Alkali silicate protective coatings

L N Nazharova, G G Mingazova and R S Saifullin
Kazan national research technical university, Kazan, Russia
E-mail: mingazova_gg@mail.ru

Abstract. The work has developed compositions of coatings based on alkali silicate. The influence of the composition of the mixtures on the drying process, resistance to temperature changes, the characteristics of the coating (adhesion, time and degree of drying, solubility in water) were studied. It has been established that the replacement of liquid glass with sodium metasilicate in the composition of the coating improves the characteristics of the coatings.

1. Introduction
High rates of industrial development, the intensification of production processes, the increase in basic technological parameters (temperature, pressure, concentration of reactants, etc.) place high demands on reliable operation of equipment and building structures. A special importance in the complex of measures to ensure uninterrupted operation of equipment is paid to the development of reliable protective coatings and use of high-quality, affordable chemical-resistant materials.

The use of alkaline silicates for the production of protective coatings is based on their ability to form a durable waterproof coating possessing the necessary technical properties in case of being rejected by chemical reagents or during heat treatment. Therefore, compositions based on alkali silicates, possessing good adhesion to many materials, good astringent, protective, anticorrosive properties, are widely used in various industries [1].

The efficiency of using sodium silicate solutions is due to the availability and cheapness of raw materials, their incombustibility, non-toxicity, and the presence of a real industrial base. In addition, silicate film formers reduce the consumption of synthetic high-molecular compounds, the production of which is associated with sources of raw materials that have limited reserves [1,2].

The disadvantage of alkaline silicate solutions is the complexity of their transportation and storage, high chemical activity. Therefore, today in many technological processes, where liquid glass is traditionally used, the use of powdered or granulated hydrated silicates, which can quickly dissolve in water under normal conditions, becomes promising.

A relatively affordable and cheap method of obtaining soluble silicates is the dissolution of minerals containing alkaline forms of silica in alkaline solutions, followed by crystallization of hydrated alkali metal silicates.

The purpose of this work was to investigate the possibility of using sodium metasilicate pentahydrate and insoluble residues obtained by alkaline treatment of Inza diatomite in the composition of heat-resistant silicate coatings.

2. Objects and methods of research
For silicate coating preparation mixtures of substances and materials were used, the compositions of which are presented in table 1. Sodium glass was used as a binder (GOST – RF standards and
Regulations - 13078-81) with a module M = 2.4 and density ρ = 1.36 g/sm³; sodium metasilicate was synthesized from diatomite. As fillers we used limestone with a particle size of d ≤ 0.086 mm and the following chemical composition in mass %: CaO - 55.82; MgO - 0.33; Fe2O3 - 0.08; MnO - 0.004; SiO2 - 0.29; K2O - 0.05; Na2O - 0.07 or maxima clay of the Republic of Tatarstan with chemical composition in % by mass: SiO2 - 58.39; Al2O3 -15.62; TiO2 - 0.79; Fe2O3 - 6.52; MgO - 3.12; K2O + Na2O - 3.24. Sodium silicofluoride was added as a hardener in accordance with Specification 6-09-1461-76, and titanium (IV) dioxide was used as a pigment in accordance with Specification 6-09-2166-77. In compositions 3 and 4, an alkaline residue obtained by decomposing natural diatomite of the Inzinsky deposit with 20% sodium hydroxide solution was used as a filler and at the same time as a binder. The number of components for the preparation of the mixture was as follows: filler: hardener: pigment: binder = 1: 0.5: 1: 2. In the composition of coating 6, urea (GOST 6691-77) was used as a modifier to increase the shelf life of the system. According to the authors [3], it reduces the rate of coagulation-condensation structure formation processes and increases the stability of the physicomechanical properties of the coating. Coatings were applied on a substrate of Steel 3.

Preparation of the mixture was carried out as follows: we mixed filler, hardener and pigment in a mortar until a homogeneous mass. Then a solution of sodium silicate binder or an aqueous solution of sodium metasilicate was added to the prepared mixture. After that, the mass was stirred for another 5-15 minutes. The mixtures prepared in this way were brushed onto the substrate. The samples were dried at a temperature of 20-250 degrees Celsius until reaching constant weight.

