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THERMOSETTING BINDER FOR FIBROUS INSULATING MATERIALS *

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Statement of the problem. The modernization of insulation systems of engineering structures, including pipelines and industrial facilities, is aimed both at solving the general problems of energy efficiency, as well as the particular tasks of heat saving and environmental safety. In this regard, the development and use of a binder that cures at much lower temperatures and does not contain phenols is an urgent task.

Results. An experiment conducted to assess the effect on adhesion to various surfaces of a complex binder, cured in the temperature range from 80 to 140 °C, allowed us to determine the optimal flow rate of the latent component and modifier, which were respectively 3.6—4.0 % and 2.6±0.1 % by weight of a binder at an optimal heat treatment temperature of 100 °C. The calculation established that when switching from heat treatment at 250 °C to heat treatment at 100 °C, direct heat costs are reduced by 60 %, and energy costs for the manufacture of mineral wool cylinders by 20—30 %.

Conclusion. The possibility of using epoxy glue on latent hardeners as a binder for highly porous systems with the distribution and curing of this binder on thin mineral fibers was justified theoretically and confirmed experimentally. The characteristic parameters of the curing process were determined, the duration of which decreases with increasing temperature and the content of latent hardener.

Keywords: mineral wool cylinders, rock wool, phenolic binder, epoxy binder, latent hardeners, heat treatment, energy efficiency.

Introduction. The energy efficiency of building systems includes two main tenets: energy saving during operation and reducing energy intensity of production, which is the basis of Federal Law No. 261-FZ (as amended on July 29, 2017, and dated November 23, 2009).

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Energy saving is achieved through the use of materials with low thermal conductivity and high operational stability, which provides energy savings on the one hand and the standard durability of the structure and long periods of maintenance-free operation on the other [1—3]. Insulation of pipelines for hot water and steam supply of gas and liquid hydrocarbon transportation involves the use of non-combustible thermal insulation. This group of materials includes products based on foam glass, mats based on basalt fiber and products (mats and cylinders) based on mineral wool. The choice of a material is determined by the operating conditions as well as the energy costs of their manufacture. Note that the production of all materials of this group is associated with high-temperature processes and is thus energy-intensive [5, 6]. Foam glass is delivered to domestic facilities for import, which implies its high cost, and, the scope, limited only by special processes. The energy costs for the production of basalt fiber are 20—30 % higher than for the production of mineral wool. Therefore, the main insulation material for industrial facilities and pipelines are products based on mineral wool, or rather, products based on rock wool having an acidity module M_k 2.0—2.4, which determines their resistance in aggressive environments and temperature resistance up to 900 °C [7, 8].

The technology of mineral wool products assumes the presence of double energy-intensive conversions: melting of raw materials and curing of the binder in the heat treatment chambers. Work to reduce the melting point of melts while maintaining its acidity modulus and fiber properties is currently underway at the NRU HSE and NRU MSCU, but the most relevant way to reduce energy costs is to optimize the heat treatment of mineral wool products at the stage of manufacturing mineral wool cylinders in off-line installations [9, 10].

In modern technologies of mineral wool products, a synthetic binder based on phenol-containing compositions is used. The curing temperature of such a binder is of the order of 250 °C, curing occurs according to the polycondensation scheme, while the product contains concentrations of free (unreacted) phenol, which is extremely undesirable from the standpoint of sanitary standards. Thus, the transition to a phenolic-free binder, curing of which occurs at lower temperatures, will allow one, on the one hand, to reduce the energy intensity of the process, and on the other, to increase the sanitary safety of the same process, and thereby to reduce costs in two areas at once: heat treatment and for the construction of sewage treatment plants that neutralize flaky air. Epoxy binders meet the requirements to the greatest extent.

The relevance of the research is due to the development of products for thermal insulation of hot water pipelines using less energy-intensive technologies and, in particular, using phenol-free binder based on epoxy resins which is cured at much lower temperatures.

