Development of methods for producing improved-quality mineral wool insulation tiles and binders for production

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Translation submitted by P. Curtis

After the issue of Resolution 18–81 (11 August 1995) of the Ministry of Construction of the Russian Federation concerning a significant increase in thermal insulation standards for buildings and structures (by a factor of ~2–3), the need arose to increase the thickness of thermal insulation on already constructed and newly built buildings and structures. In this context, it was required to create new low-toxicity thermal insulation, including mineral wool tiles (MWTs) of increased strength, water resistance, and durability. These properties of MWTs largely depend on the nature of the binder being used.

At present, a number of enterprises, including enterprises in the Urals region, are producing MWTs based on carbamide–formaldehyde resin of grade KS-11. Resin KS-11 is highly toxic, since it contains up to 4.5% free formaldehyde. The emission of formaldehyde from finished mineral wool tiles exceeds the safety norms, and therefore such tiles are authorised for application only in industrial building.

At the Urals State Wood Technology Academy (USWTA), in the Faculty of Plastics Processing Technology (PPT), a method has been developed for producing new carbamide–formaldehyde resin of grade MWTs for the production of PPT by forming a mineral wool carpet from pulp. The given resin contains 20 times less free formaldehyde than KS-11 (Table 1). PKP-52 resin is synthesised in three stages.

The functional composition of PKP-52 resin differs from that of KS-11 resin (Table 2). PKP-52 resin contains cyclic condensation products; its molecules have a branched structure. In KS-11 resin, cyclic condensation products are absent, and the structure of its molecules differs in a greater degree of branching and content of methylol groups by comparison with PKP-52.

The method for synthesising PKP-52 resin is protected by Russian Patent 21141306, MKI C 08 G 12/12. The production of resin PKP-52 has been assimilated at the “Uralkhimplast” Joint Stock Company (Nizhni Tagil, Sverdlovsk region), and the resin has a safety certificate.

| Table 1. Properties of carbamide–formaldehyde resins of grades KS-11 and PKP-52 |
|-----------------------------------------|----------------|----------------|
| Standard for grades                    | KS-11          | PKP-52         |
| Mass fraction of dry residue, %        | ≥62            | ≥67            |
| Mass fraction of free formaldehyde, %  | ≤5.0           | ≤0.25          |
| Nominal viscosity at 20.0 ± 0.5°C according to VS viscometer after preparation, s | 5–15           | 15–65          |
| Miscibility of resin with water by volume at 20 ± 1°C in 1:10 ratio | Full           | Full           |
Prior to this, under laboratory conditions, using resin PKP-52, series of sand–resin bars (SRBs) were manufactured to model MWTs. To confirm that SRBs were proper models of MWTs, a correlation analysis was made of the properties of bars and tiles having an identical binder content.

The analysis showed that, with increase in formaldehyde emission from the bars [Figure 2], there is a consistent increase in formaldehyde emission from the tiles. The correlation between the toxicity of the bars and tiles is fairly close. The paired linear correlation coefficient is 0.81.

With increase in the water absorption of sand–resin bars [Figure 1], there is likewise an increase in water absorption of MWTs. The correlation between the water absorption of SRBs and MWTs is close. The paired linear correlation coefficient is 0.8297.

### Table 2. Functional composition of PKP-52 and KS-11 resins (in rel.%)

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>KS-11</th>
<th>PKP-52</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylol groups [$\text{\text{CH}_2\text{OH}}$]</td>
<td>26</td>
<td>12</td>
</tr>
<tr>
<td>Total rings</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Triazinone rings</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Tertiary nitrogen atoms</td>
<td>33</td>
<td>26</td>
</tr>
</tbody>
</table>

**Figure 1.** Correlation field of water absorption of SRBs and MWTs

**Figure 2.** Correlation field of formaldehyde emission from SRBs and MWTs
absorption of the mineral wool tiles. The dynamics of increase in water absorption in the quantitative expression is identical on bars and on tiles. The correlation is closer than in the case of toxicity. The correlation coefficient is higher and amounts to 0.9. Thus, correlation analysis showed that, from the properties of sand-and resin bars, it is possible, with fairly high accuracy, to predict the properties of mineral wool tiles.

A study of the properties of SRBs manufactured using two carbamide resins showed that the cross-breaking strength of SRBs based on PKP-52 is similar, the water absorption is ~5% higher, and the formaldehyde emission is 3.4 times lower than in the case of SRBs based on KS-11 (Figure 3). The higher strength and water resistance of SRBs based on resin KS-11 is evidently connected with the greater number of methylol groups in this resin, and with the formation of a denser network and greater density of the resin after curing. The low formaldehyde emission from SRBs based on PKP-52 is due to the additional combination of formaldehyde in triazines rings in the presence of considerable quantities of ammonia in the resin.

The results of laboratory tests of SRBs were reproduced well on MWTs under industrial conditions.

At two enterprises of the Sverdlovsk region ("Tizol" AOOT, Nizhnyaya Tura; the "Bilimbai Thermal Insulation Materials Works" Open Joint Stock Company, Bilimbai), the production of rigid and semirigid MWTs and high-rigidity MWTs has been assimilated using PKP-52 resin, with a total volume of 30 000 m³/year. The new, low-toxicity thermal insulation mineral wool articles are protected under the trade name "TIMLAK".

