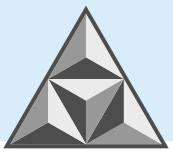

SCIENTIFIC ARTICLE

Production of a modified sodium liquid glass binder for construction work

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The paper considers the possibility of obtaining a high-quality binder based on sodium liquid glass suitable for construction works. According to the author, by varying the dilution of sodium silicate solution and carbamide concentration at a fixed elevated temperature (353 K) we can obtain a modified product with a certain molecular weight and a given particle size in the solution. Based on the data of thermomechanical analysis and testing the properties of 200-270 μm thick films obtained by curing the system "sodium liquid glass with a density of 1.36-1.41 g·cm^{-3} – carbamide", we have identified the conditions for providing the necessary hardness and tensile strength of the material. The author recommends the resulting modified material for using in silicate compositions for the protection and decorative finishing of mineral surfaces of building structures.

Keywords: sodium liquid glass, carbamide, modified binder, particle size, molecular weight, hardness, tensile strength of films

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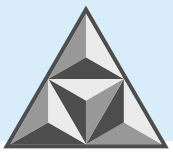

НАУЧНАЯ СТАТЬЯ
УДК 546.284 + 547.245

Получение модифицированного связующего материала из натриевого жидкого стекла для строительных работ

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Рассмотрена возможность получения качественного связующего материала на основе натриевого жидкого стекла, пригодного для проведения строительных работ. Показано, что путем варьирования разведения раствора силиката натрия и концентрации карбамида при фиксированной повышенной температуре (353 К) можно получить модифицированный продукт с определенной молекулярной массой и заданным размером частиц в растворе. На основании данных термомеханического анализа и испытания свойств пленок толщиной 200–270 мкм, полученных при отверждении системы «натриевое жидкое стекло с плотностью 1.36–1.41 г·см$^{-3}$ – карбамид», выявлены условия для обеспечения необходимой твердости и разрывной прочности материала. Полученный модифицированный материал рекомендуется использовать в составе силикатных композиций с целью защиты и декоративной отделки минеральных поверхностей строительных объектов.

Ключевые слова: натриевое жидкое стекло, карбамид, модифицированный связующий материал, размер частиц, молекулярная масса, твердость, разрывная прочность пленок

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INTRODUCTION

Previously [1-4] we have presented studies highlighting the prospects of introducing carbamide into liquid glass solutions (potassium, sodium, lithium) to produce a promising bonding material used for the protection and decorative finishing of building facades. We found, firstly, that it is possible to obtain a qualitatively new film-forming agent with improved properties (higher hardness, water resistance, and film flexibility) at higher temperatures (333-353 K). Secondly, the conditions for maintaining the rheological properties of the modified product [3] are established at a level required and sufficient for producing one-pack silicate materials, the benefits of which at the construction site are very substantial. For example, materials based on modified liquid glass are very cost-effective, environmentally friendly, fire-safe and have a long service life (at least 10 years). It is evident in the protection and decorative finishing of mineral and metal surfaces of building structures with compositions containing liquid glass modified with additives of various genes.

The materials of liquid glass with inclusion of carbamide are used in Russia to increase the adhesion and water resistance of the resulting materials [3, 5], as well as to make them cheaper in comparison to other materials suitable for surface protection of building structures. Sodium silicate liquid glass is thus of particular interest as an economical raw material compared to potassium silicate (potassium silicate liquid glass).

The purpose of this paper is to study the production conditions and strength properties of new binder materials based on non-deficient sodium liquid glass and a carbamide modifier. These conditions should provide a production of a new bonding material for single-pack sand lime paints, suitable for surface protection of modern construction sites.

EXPERIMENTAL PART

Materials

Sodium liquid glass, sand lime modulus 2.7-3.3, initial density 1.36-1.41 g·cm^{-3}; total sodium oxide and silicon oxide content 30.2-38.5 wt%.

Carbamide is of type "h"; melting point is 405.7 K at 1 bar, boiling point is decomposable.

Producing a modified binder

We filled sodium liquid glass with a modulus of 2.7-3.3 and a density of 1.36-1.41 g·cm^{-3} in the raw state or after dilution with water to a density of 1.12-1.24 g·cm^{-3} into a 250 mL three-neck flask with connections to a reflux condenser, thermometer, and stirrer. We added carbamide at an amount of 5.0-17.5 wt% to the system at room temperature and rotation of the stirrer at 60-90 s^{-1}, heated the mixture to a temperature of 343 K at a drift of ±1 K, incubated at this temperature until a conditional viscosity (system run out time) of 25-30 s was reached using a 100 ml VZ-4 funnel. The treatment time was 1-6 h, after which the modified binder was discharged, and its properties were analyzed.