1. Statement of the problem. Epoxy oligomers are widely used in various fields of technology, in particular, as a component of binders for various composite materials with high physicochemical characteristics.

Epoxy adhesives have good adhesion to a large number of a wide variety of materials due to the presence of ether and hydroxyl groups, as well as excellent chemical resistance, and resistance to solvents, easily and quickly cure almost without emission of volatile substances. Small shrinkage during curing promotes the formation of adhesive films with a low level of stress. However, not always epoxy materials have sufficient ductility, i.e. resistance to brittle fracture, which is especially important for adhesives [11, 12].

The known methods for increasing the ductility of epoxy materials are reduced mainly to four directions: reducing the crosslink density, internal plasticization, creating a multiphase structure and using a flexible molecular structure. The crosslinking density is reduced by the use of high molecular weight diene oligomers, bifunctional components, e.g., diamines. Internal plasticization is achieved by the formation of a branched structure. The increase in the ductility due to the double-phase structure is carried out by introducing plasticizers (external plasticization), dispersing elastomer particles, creating interpenetrating systems of double polymers (epoxy-polyacrylic, epoxy-polyurethane, epoxy-polyester). A more flexible molecular structure is designed by using the starting reagents with long flexible molecules.

The use of various hardeners, fillers, modifiers allows one to control their structure and properties [13, 14] of the epoxy binder, but the temperature factor is important for curing the binder in mineral wool products, in addition to its durability and good adhesion. Hardeners of temperature action are materials that cause gelation only at elevated temperatures from 80—100 °C to 200—250 °C.

Curing accelerators are usually added in the amount of 1—3 % by weight of the epoxy resin. The same substances in the amount of 5—10 % are independent hardeners of epoxy resin by the polymerization mechanism. Depending on the activity of the hardener and the temperature, complete curing can be achieved in a time from a few seconds to 2—3 hours.

Based on the results of studying the state of the issue, a hypothesis has been set forth that an increase in the strength and service life of mineral wool cylinders can be achieved through the use of low-toxic thermosetting epoxy binder containing latent components (enhancing the adhesion of the binder to the fiber, regulating the curing temperature) during the heat treatment of mineral wool cylinders.

In accordance with the hypothesis, the aim of the study was to formulate the scientific foundations of energy-saving technology for mineral fiber cylinders with increased strength and

operational stability as well as to develop an energy-efficient technical thermal insulation system using mineral wool cylinders. To achieve the goal, the following tasks were performed:

- to analyze the technologies, types of binder and formulations of thermal insulation products and the use of these products in order to increase the energy efficiency of technical insulation systems;
- to research on the possibility of using thermosetting epoxy compositions on latent modifiers in order to use it as a binder for mineral wool cylinders.

The scientific novelty of the work was that it was theoretically justified and experimentally confirmed the possibility of using epoxy glue on latent hardeners as a binder for highly porous systems with the distribution and curing of this binder on thin mineral fibers. The characteristic parameters of the curing process were determined, the duration of which decreases with increasing temperature and the content of latent hardener.

2. Experimental methods of adhesive joint properties investigation. Studies of the properties of the adhesive joint were carried out in accordance with the methods of domestic standards. Shear strength was determined on the machine and for testing the strength of adhesive joints, allowing tensile tests and measuring the value of the load with an error of not more than $\pm 1\%$. The machine was equipped with special clamping heads (Fig. 1).

Fig. 1. INSTRON 3382 machine for testing adhesive joints:
a — general view; b — clamping head with the test sample

Research was carried out on various binder compositions, the adhesive properties of which were also investigated by applying a binder to metal plates followed by heat treatment.

