene, styrene-acrylate, and polyvinyl-acetate latexes, aqueous dispersions of the copolymers of acrylic family, polyvinyl acetate, polyvinyl chloride, polyurethane, etc. [4–9]. Aqueous latexes and dispersions have important advantages over the binders diluted by organic substances, namely, fire and explosion safety, high concentration of the desired component, and the absence of release of harmful substances.

Sometimes, mixtures of latexes and dispersions can be used as a binder. In this case, it becomes possible to attain the required level of vapor permeability of the coatings and their adhesion to the protected surfaces; moreover, it becomes possible to extend the range of their operating temperatures. Thus, to obtain coatings capable of withstanding multiple jumps of temperature from – 70 to + 100°C, the composition of the mixture of aqueous binder is enriched with high-elasticity latexes, e.g., with butadiene-styrene, butadiene, and polyvinyl chloride latexes, or with latexes based on the copolymers of the above-mentioned polymers [5].

It was shown that earlier developed heat-shielding, heat-insulating, and fire-resistant compositions of SFP based on water-diluted polymeric materials are not intended for the protection of structural elements of spacecrafts and, moreover, according to their characteristics, cannot be used in this branch of engineering.

In view of their operating conditions, fairly severe requirement are imposed on the EHSC protecting the structural components of spacecrafts. In particular, their high physicomechanical characteristics must be preserved in the case of abrupt increase in temperature up to 350–450°C under the conditions of high-speed aerodynamic heating and strong vibration. The heat-conduction coefficient and specific heat capacity must be on the levels of 0.13 W/(m ·°C) and 1.71 kJ/(kg ·°C), respectively [2]. Moreover, these materials should be nonflammable in the course of flight.

The "KB Yuzhnoe" State Enterprise in cooperation with the "Ukrainian State Chemicotechnological University" State Higher School developed incombustible SFP of sprayed type (NTZP-U) based on polyurethane aqueous dispersions, glass and polymeric microspheres, powder antipyrenes, and technological admixtures [13]. The NTZP-U is thermally stable up to 250°C and has a fairly good complex of physicomechanical properties: a density of 0.4–0.6 g/cm^3, a tensile strength of 0.80–1.65 MPa, a relative elongation of 12.8–69.0%, and an ultimate strength of 0.98–1.04 MPa [14].

To get the indicated strength characteristics, as a polymeric matrix, we used mixtures of polyurethane aqueous dispersions. Moreover, one of these dispersions is self-crosslinking [Joncryl HYB-6336 polyurethaneacrylic dispersion (Neoresins, Holland)] and must guarantee the formation of coatings with spatially cross-linked structures and high thermal stability and the second dispersion (NeoPack E-106 polyurethaneacrylic dispersion, BASF, Germany) must guarantee the elasticity of the developed compositions.

In what follows, we compare the results of investigation of the thermal properties and the results of thermoerosion tests obtained for the developed sprayed NTZP-U SFP and for the TTP-FSU coating used in manufacturing the SE. The NTZP-U materials were obtained as a result of layer-by-layer deposition with the use of airstream spraying (the thickness of one deposited layer was 0.3–0.4 mm) of its liquid compositions on the surface of aluminum foil. Each layer of the coating was dried at room temperature and at 60–70°C every time when the coating became 1 mm thicker. By the method of optical microscopy, we obtained micrographs of the SFP both with the NTZP-U composition and with the earlier developed TTP-FSU composition (Fig. 1).

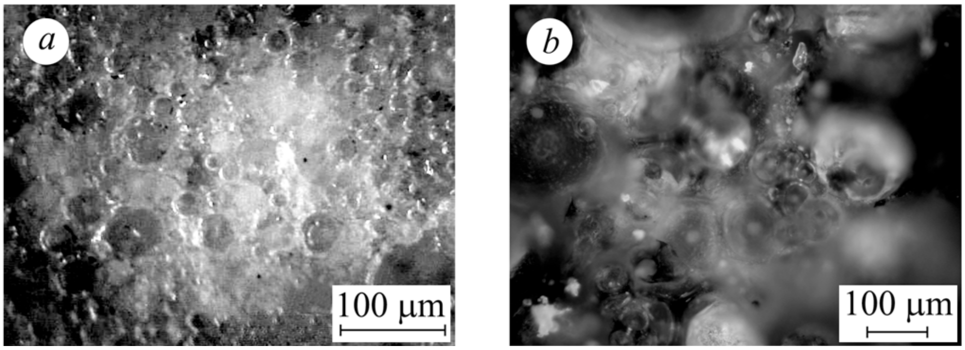

Fig. 1. Micrographs of the fractures of syntactic foam plastics based on the NTZP-U composition (with a content of microspheres of 28.7 wt.% and a density of 0.51 g/cm^3) (a) and on the TTP-FSU composition (10.0 wt.% and 0.39 g/cm^3) (b).