Determination of particle size and molecular weight of the modified material

We estimated the average mass size of particles (r) by expressions (1)-(4), defining it through turbidity (expression (1)) and the optical density of the system (D), particle volume (v) (expression (2)) and index of refraction of the dispersed phase (expression (3)):

$$\bar{\tau} = \frac{2.303 \cdot D}{L}; \quad (1)$$

$$v = \frac{\bar{\tau}}{C_v \cdot P}; \quad (2)$$

$$P = \frac{24\pi^3}{\lambda^4} \cdot \left(\frac{m^2 - 1}{m^2 + 2}\right)^2; \quad (3)$$

$$r = \left(\frac{3v}{4\pi}\right)^{1/3}. \quad (4)$$

It should be noted that to calculate by formula (4), it is necessary to know the following parameters:

L is cuvette thickness (9.995 mm);

Cv is the volume concentration (proportion) of the dispersed phase [6];

$m = n_1 / n_0$ is the ratio of the refractive index of the "dry" film-forming substance (dispersion phase) [6] to the refractive index of the dispersion medium (water);

λ is the wavelength of light in a dispersive medium;

$\lambda = \lambda_{vac} / n_0$; λ_{vac} (wavelength in vacuum) = 665 nm [7].

We calculated the molecular weight of the formations in the sodium liquid glass solution according to the method of Tager [8]. According to Einstein's theory of fluctuational light scattering and Debye's provisions for sodium liquid glass (sodium silicate) solutions the following dependence is fulfilled:

$$\frac{Hc}{\bar{\tau}} = \frac{1}{RT} RT\left(\frac{1}{\bar{M}} + 2A_2 c\right) = \frac{1}{\bar{M}} + 2A_2 c. \quad (5)$$

Within the range of concentrations, we use

$$H = \frac{32\pi}{3} \cdot \frac{n_0^2}{N_A \cdot \lambda^4} \left(\frac{n - n_0}{c}\right)^2, \quad (6)$$

where N_A is Avogadro's number;

c is the concentration of the solution;

A_2 is concentration factor;

M is the average molecular weight of the compounds in solution;

λ is assumed in this case to be 665 nm.

We determined at the first stage $\frac{Hc}{\bar{\tau}}$ for sodium liquid glass solutions (1.5-4.5 g in 100 ml).

We have extrapolated on the ordinate axis the dependence obtained $\frac{Hc}{\bar{\tau}} = f(c)$ and at $c \to 0$ we found the value: $\frac{Hc}{\bar{\tau}} = \frac{1}{\bar{M}}$.

Also we determined the average molecular weight of the formations in the modified material.

Since the condition was met where the particle size (r) did not exceed the value $\lambda/20$, the necessary precision of the results was ensured experimentally.

Thermo-mechanical curve acquisition

We put samples of modified sodium liquid glass on a lavsan substrate. We dried the films at (273±5) K for 24 hours. Then we separated the film from the substrate and measured its thickness with a micrometer MK-0.25 with a division value of 0.01 mm. We selected the sample width so that the sample load was 0.8-1.0 kg·cm^{-2}; the sample length was 35 mm. We shot the thermo-mechanical curves on the UMIV-3 device at a diagram rate of 60 mm·h^{-1}. The rate of temperature rise was 1.8 K·min^{-1}.

RESULTS AND DISCUSSION

Dilution of sodium liquid glass with water with an initial density of 1.41 g·cm^{-3} to a density of 1.18-1.24 g·cm^{-3} causes intensive growth over time (2-6 hours) of particles when treated with carbamide at high temperatures (343 K) (Table 1).

Table 1. Particle size in sodium liquid glass solution at different degrees of dilution with water and carbamide treatment at 343 K

Processing time of sodium liquid glass, hours	Particle diameter in the system, nm			
	Sodium liquid glass (1.41*) + carbamide	Sodium liquid glass (1.36) + carbamide	Sodium liquid glass (1.24) + carbamide	Sodium liquid glass (1.18) + carbamide
0	8.0	8.5	8.8	9.3
2	8.7	10.2	10.3	10.8
4	9.1	10.9	11.5	12.3
6	9.3	11.2	11.8	12.5

* Density of the liquid glass solution is given in brackets, g·cm^{-3}

The author explains this with phenomenon by the accumulation of silica-type formations as described in the fundamental study [9]. The performed experiment and the following calculation of average molecular weights showed that at 343 K in diluted sodium liquid glass solutions with a density of 1.18 g·cm^{-3} with the introduction of 10 wt% carbamide modifier in time (up to 6 h), along with hydrolysis, the polycondensation process proceeds rather intensively. The molecular weight of the formations increases from 480 to 1200.