During the tests we determined water losses during the drying process and the main operational properties of the coatings: adhesion of the coatings to the base according to GOST 15140-78. Tests for resistance to temperature differences were carried out according to the method of GOST 27037-86, time and degree of drying in accordance with GOST 19007-73.

3. Experimental results and discussions

We define silicate coatings as suspension of mineral fillers, hardeners and pigments in aqueous solutions of water-soluble silicates.

The choice of filler for silicate coatings was carried out on the basis of the operational requirements for these materials and their cost. In this case, to ensure the stability of the coatings to temperature extremes, refractory fillers of natural origin were used, such as limestone and clay, as well as the residue from the alkaline treatment of diatomite.

At the stage of preliminary studies we carried out the treatment of diatomite, which has the following mineralogical composition, %: X-ray amorphous silica - 70; montmorillonite - 14; mica - 7; kaolinite - 1; quartz - 8; feldspars - 1 sodium hydroxide solution for 3 hours. At the end of the synthesis process, the sodium silicate solution was separated from the undissolved diatomite particles by filtration. The solutions were evaporated and, upon cooling, sodium metasilicate pentahydrate was crystallized. According to the X-ray phase analysis and chemical analysis, the crystallization product corresponded to Specifications 6-18-161-82 on sodium metasilicate and was used in the composition of coatings 1, 2, 3, 6 as a binder. The undissolved part of the diatomite after separation on the filter was used in the composition of silicate coatings as a filler and binder in compositions 4 and 5. The results of XRPA showed that due to leaching of amorphous silica from diatomite, clay minerals (49%), quartz (33 %), feldspars (18%), residual content of amorphous silica (3.5%) [8].

Table 1. The qualitative composition of the studied mixtures.

| Components   | Solution 1 | Solution 2 | Solution 3 | Solution 4 | Solution 5 | Solution 6 |
|--------------|------------|------------|------------|------------|------------|------------|
| Limestone    | +          | -          | -          | -          | +          | +          |
| Clay         | -          | +          | -          | -          | -          | -          |
| Titanium Oxide (IV) | +          | +          | -          | -          | +          | -          |
| Sodium fluoride | +          | +          | +          | +          | +          | +          |
| Sodium Metasilicate | +          | +          | +          | -          | -          | +          |
| Water        | +          | +          | +          | -          | -          | +          |
During the preparation of mixtures we marked different viscosity and fluidity of the systems. In compositions 1 and 5 (with limestone), masses of a liquid consistency were obtained, hardening relatively quickly, possibly due to the formation of an insoluble double salt of the composition \( x\text{CaCO}_3 \cdot y\text{Na}_2\text{SiO}_3 \)\[^{[4]}\]. In the preparation of mixtures 2 and 4, which include clay, the masses had a higher viscosity, thick texture, which is associated with high absorption capabilities of clay and diatomite.

After applying the mixtures to metal substrates, the coating was dried under natural conditions and the mass loss in time was determined. The research results are presented in figure 1. As it can be seen from the curves, the loss of water mass by the coatings, which include limestone as a filler, is significantly less than that of the coatings that contain clay and an alkaline residue. This is due to the high absorption capacity of clay and the porous structure of diatomite. The use of metasilicate as a binder also increases the weight loss of coatings during the drying process, which is associated with increased water consumption in the preparation of solutions of metasilicate with a working viscosity.

![Figure 1. Weight loss of coatings during drying in natural conditions.](image)

It also has been observed that drying of mixtures with an aqueous solution of metasilicate takes longer than drying of the same mixtures with liquid glass, for example, the time during which the degree of drying 3 was reached for composition 1 was 40 minutes, for composition it was only 5-15 minutes.

As a result of testing the coatings for resistance to temperature changes from 200 to 20 °C, it was noted that coatings based on sodium metasilicate retain their solidity, do not swell, do not peel off. Coatings where liquid glass was used as a binder, bulged and exfoliated, which is probably due to enhanced and rapid moisture removal. Heating liquid glass to 110-120 °C causes the formation of a thin, low-porous film on the surface, making it difficult to filter water vapour and accumulate them under a layer of film. Thermal decomposition of silica gel and an increase in the volume of the coating occur with possible burnout of the binder due to the removal of adsorption and physically bound water, which leads to deformation and increased brittleness of the coating\[^{[6]}\].