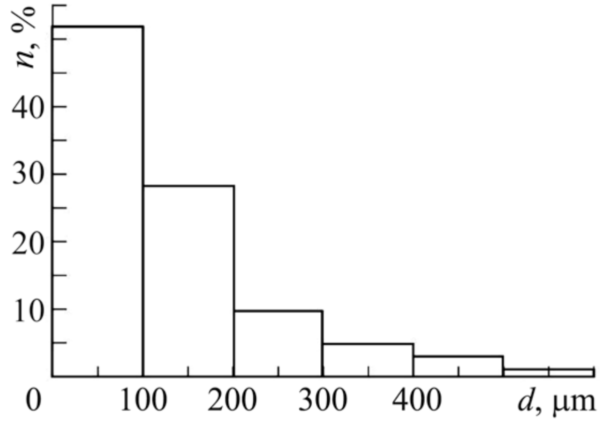

Fig. 2. Histogram of distribution of the particles of BV-01 phenol microspheres over the diameter after screening through a sieve No. 0.63.

It was established that the NTZP-U-type SFP is uniformly distributed and has a dense packing of microspheres, whereas the TTP-FSU material contains microspheres with a broader range of the diameters of particles. This is explained by the specific feature of the technology of manufacturing of liquid SFP compositions based on the introduction of preliminarily fractionated hollow microspheres of two types (namely, polymeric and glass) taken in the mass ratio 1:1 in the NTZP-U composition. As polymeric microspheres we used Expancel® 461 WE 20 d 36 and Expancel® 461 WE 80 d 36 microspheres based on a copolymer of acrylonitrile, vinylidene chloride, and methyl methacrylate (Akzo Nobel, Holland) with particle sizes of 40 and 80 μm, respectively, and HGS 16 and HGS 130 glass microspheres (Larand Chemical Corporation, USA) with particles 30 and 40 μm in size, respectively.

The authors of the patents [5, 6] believe that microspheres with different sizes and different bulk densities are distributed most uniformly in the volume of the composite material. Moreover the difference between these parameters should be maximum possible. At the same time, the BV-01 phenol microspheres introduced in the TTP-FSU are characterized by a quite wide distribution of hollow particles in diameter. They are preliminarily screened through a sieve No. 0.63. In this case, it is established (Fig. 2) that, after screening, up to 53% of phenol microspheres have diameters smaller than 100 μm and the diameters of the remaining particles vary within the range ~ 200–600 μm.

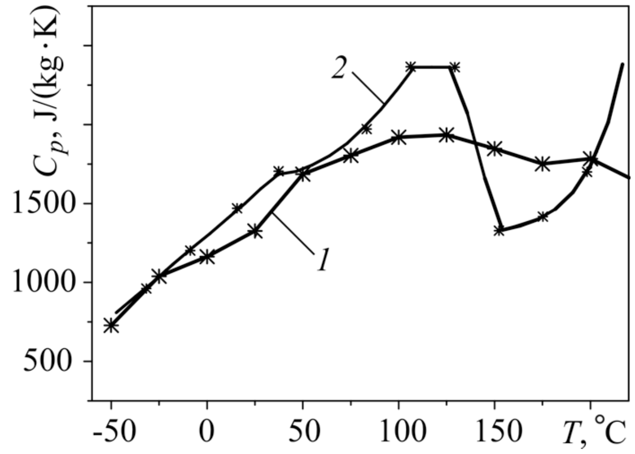

Fig. 3. Temperature dependences of the specific heat of the NTZP-U (curve 1) and TTP-FSU (curve 2) materials.

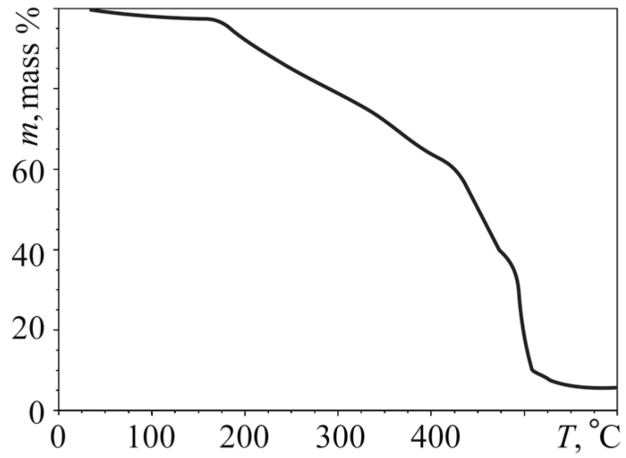

Fig. 4. Data of thermogravimetric analysis of the TTP-FSU standard coating (with a density of 0.39 g/cm^3).