At the same time, the molecular weight of the modified film-forming material for construction works increases weakly from 710 to 780-800 with the transition to higher dilution solutions (density 1.12 g·cm^{-3}). This is due to the significant counteracting effect of depolymerization.

Dilution with water promotes the formation of polysilicon formations which should have negative impact on the film-forming properties of sodium liquid glass-carbamide systems [10]. In this regard, we propose to use sodium liquid glass with a density in the range of 1.36-1.41 g·cm^{-3} as an effective binder for construction works.

We studied particle growth (from 9 to 14 nm) in the system 'sodium liquid glass with a density of 1.36 g·cm^{-3} - carbamide' at a fixed temperature (343 K) by increasing the content of the modifier in the range from 5 to 15 wt% (Fig. 1).

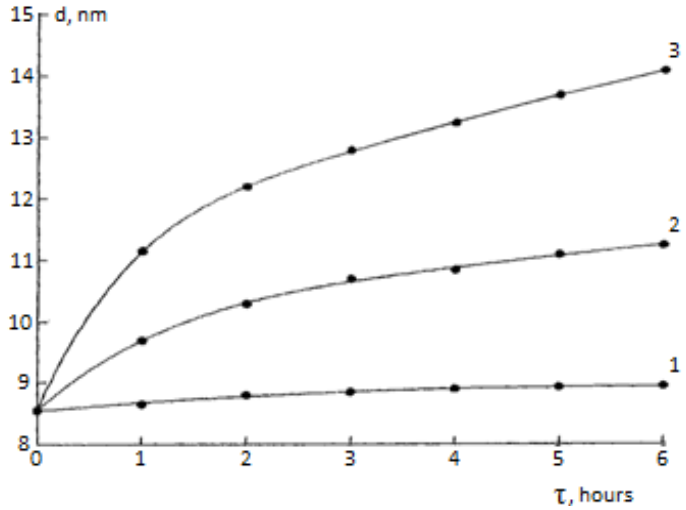

Fig. 1. Dynamics of particle entropy over time in a sodium liquid glass solution (1.36) when carbamide is introduced into the solution. Conditions: temperature 343 K; modifier concentration, wt%: *1* – 5; *2* – 10; *3* – 15

The average molecular weight of the modification product increases simultaneously with the increasing of colloidal particles in the solutions. It increases from 380 to 450 in treatment time (6 hours) at a concentration of 5 wt% carbamide. The increase of the carbamide concentration to 10 wt% doubles the average molecular weight of the product (380 to 760). However, the functional silanol groups in the binder solutions may be blocked by carbamide if the content of the modifying additive is high. The bonding is both chemical and physical in nature. In this case some of the carbamide, not interacting with the sodium liquid glass molecules, will contribute to the production of low-base silicates in the process of redistribution of solvation water. The study of the character of the thermomechanical curves (Fig. 2) indicates an increase in creep as the modifier is introduced.

To maintain a suitable binder/modifier ratio we recommend not exceeding 12-14 wt% of the latter. The presence of carbamide in the system in an amount of 15-17 wt% or more in sodium liquid glass (1.36) has a negative effect on the physico-chemical properties of the cured films.