Testing of water absorption coatings showed that all the studied coatings obtained by the method of natural drying were dissolved in water during the day, however, after their temperature treatment at 200 °C, the solubility of the samples decreased. The residual content of the coating on the Steel 3 plates after their exposure in distilled water under natural conditions during the day for samples 1, 2, 3, 6 was 0.17
%, respectively; 2.69%; 22.4%; 31% respectively. Samples 4 and 5 when heated to 200 °C swell and were not used in the solubility tests.

The unique ability of sodium silicate solutions is their high adhesive properties to substrates of various chemical nature, which is explained by the formation of interfacial chemical bonds at the adhesive-substrate interface [7]. The test results are presented in table 2. The coatings based on sodium metasilicate have the best adhesion to the metal substrate. Apparently, this is due to complex colloid-chemical processes occurring during the hardening of the composition. When mixed with grains of fillers in the dry state, metasilicate particles are well adsorbed on their surface and envelop it (a silicate film is created on the surface of the filler grain). When moistening the mixture, the particles of metasilicate dissolve in water, forming a sticky colloidal solution of alkaline silicate, the latter, enveloping the surface of the filler grains, cements them together. When the coatings are dried, the alkali silicate solution is concentrated and firmly binds the filler grains together into a single strong conglomerate [5]. In addition, a certain part of the silicate is hydrolysed by drying the coating. A gel of silicic acid is formed, which, enveloping the grains of the filler and compacting, additionally cements them. The adhesion index for the coating of a mixture of 6 is 1 point. Apparently, this is due to the presence of carbamide in the composition of the mixture, which enters into the role of “bridges”, crosslinking sodium silicate molecules, which possibly leads to the strengthening of the system [3].

Table 2. Adhesion evaluation of the investigated coatings.

| Composition | Score | Description of the coating surface after cutting |
|-------------|-------|-------------------------------------------------|
| 1           | 2     | Slight flaking of the coating in the form of small scales at the intersection of the grid lines |
| 2           | 3     | Partial or complete flaking of the coating along the grating lines of the lattice or at the points of their intersection |
| 3           | 1     | No damage and integrity of coatings at the intersection of the grid lines |

On the basis of the experimental data obtained, it can be concluded that it is possible to use sodium metasilicates and residues from the leaching of diatomite with sodium hydroxide solutions as silicate coatings. Sodium metasilicates have a favourable effect on the increase in the resistance of coatings to temperature differences in the range from 200 to 20 °C, improve their drying time and adhesion properties.

Acknowledgments
The authors acknowledge the assistance in performing x-ray and chemical analysis of minerals from Taliya Lygina, Alfia Gubaydullina and Alexey Shinkarev, staff of Central Research Institute of Nonmetallic Minerals Geology (Kazan).

References
[1] Korneev V I and Danilov V V 1991 Production and use of soluble glass: Liquid glass (Leningrad: StroyIzdat)
[2] Matveev M A and Rabukhin A H 1954 On the use of soluble glass for waterproof forms in precision casting Proceed. of Moscow Chem. Techn. Univ. 27 156-71
[3] Razgovorov P B 2008 Scientific basis for the creation of composite materials from technical and natural silicates (Ivanovo) p 37
[4] Pashenko A A, Serbin V P and Starchevskaya 1975 Binding materials (Moscow: High school)
[5] Matveev M A 1954 Getting unburned abrasive products based on hydrosilicate glass Proceed. of Moscow Chem. Techn. Univ. 18 135-41
[6] Ryzhov I E and Tolstoy V S 1987 Physico-chemical principles of the formation of the properties of liquid mixtures with liquid glass (Moscow: High school)
[7] Zhivykh V 2001 Structure and adhesive properties of epoxy resins (Moscow: RSTU)
[8] Filippovich E N, Khartsinov A I and Nazharova L N 2011 Synthesis of crystalline hydrates of
sodium metasilicate from diatomite of the Inzenskoe deposit. *Technics and technology of silicates* 18(3) 27-30