We plotted (Fig. 3) the temperature dependences of specific heat of the NTZP-U material (with a content of microspheres of 28.7 wt.% and a density of 0.50 g/cm^3) and the TTP-FSU material (with 10.0 wt.% and 0.39 g/cm^3, respectively) in the form of an array of the experimental data, their mean values, and the approximating curve. The specific heat was determined within the temperature range (– 40)–250°C by using an IT-S-400 device.

It was discovered that the specific heat of all tested NTZP-U samples is much lower than for the TTP-FSU standard coating. Its decrease observed for TTP-FSU within the range 150–175°C is obviously connected with the decomposition of the binder (film-forming agent) of this material, namely, of chlorosulfonated polyethylene (Fig. 4)

It was established (Fig. 5) that the heat-conduction coefficients of both materials monotonically increases with temperature. Thus, for the syntactic TTP-FSU-type foam within the temperature range from – 50 to 50°C, its values are higher than for the NTZP-U material. This may be caused by a much lower content of hollow microspheres in the TTP-FSU composition than in the NTZP-U composition.

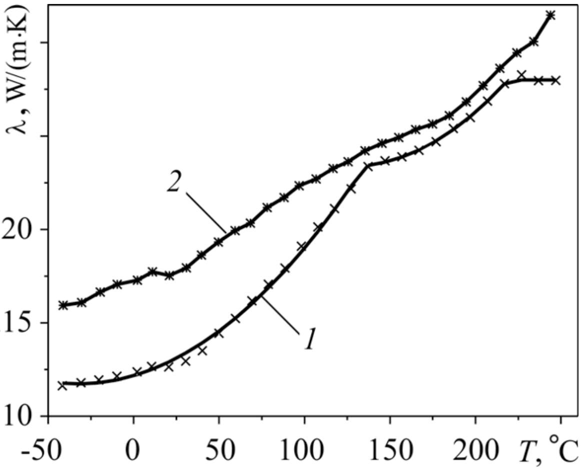

Fig. 5. Comparison of the temperature dependences of the heat-conduction coefficient for the NTZP-U (curve 1) and TTP-FSU (curve 2) materials.