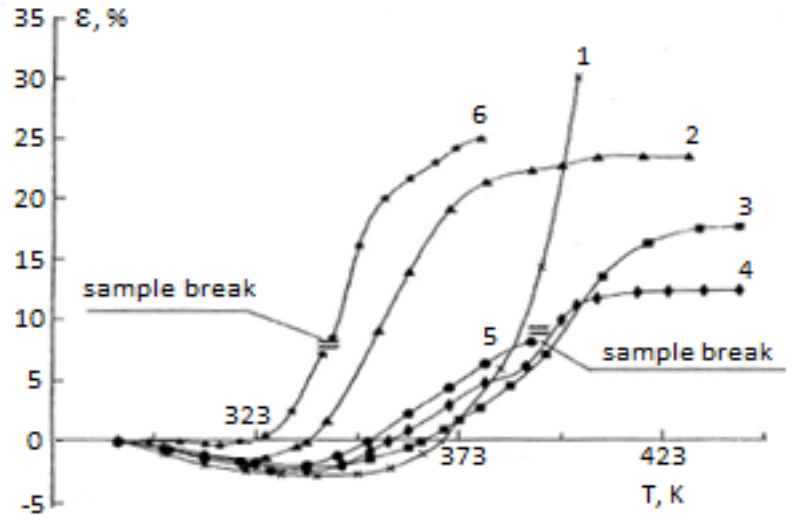

Fig. 2. Thermomechanical curves of films (270 μm thickness) made of sodium liquid glass (1.36) modified with carbamide in an amount, wt%: *1* – 0; *2* – 7.5; *3* – 10.0; *4* – 12.5; *5* – 15.0; *6* – 17.5. Conditions: Treat temperature with carbamide is 343 K, time 2 hours

Such negative consequences, which are a consequence of violation of the optimum ratio of crystalline and amorphous phases in the film, are described in the studies of V.A. Kargin [11, 12]. In particular, the tensile strength (σ) and absolute hardness (T, s) of modified product specimens decrease sharply due to an increase in the number of defects. According to the analysis of thermomechanical curves (Fig. 2, curve *6*), fracture of test specimens, which are characterized by "oversaturation" with modifier, can be realized already in the working zone of 333-338 K.

An excess of carbamide (from 12.5 to 17.5-20.0 wt%) contributes to a significant decrease (from 1230-1900 to 430-480) in the calculated molecular masses of the formations (M_r) in the modified binder (see fig. 3, curve *2*). In addition, the disruption of the molar ratio between the liquid glass and the modifier as well as the prolonged (τ = 6 hours) treatment at 343 K led to a sharp increase in the viscosity of the system. Stirring becomes problematic [13]; at the same time, a reduction in the performance of the resulting material is to be expected.

A relatively fast treatment (see Fig. 3, curve 1, τ = 2 hours) is, at the same time, possible with the specified amount of modifier. However, it would require a minimum variation of reagent concentrations (≤ 0.5 wt%) in the reactor volume. Thus, a suitable addition of carbamide to the sodium liquid glass solution should not exceed 10-12 wt%, and the treatment at 323-343 K is recommended to be conducted within 1-2 hours.

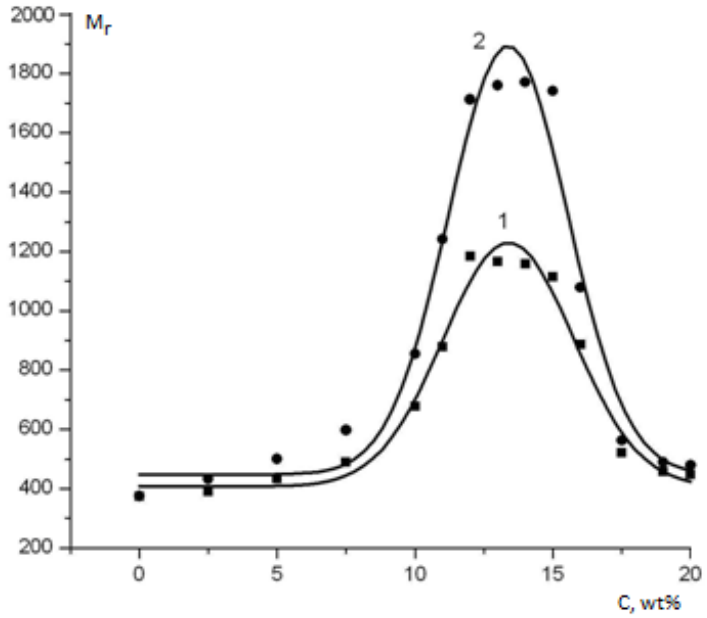

Fig. 3. Molecular weight of the formations in the modified sodium liquid glass (1.36) at different carbamide contents in the mixture
Conditions for carbamide treatment: temperature 343 K; time, hours: *1* – 2; *2* – 6

The molecular weight (Y) of carbamide-modified sodium liquid glass (1.36) changes according to equation (7) depending on the additive content in the solution (X, wt%):

$$Y = Y_0 + Ae^{-\frac{(x-x_C)^2}{2w^2}}. \quad (7)$$

If the treatment time is 1-2 hours, the following calculated coefficients for equation (7) are revealed: A = 822.9 ±36.6; x_C = 14.0±0,1; w = 2.37±0.15; Y_0 = 407.4±24.4.