Table 1

Experimental conditions

Name of factor	Symbol X_i	The average value of the factor, X_i	Range of variation, ΔX_i	Factor values at levels	
				–1	+1
The content of the latent component in the composite binder, %	X_1	3.0	2.5	0.5	5.5
Curing heating temperature, mm	X_2	110	30	80	140
Modifier content, %	X_3	2	1	1	3

In the process of testing adhesive contacts, an experiment was conducted to determine the relationship between the shear strength of the adhesive joint and variable factors. The following factors were considered as variable factors: latent component and modifier contents, heat treatment temperature. Binder curing and gluing of samples at temperatures in the range specified in Table 1 was fully completed within 4-6 minutes.

The full factorial experiment was carried out according to the D-optimal plan of type $2^3 + 2 \cdot 3 + 1$. In total, the plan provided for 15 experiments, at each point of the plan the experiment was repeated three times. By testing statistical hypotheses, a confidence interval of 0.5 MPa was determined. All coefficients smaller than the confidence interval were considered insignificant and equated 0.

3. Results. As a result of the experiment and processing, this obtained a mathematical polynomial (regression equation) of the form:

$$Y = 7.0 + 3.2X_1 + 1.2X_2 + 1.0X_3 - 1.2X_1X_2 + 0.8X_2X_3 - 0.6X_3^2. \quad (1)$$

The analysis of the coefficients of the regression equation shows that the consumption of the latent component has the greatest influence on the result (the coefficient at X_1 is 3.6), and with increasing consumption, the strength increases. The influence of the heating temperature is manifested to a lesser extent (coefficient at X_2 equal to 1.2) but also significantly. The effect of plasticizer consumption is not linear (the coefficients at X_3 and X_3^2 are equal to 1.0 and –0.6, respectively) and is extreme in nature. The magnitude of the extremum can be established by the method of local optimization [15, 16].

A coefficient at X_1X_2 equal to –1.2 indicates that the combined effect of the flow rate of the latent component and the heating temperature on the contact strength is significantly and inversely proportional, i.e., the strength increases (when factors change in the intervals of the experimental conditions). This antagonistic co-influence can be formulated as follows: as the consumption of the latent component increases and the heating temperature decreases, or the other way around, as the consumption of the latent component decreases and the temperature increases, the adhesive strength of the contact rises. The combined effect of modifier con-

sumption and temperature manifests itself as a synergistic effect: the strength increases not only due to a direct increase in the temperature and plasticizer consumption (all of them in the intervals established Table 1), but also due to the combined influence of these factors.

The complex effect of the modifier can be explained as follows. The introduction of a modifier with the plasticizing properties of the plasticizer into the initial binder improves the mobility of the mixture (as well as the temperature factor) and the wettability of the surface of glass fibers, and, accordingly, the concentration of thin binder films in the contact areas of the fibers (Fig. 2), which explains the increase in the contact strength in modified binder. An increase in the consumption of this substance in excess of the optimum reduces the strength of the binder adjacent to the glass fibers, which determines the decrease in the strength.

Fig. 2. The distribution of the binder in homogeneous contacts between the fibers

When studying the formation of adhesive compounds of adhesives and composite materials, wetting is considered as one of the main factors in the formation of reliable contacts [17—19]. Wetting depends not only on the energy of the bonded surface, but also on the temperature, degree of conversion and other factors. The viscosity of epoxy adhesives also has a significant effect on the strength of the contact (adhesive properties).

Equation (1) is a function of three variables ($Y = f(X_1, X_2, X_3)$) to which the methods of mathematical analysis and analytical optimization are applicable. Having found the partial derivative with respect to X_3 and equalizing it to 0, we can determine the local extremum of the base function (1) with respect to X_3 : $X_3 = 0.6 + 0.5X_2$ or with an average value of the temperature of heat treatment (120 °C), factor X_3 in the encoded values the flow rate of the modifier is 0.6, and in real terms 2.6 ± 0.1 %.

