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Розроблено технологію виготовлення склозв'язок-активаторів для інтенсифікації спікання керамічних матеріалів, зокрема – ангобних покриттів. Проведено порівняльний аналіз склозв'язок, отриманих за допомогою традиційної варки скла та шляхом золь-гель синтезу. Встановлено значну ефективність останнього, оскільки зменшуються енерговитрати на термообробку композиції (замість варки скла при 1300–1400 °С потрібна термообробка гелю до 600 °С) та підвищується однорідність склозв'язки (хімічний склад композиції усереднюється на молекулярному рівні).

Досліджено також різні золь-гель способи одержання склозв'язок-активаторів: порошковий золь-гель спосіб без прожарювання; золь-гель спосіб приготування розчинів солей; порошковий золь-гель спосіб з плавленням композиції. Зазначені способи відрізняються послідовністю та методом змішування вихідних компонентів, але обов'язковою є диспергація в гелеутворюючому агенті – етилсілікаті ЕТС-40. В якості основних складових активатора обрано розчинні солі $Al(NO_3)_3 \cdot 9H_2O$, $Ca(NO_3)_2$ та $NaNO_3$. Вивчено особливості зміни фазового складу склозв'язок під час їх нагріву до 600 °С та встановлено, що отримані композиції наближуються до аморфного стану при температурах ~600 °С. При подальшому нагріванні дослідних склозв'язок до 1000 °С відбувається їх інтенсивне плавлення, при чому у перших двох способах в'язкість та поверхневий натяг розплавів є меншим, у порівнянні зі звичайним склорозплавом, тому змочувальна здатність склозв'язок-активаторів є вищою.

При введенні даних активаторів спікання до складів керамічних покриттів встановлено, що найбільш ефективним є активатор, отриманий способом приготування розчинів солей. Саме він після випалу при 1170 °С забезпечує формування найбільш щільної структури спеченого покриття зі зниженим водопоглинанням (не більше 0,05 %) та високою білизною поверхні (87–88 %). Розроблені активатори можуть стати альтернативою традиційним склозв'язкам, для варки яких потребуються значні енергоресурси.

Ключові слова: золь-гель спосіб, активатор спікання, ангоб, випал, водопоглинання

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DEVELOPMENT OF A SOL-GEL TECHNIQUE FOR OBTAINING SINTERING ACTIVATORS FOR ENGOBE COATINGS

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1. Introduction

Under conditions of constant growth of energy costs and the deficit of energy resources, a pressing issue in the ceramic industry where products are annealed at high temperatures is energy efficiency. In order to ensure the intensive sintering process of ceramic products and coatings, it is required to achieve a high degree of activity of all components in the ceramic charge [1]. However, the activity of starting components under actual industrial conditions is often quite

low, which leads to the necessity to sinter materials at high temperatures. Otherwise, one observes a deterioration in the physical-mechanical characteristics of the fabricated products.

One of the possible solutions to the specified task is the application as part of the charge of specialized sintering activators [2], which would make it possible to significantly improve products quality, without introducing radical changes to the technological process, and to considerably reduce the temperature of their annealing.

The most common method in the ceramic technology is the application of glass ligaments as the sintering activators [3]. However, obtaining in line with a conventional technology implies glass melting at temperatures of 1,250–1,400 °C to be followed by fritting, which is rather energy intensive. Therefore, there is the constant search for promising new methods for obtaining compositions with a polyoxide formulation, and a sol-gel could become one of them.

At present, the sol-gel method is the most promising one for obtaining highly-active compositions. It is implemented at the expense of hydrolysis of the appropriate compounds of elements that are included in the composition of an oxide system [4]. A special feature of the sol-gel synthesis is that the fragments of a would-be composition occur in a gel, thereby minimizing the diffusion barriers during a solid-phase interaction between components.

The advantages of the sol-gel technologies include: high chemical uniformity of multicomponent systems, high surface energy of gels and powders, which contributes to a decrease in the temperature of sintering. In addition, there is a possibility to obtain products in the form of powders, films, microspheres, glass, fiber. It is possible to implement a direct transition of synthesis products from the amorphous to crystalline state without the need to introduce mineralizers. In addition, it is possible to control the properties of the synthesized ceramic materials and glass with high precision.