Calculation factors for the polycondensation process when treating sodium liquid glass with carbamide for 6 hours are: A = 1445.7±74.9; x_C = 13.4±0,1; w = 2.16±0.16; Y_0 = 448.1±45.8.

The R^2 coefficients in the range 0.975-0.983 confirm that equation (7) adequately describes the formation of new structures in sodium liquid glass at carbamide modifier concentrations of 0-20 wt%.

The curves of tensile strength and average hardness (Fig. 4) show resulting modification of liquid glass solutions with a density of 1.41 g·cm^{-3} and the formation of a three-dimensional lattice structure. The predictions about increase of cross-linking degree of compounds during carbamide treatment of sodium silicate are confirmed [3, 4]. The presence of a maximum on the σ-curve can be explained both by cross-linking between OH groups, which is reflected in film hardening, and by the factor of internal stresses growth. These stresses stimulate the growth of microcracks in the resulting product.

The growth of internal micro-cracks on structure defects during fast polycondensation processes is not compensated by polymer thickening (light refraction index decreases only by 0.001-0.002 units). In this case, the strength of the cured films increases. If the modification process lasts at least 4 hours, the micro-crack growth factor already dominates. As a result, the breaking strength (σ) decreases. As for the average absolute hardness of the films, already in the first 2-3 hours of carbamide treatment acceptable hardness values (98-105 s) are reached (see Fig. 4).

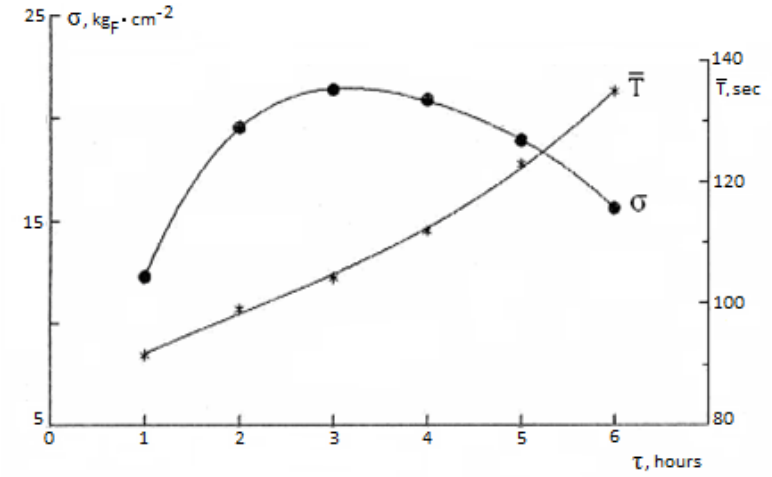

Fig. 4. Dynamics of changes of strength and average hardness of films (200 μm thickness) from the system "sodium liquid glass (1.41) – carbamide (12.5 wt%)" during treatment with the modifier at 343 K

The presented data confirm the possibility of mixed nature of interaction of sodium liquid glass molecules and carbamide modifier to obtain a quality binder suitable to produce protective building materials. A new product with silazanic bonds can be expected at 333-353 K under conditions of stirring the system with an intensity of 60-90 s^{-1} [4]. On the other hand, an increased content of carbamide in the system (> 12.5-15.0 wt%) should not be excluded an intensification of the desalting effect of carbamide on the liquid glass. In this case the redistribution of solvation water will contribute to the formation of low-base silicates.

CONCLUSIONS

Therefore, to maintain the necessary film-forming properties of sodium liquid glass used to prepare protective materials in the construction industry, the density of its solutions diluted with water should be in the range of 1.36-1.41 g/cm^3.

The introduction of carbamide as a sodium silicate liquid glass modifier at 333-353 is reasonable and justified for all cases, provided the threshold concentration of the introduced additive is 12.5-15.0 wt%, and the treatment under stirring does not exceed 2-3 hours. The particle size in modified sodium silicate solutions should not exceed 15 nm and the average molecular weight of the polymer compounds should not be higher than 1600-1800. Otherwise, defects in the modified product will be activated and the sample will be damaged already in the temperature range of 333-338 K.

We obtained data on the change in molecular weight, breaking strength, and absolute hardness of the modified binder during the treatment of sodium liquid glass with a modifier. We obtained regression equations describing with a high degree of accuracy (R^2 = 0.975-0.981) an increase in the average mass of polymer formations in the system as the urea modifier addition increases.

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