The optimized basic equation (1) when substituting the optimization function takes the form:

$$Y = 7.2 + 3.2X_1 + 2.1X_2 - 1.2X_1X_2. \quad (2)$$

A graphical interpretation of the optimized polynomial (2) was carried out and a nomogram of the relationship between the shear strength of the adhesive joint and the consumption of the latent component in the composite binder and the heating temperature during curing was obtained (Fig. 2).

Fig. 2. The relationship between the shear strength of the adhesive joint and the flow rate of the latent component in the composite binder and the heating temperature during curing, MPa:
1 — 2; 2 — 4; 3 — 6; 4 — 8;
5 — 10; 6 — 12; 7 — 14

The optimal content of the latent component in the complex binder is determined by means of the method of analytical optimization:

$$\frac{\partial Y}{\partial X_1} = 3.6 - 1.2X_1 = 0 \rightarrow X_1 = \frac{1.2}{3.6} = 0.33.$$

We carry out the transition from coded values to natural ones:

$$R_1 = 3.0 + 2.5 \times 0.33 = 3.7 \pm 0.1 \text{ \%}.$$

Taking into account the experimental error (5 %), the optimal content of the latent component should be within the range of 3.6—4.0 %.

As a result of the experiment, it was found that with a low content of the latent component of the composite binder, i.e., with compositions close to pure epoxide, the shear strength of the adhesive joint reduces significantly.

The combined effect of the flow rate of the latent component and the heating temperature on the contact strength is significantly and inversely proportional, i.e., the strength increases (with changing factors in the intervals of the experimental conditions) as does the flow rate of the latent component and the heating temperature decreases, or the other way around as the flow rate of the latent component and temperature decrease. The optimal content of the latent component is within the range of 3.6 to 4.0 %, and the optimal consumption of the modifier is within the range of 2.5 to 2.7 % by the weight of the binder.

The energy efficiency of new technological solutions was evaluated by the change in heat loss during heat treatment of mineral wool cylinders. Lowering the curing temperature of the epoxy binder on latent hardeners to 80—110 °C allowed us to reduce the heat treatment temperature to 100 °C, while for the curing of phenolic alcohols, the coolant temperature was 250—260 °C.

The heat content of the heat flux (kW) was taken as an evaluation criterion. In the first case, it was 913 kW, in the second 365. In relative units, the decrease in heat consumption by heat flux was $(913 - 365) / 913 = 0.6$ (or 60 %).

As for the energy performance of production of mineral wool cylinders, it is necessary to take into account the energy component associated with the production of mineral fiber, energy consumption for technological needs, etc. In this case, the estimated economic effect of reducing the heat treatment temperature by 150 °C is assumed to be 20—30 %.

The developed methodology for calculating the thickness of the insulating layer according to the standard value of the specific heat flux made it possible to establish the optimal flow rate of the insulating material, which enabled its consumption in insulation systems to be optimized both for thermal devices operating at temperatures not exceeding 80 °C and for devices and pipelines with an operating temperature of more than 100 °C.

Conclusions. The products for thermal insulation of hot water pipelines were manufactured using less energy-intensive technologies and, in particular, a binder based on epoxy resins that cured at significantly lower temperatures than the binders based on phenol compounds, have been developed.

The studies took into account that epoxy adhesives have good adhesion to glass and metal, as well as chemical resistance and resistance to solvents and easily and quickly cure almost without emission of volatile substances. Small shrinkage during curing promotes the formation of adhesive films with a low level of stress, which is specifically important at monolithic contacts of mineral fibers.

The scientific foundation of energy-saving technology for mineral fiber cylinders with the increased strength and operational stability, as well as the development of an energy-efficient technical thermal insulation system using mineral wool cylinders have been completed.

The result of the research was the rationale for the use of a complex epoxy binder on latent hardeners. Having obtained a low toxic binder for mineral wool products, one can reduce the curing temperature of the binder to 100 °C. The economic calculations justified a reduction in the energy consumption in the manufacture of products by 20–30 % while maintaining regulatory conditions for the maximum heat flow.

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