The formaldehyde content in the air of the working zone of plants producing "TIMLAK" based on resin PKP-52 was reduced by a factor of 2–3 and amounted to 0.2–0.5 mg/m³, which is below the MPC of formaldehyde in the working zone.

The method for manufacturing reduced-toxicity "TIMLAK" based on resin PKP-52 is protected by Russian Patent 2114080 (MKI C 04 B 26/12). The new tiles have been granted a safety certificate from the Sverdlovsk Regional Health and Safety Inspectorate (certificate No. 10/10-271, 24 April 1996). The ecological safety of "TIMLAK" is confirmed annually by test results from the Sverdlovsk Regional Health and Safety Inspectorate. Owing to its low toxicity, the material has been authorised for use in civil housing.

"TIMLAK" produced by the Bilimbai Works is a fire-resistant material according to GOST 30244–94 and building codes, as indicated by fire safety certificate SSPB, RU UP001, B00414 issued on 8 June 1998 by the All-Russia Scientific Research Institute of Fire Prevention of the Russian Ministry of Internal Affairs.

Thus, the use of ammonia in synthesis made it possible to produce low-toxicity carbamide–formaldehyde resin of grade PKP-52 and ecologically safe and fire-resistant thermal insulation material "TIMLAK" based on it. However, as regards water resistance, "TIMLAK" is slightly inferior to analogous thermal insulation produced by the leading European companies – "ROCKWOOL", "URSA", etc.

Taking into account the experience of foreign companies and published data on the fact that increased water repellancy and strength is given to materials by phenol–formaldehyde resins, subsequently, for the manufacture of SRBs, use was made of different composites of PKP-52 resin and low-toxicity phenolic alcohol of grade FS-K(n), the production method of which was also developed in the PPT Department of the USWTA. The specifics of the production of phenolic alcohol FS-K(n) consisted in using the optimum quantity of catalyst calcium hydroxide in the form of an aqueous suspension.
In order to establish the optimum total quantity of composite binder in SRBs and the optimum proportion of phenolic alcohol in the composite, tests were conducted by a full factorial experiment design of type $N = 22$. Regression analysis of the obtained experimental data revealed the following adequate regression equations:

For the water absorption of bars
$$\hat{Y}_{[\text{water}]} = 2.9 - 1.65X_1 + 0.125X_2 + 0.15X_1X_2$$

For the emission of formaldehyde
$$\hat{Y}_{[\text{formaldehyde}]} = 8.12 - 1.245X_1 + 0.02X_2 + 0.355X_1X_2$$

For the cross-breaking strength
$$\hat{Y}_{[\text{strength}]} = 5.875 + 1.425X_1 + 2.575X_2 + 0.425X_1X_2$$

The equations confirmed previously obtained data from single-factor experiments which had indicated that, with increase in the proportion of phenolic alcohol in the composite, the strength of the bars increases, the water absorption and toxicity decrease, and, with increase in the total content of binder in the SRBs, their water absorption and strength increase, while the emission of formaldehyde hardly changes.

The regression equations were used to optimise the conditions for producing SRBs under the following constraints: water absorption 1–3%, formaldehyde emission 0–8 mg/100 g, strength $\geq 4$ MPa.

As a result of the optimisation, nine optimum variants were found with an identical 78% level of confidence. Among these, for economic reasons, the variant with a total binder content of 6% and a proportion of phenolic alcohol in the composite to 26% was chosen. The calculated water absorption of SRBs under conditions of the optimum amounted to 1%, the cross-breaking strength to 6.4 MPa, and the formaldehyde emission to 7.4 mg/100 g.

Control tests, conducted to assess the reproducibility of the calculated data, confirmed the agreement between actual and calculated values with respect to the formaldehyde emission and strength of SRBs but revealed a slightly higher experimental value of water absorption, which is easily explained by the achieved confidence level during optimisation.

Thus, the use of a composite binder based on low-toxicity carbamide-formaldehyde resin of grade PKP-52 and phenolic alcohol of grade FS-K(n) makes it possible to improve considerably the combination of service properties of articles. In the preparation of such a binder it is expedient to bring the proportion of FS-K(n) in the composite to 26%, and the amount of composite binder in the articles to 6%.

Since the industrial production of low-toxicity phenolic alcohol of grade FS-K(n) has yet to be assimilated, while phenolic alcohols of grades FS-B (based on potassium hydroxide) and FS-D (based on barium hydroxide) are produced by industry, these phenolic alcohols were also tested for the preparation of composites under the optimum conditions found.

The results showed (Figure 4) that similar and good properties are possessed by SRBs on composites with phenolic alcohols produced using alkaline-earth element hydroxides as catalysts. Bars based on composites of PKP-52 and phenolic alcohol of grade FS-B have worse indices with respect to water absorption and are characterised by greater toxicity.

Generalising the data obtained, and taking into account the greater availability of calcium hydroxide $Ca(OH)_2$ by comparison with barium hydroxide $Ba(OH)_2$, it is recommended in future to use a composite of carbamide resin of grade PKP-52 with phenolic alcohol of grade FS-K(n) as the binder for the production of mineral wool tiles. The total content of binder in the MWTs must be kept at a level of 6%, and the proportion of FS-K(n) in the initial composite binder must be kept at 26%.

The introduction of the new composite binder in MWT production will make it possible to produce a new-generation “TIMLAK” material which, in its entire combination of properties, will correspond entirely to equivalent foreign thermal insulation.