Therefore, it is a relevant task at present to undertake a study the results of which would establish the technological parameters for obtaining glass ligaments-activators by using a sol-gel technique in order to produce the engobe coatings.

2. Literature review and problem statement

The largest body of scientific research addresses the obtaining of synthetic silica via a sol-gel method [5] and the basic processes that accompany it. The monomer solutions of silicon compounds can be obtained through the hydrolysis of halides, complex ethers, or acyl derivatives, for example, silicon tetraacetate. Subsequently, ethyl silicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ [4] and silicon tetrachloride SiCl_4 have become the most common starting raw materials.

It is known [6] that there is possibility to obtain, by applying a sol-gel technique, glass coatings in the system $\text{SiO}_2\text{--CaO--P}_2\text{O}_5$ on the porous ceramics of β -tricalcium phosphate. The received materials are intended to restore bone tissue through the high activity of glass when the frames are thermally treated. However, they are too expensive for large-tonnage production.

Paper [7] described a scheme of sol-gel method in order to make eyeglasses and related materials. Such a method makes it possible to synthesize glass at relatively low temperatures, as well as prepare new optical glasses, which cannot be made via conventional melting technologies. However, it is a multistage and complicated method, while the composition of glass typically includes compounds of TeO_2 , B_2O_3 , AlF_3 and others, which are costly and thus impractical for use in the construction industry.

Work [8] employed a modified sol-gel method in order to synthesize ceramics of the ilmenite type with controlled dielectric properties, which demonstrates broad applicability of a given method not only to glass-like, but also to ceramic, materials. However, the work applied this method to the

system $(\text{Zn}_{1-x}\text{Cd}_x)\text{TiO}_3$, whose synthesis requires scarce soluble compounds and is appropriate for a narrow circle of specific dielectrics.

A sol-gel method is also used in [9] for the synthesis of cordierite ceramics with high thermal stability, which, when manufactured by conventional methods, is expensive because it requires finely-dispersed chemically pure reagents and high temperature of annealing. The sol-gel method ensures a lower temperature of material synthesis, improved uniformity, and tighter control over the composition and manufacturing conditions for products. However, the materials obtained based on the system $\text{MgO--Al}_2\text{O}_3\text{--SiO}_2$ have high-temperature eutectics; these materials cannot be used as glass ligaments.

There are data [10] about obtaining pigment compositions using the aqueous solutions of sol-gel. It is noted that the structure in the gel-like state is capable of absorbing a greater amount of coloring ions than that in the crystalline state. In the specified work, there are interesting techniques for mixing the components and the substantiation of gel-forming processes, though it fails to consider the way in which a colorless glass-like composite could be obtained.

Therefore, the above data [5–10] clearly shows the advantage of materials that were received via sol-gel methods in comparison with the conventionally made analogs, as well as the dependence of synthesis products on a large number of technological factors [4, 10–12], production conditions, raw materials, as well as the ratio between components, etc. Most of the developed materials belong to complex oxide systems that have specific properties maintaining which requires the use of scarce and expensive materials. No data about obtaining the most common fusible glasses, specifically the system $\text{Na}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2$ [13], have been found. That can be explained by that in the large-tonnage production of glass the sol-gel process does not make much sense because of the extremely large consumption of raw materials. Industrial glasses (window, tare) will always be made through the conventional melting. However, it is of interest to obtain, within a specified system, the fusible oxide glass ligaments, which could be added in small quantities to the composition of ceramic masses or coatings, and to act as the “activator” of sintering. Thus, there is a need to conduct thorough research into development of the composition and the sol-gel technology for obtaining activators- glass ligaments in the system $\text{Na}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2$.

3. The aim and objectives of the study

The aim of this work is to establish the effect of sintering activators, obtained through the conventional melting, and activators, received from different variants of sol-gel techniques, on the properties of engobe coatings, and to identify the most rational technique for obtaining a glass-like activator. This would make it possible to improve the quality of engobe coatings and to reduce the labor- and energy- intensity of their production.

To accomplish the aim, the following tasks have been set:

- to synthesize glass-like sintering activators by various techniques, based on the sol-gel processes, and to explore their properties by comparing them with the activator that is obtained via glass melting;

- to establish the effect of activators on the technological properties and quality characteristics of engobe coatings;

– to identify the most rational technique for obtaining a glass-like activator.