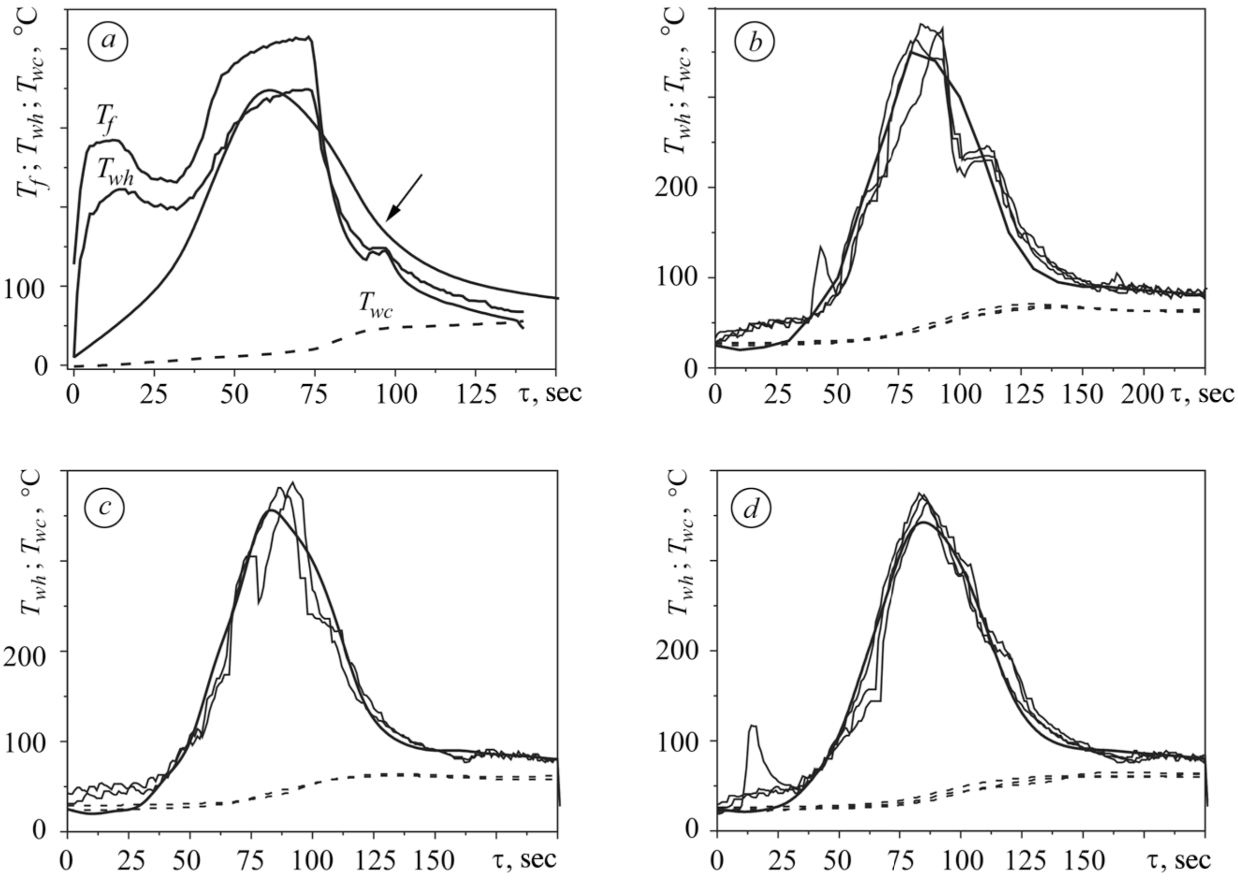

Fig. 6. Temperatures of the incident air flow T_f, heated surface T_{wh}, and lower surface T_{wc} of the samples of syntactic foam plastics based on the NTZP-U composition (a–c) and containing 28.7 (a), 30.4 (b), and 32.6% (c) of the mixture of glass and polymeric microspheres (in the mass ratio 1:1) and on the TTP-FSU composition (d) under conditions simulating the temperature conditions formed on the surface of the nose cone of the "DNEPR" launch vehicle in the course of flight. The arrow indicates the curve of the indicated temperature conditions [(b–d) T_{wh} is plotted by the solid curve and T_{wc} is plotted by the dashed curve]. The thickness of the tested samples is 3.0–5.2 mm.

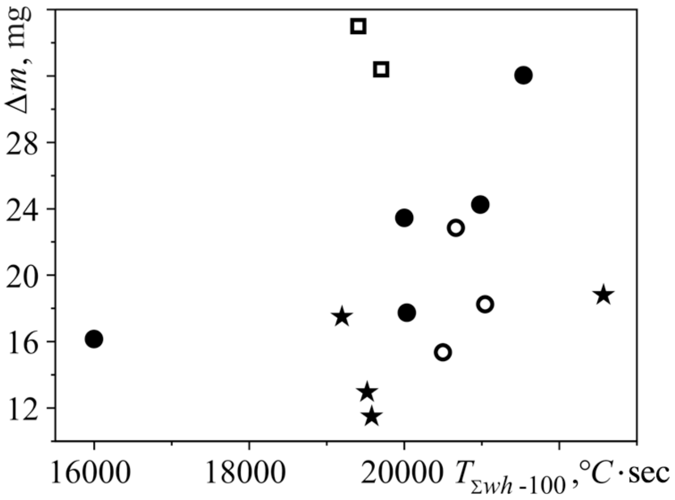

Fig. 7. Dependence of the mass loss Δm of the materials of EHSC on the integral temperature of the surface for the surface temperature higher than 100°C: (●) TTP-FSU; NTZP-U with various contents of microspheres: 28.7% (★), 30.4% (○), and 32.6% (□).

For the determination of the principal possibility of application of the developed NTZP-U composition, we used the results of testing under the thermal conditions simulating the temperature conditions formed on the surface of the coating of the nose cone of the "DNEPR" launch vehicle (LV) in the course of flight.

The tests were carried out in an installation developed at the Frantsevich Institute for Problems in Materials Science. A sample was heated by a flow of hot air, which (in turn) was heated by an industrial fan (GHG660 LCD, Bosch, Germany) with electronic control of temperature and air flow mounted on a tripod with a possibility of vertical displacements. The temperature of the surface T_h was regulated according to a prescribed program in the manual mode by varying the modes of operation of the fan and the distance from its nozzle section to the surface of the sample. The heater gave the temperature of air T_f within the range from 50 to 660°C with steps of 10°C and an accuracy of stabilization of $\pm 5\%$. The air flow was $0.25\text{–}0.5\ \mathrm{m^3/min}$. The exit diameter of the nozzle was 20 mm. The maximum heat flow toward the cold wall equal to $60\ \mathrm{kW/m^2}$ was attained in the case where the temperature of air was equal to 660°C for the minimum distance from the nozzle section (25 mm).

The temperature T_h was measured by a Flus IR-86-1U recording pyrometer with a spectral sensitivity within the wavelength range $\lambda = 8\text{–}14\ \mu\mathrm{m}$ and the accuracy of measurements equal to $1.5\% \pm 2°\mathrm{C}$ within the temperature range 0–500°C. The pyrometer was placed at a distance of 250 mm from the surface of the sample on which the diameter of the measurement spot was equal to 5 mm. The emissivity was set equal to $\varepsilon = 0.9$. The integral temperature of the surface (the integral of the surface temperature over the time of testing) for the entire period of operation was $T_{\Sigma(\tau=200)} = 27{,}450°\mathrm{C} \cdot \mathrm{sec}$. At the same time, for the period when the surface temperature was higher than 100°C, the integral temperature $T_{\Sigma(Tw>100)} = 19{,}775°\mathrm{C} \cdot \mathrm{sec}$.

In the course of experiments, we also measured the temperature of the lower surface of the sample (T_{wc}) characterizing the heat-insulating properties of the investigated materials.

In Fig. 6, we illustrate the behaviors of temperatures of the hot (T_{wh}) and cold (T_{wc}) surfaces of the samples of syntactic foams of the NTZP-U-type with different contents of microspheres and densities (28.7% and $0.51\ \mathrm{g/cm^3}$; 30.4% and $0.45\ \mathrm{g/cm^3}$; 32.6% and $0.39\ \mathrm{g/cm^3}$) and of the TTP-FSU material in the course of the tests.

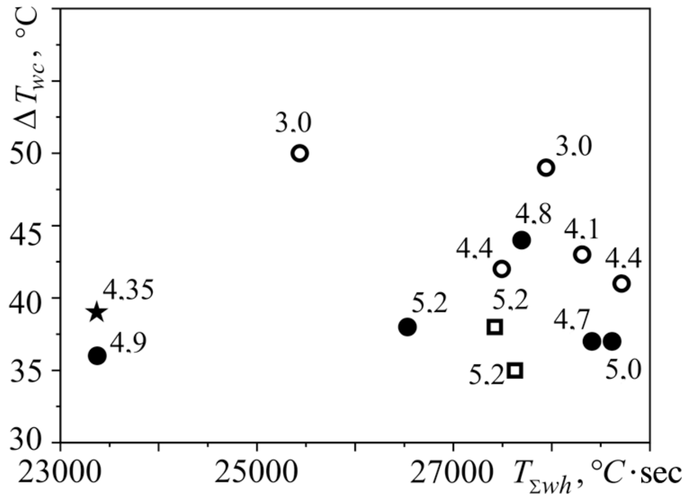

Fig. 8. Dependence of the maximum heating of the back wall ΔT_{wc} of the materials of EHSC on the integral temperature for the heating time $T_{\Sigma wh}$ (numbers near the experimental symbols correspond to the thicknesses of the samples in mm): (●) TTP-FSU; NTZP-U with various contents of microspheres: 28.7% (★), 30.4% (○), and s32.6% (□).

By using the experimental data, we plotted the dependence of the mass loss Δm (mg) on the integral temperature $T_{\Sigma wh-100}$ (°C · sec) for the surface temperatures higher than 100°C and the dependence of the temperature of heating of the back wall ΔT_{wc} (°C) on the integral temperature $T_{\Sigma wh}$ (°C · sec) for the testing time $\tau = 200$ sec (Figs. 7 and 8). The integral temperature obtained for the surface temperature higher than 100°C was chosen as an argument of the first dependence under the assumption that, for lower values of temperature, the rate of mass loss is insignificant.

CONCLUSIONS

Thus, we have developed a domestic sprayed syntactic foam plastic. It is called the NTZP-U material and can be recommended as a heat-shielding material in the production of SE instead of the TTP-FSU-type material used earlier at the "KB Yuzhnoe" State Enterprise. The NTZP-U syntactic foam plastics contain up to 28.7–32.6% of the mixture of glass and polymeric microspheres (in the mass ratio 1:1) and have a lower mass loss than the TTP-FSU-type materials. Since, parallel with heat conduction, the temperature of heating of the back wall of the heat-shielding material is also determined by the total heat flow (characterized by the integral temperature of the heated surface) and by the thickness of the sample, all NTZP-U materials presented in Fig. 8 have the heat-insulating properties comparable with the corresponding properties of the TTP-FSU coating and satisfy the requirements imposed by the operating conditions of SE.

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