4. Materials and research methods

In order to manufacture a glass ligament-activator, we have chosen the silicate system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, which includes eutectic compositions with melting temperatures of 740–1,050 °C [13], which is sufficient to intensify the sintering of many types of ceramics and coatings. Chemical composition of the base glass is given in Table 1.

To fabricate a glass ligament in line with a conventional technique that involves glass melting, we used enriched quartz sand and chemically pure oxides Al_2O_3 , CaO and Na_2O . Glass melting was carried out at the laboratory silite furnace at a temperature of 1,350 °C.

Table 1

Chemical composition of basic glass, % by weight

SiO_2	Al_2O_3	CaO	Na_2O	Σ
72.39	2.44	11.65	13.53	100.00

In order to synthesize a glass ligament via a sol-gel technique, we used the ethyl silicate ETS-40 as the base of the composition, and soluble salts $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 , graded “pure”. The formation of sol was carried out at a constant agitation of ingredients [4]. Following the poly-condensation, the resulting gels were dried under natural conditions, sintered, ground; the received ultra-disperse powders were then introduced to the composition of engobe.

The qualitative phase composition of the examined materials was determined using the X-ray general-purpose diffractometer DRON-3 (made by NVP “Burevisnyk”, Russia).

The microstructure of glass ligaments was examined in the passing light using the optical microscope NU-2 (Carl Zeiss Jena, Czech Republic).

For the engobe ceramic slurry, we defined a yield indicator using the Ford bowl, which specifies the time required for 100 ml of suspension to flow through the opening in the bowl the size of 4 mm.

For the sintered engobe coatings, we determined water absorption [14] based on the amount of water absorbed by a sample, saturated in a vacuum; coefficient of diffuse reflection – by using the color comparator KT-3 (AOOT “Zagorsky optical-mechanical plant”, Russia).

5. Results of research into glass ligaments, obtained by different techniques, and their effect on the sintering of engobe coatings

5.1. Synthesis and examination of the base glass

In order to receive a densely-sintered ceramic coating, a composition of the charge is typically introduced with a finely-ground glass-like component (glass, cullet, or frit). Formation of the liquid phase at temperatures lower than the sintering temperature of a ceramic coating leads to the intensification of high-temperature processes that form a dense structure [15]. However, the use of the specified products is accompanied by considerable difficulties: for case of utilizing cullet, they are related to the need to provide a constant amount of the recycled product with a certain per-

manent chemical composition; for the case of applying glass or frit, an additional high-temperature melting is required, which significantly increases the cost of a product.

In order to compare the properties and influence of the examined activators, in this work the glass ligament was received via conventional glass melting. The base glass was the synthesized glass with a predefined chemical composition (Table 1). To this end, the purified silica sand was thoroughly mixed with chemically pure oxides of Al_2O_3 , CaO and Na_2O ; glass melting was carried out at the laboratory silite furnace at a temperature of 1,350 °C; the melt of glass was then fritted in water. For the further research, the glass was crushed until its complete passage through sieve No. 0063. The resulting glass (Fig. 1) was in the X-ray amorphous state, which is confirmed by the presence of an X-ray amorphous halo at the radiograph. We also registered diffraction maxima for such crystalline substances as $\text{CaO} \cdot \text{SiO}_2$ (3.31; 2.95; 2.45; 2.16; 1.81; 1.73 Å) and $\beta\text{-SiO}_2$ (4.25; 3.34; 1.81 Å).

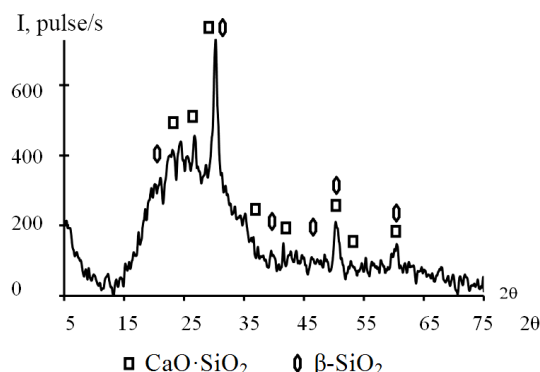


Fig. 1. Radiograph of the examined base glass

5.2. Synthesis and examination of activators-glass ligaments by different sol-gel techniques

In order to obtain glass-like sintering activators via a sol-gel method, we have chosen water-soluble nitric acid salts, whose characteristics are given in Table 2. The choice of these salts is predetermined by the relatively low temperatures of decomposition. The source of silicon oxide and the gel-forming agent used in the examined activator is the ethyl silicate ETS-40. Material composition of the examined glass ligaments-activators is given in Table 3.

Table 2

Properties of starting materials [16]

Material title	Melting temperature, °C	Decomposition temperature, °C	Water solubility, %
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	70.0	150	70.7
$\text{Ca}(\text{NO}_3)_2$	561.0	561>	55.8
NaNO_3	306.8	380	46.8
Ethyl silicate ETS-40 (SiO_2)	1,728	–	–

Ethyl silicate ETS-40 ($(\text{C}_2\text{H}_5\text{O})_{12}\text{Si}_5\text{O}_4$) is an organosilicon fluid that is a mixture of polysilicon acids [4]; it is not a binding material as long as there is no hydrolysis, that is, until it interacts with water.

During hydrolysis, ethoxy groups ($\text{C}_2\text{H}_5\text{O}$) are substituted with hydroxyl groups (OH). The result is the formed sols, that is, colloidal solutions of acids. The hydrolysis can

be performed when adding any amount of water; in this case, the reaction takes place:

Table 3

Material composition of the examined glass ligaments-activators No. 1, No. 2, and No. 3, % by weight

Component title	Quantity, g	% by weight
Ethyl silicate ETS-40	180.98	74.04
Water-soluble salts:		
Al(NO ₃) ₃ ·9H ₂ O	10.78	4.42
Ca(NO ₃) ₂	34.11	13.95
NaNO ₃	18.55	7.59
Total	63.44	100.00



The products of hydrolysis undergo polymerization, forming polymers of linear structure, in which inorganic main chains of molecules, built from atoms of silicon and oxygen (–Si–O–Si–) are combined in ethoxy groups.

A sol-gel process includes obtaining a sol and its consistent conversion into a gel. At the first stage of the sol-gel process, there forms a chemical composition of the product (the chemical form of a substance and the ratio between components), which is received in the form of a highly-dispersed colloidal solution – sol. The particle size in the disperse phase in a stable sol is 10⁻⁹–10⁻⁶ m. Increasing the concentration of a disperse phase leads to the occurrence of coagulating contacts between particles and to the onset of structure-formation – the gel-formation (the second stage in the sol-gel process). Coagulating structures are characterized by a low strength, determined by van der Waals forces; in this case, interaction between particles is enabled through the layer of the dispersion medium; its thickness is in equilibrium. For the so-called coagulating structures of distant interaction, the force of interaction between particles is 10⁻¹¹–10⁻¹⁰ N/contact, while the distance between them is 10⁻⁸–10⁻⁷ m [4]. Such structures are characterized by the complete spontaneous restoration after mechanical destruction (thixotropy).

A further increase in the volumetric concentration and the surface of the disperse phase leads to a gradual disappearance of the capacity for thixotropic recovery, and, in proportion to a decrease in the content of the dispersion environment, the elastic and plastic properties are lost. When fixing the particles in the structure, corresponding to the close coagulation, the strength of coagulating contacts increases to 10⁻⁹–10⁻⁸ N, while the distance between the particles reduces to 10⁻⁹ m. At this stage, there may also occur the atomic (point) contacts that are characterized by a strength of 10⁻⁸–10⁻⁶ N/contact. Under actual conditions, most often occurring are the coagulation structures of both types.

Following the removal of a dispersion medium (the third stage of the process), the solid phase contacts emerge; in this case, the thixotropic properties are lost and the mechanical destruction of the structure becomes irreversible. When dried, gel turns into a solid fine-porous body (xerogel) that has a condensation-crystallization structure. In the process of drying, there may occur a noticeable compaction of gel, as well as a change in its structure.

Taking into consideration the mechanism of gel-formation, as well as known practice [4, 11, 17, 18], in this study we

have selected three possible techniques for the synthesis of glass ligaments, which were conditionally termed as follows:

- 1) a powder method without calcination;
- 2) a method for the preparation of solutions of salts;
- 3) a powder method with salt melting.

The specified methods differed by a technique for mixing the starting components, while their dispersion within the gel-forming base (ethyl silicate) was mandatory.

I. Obtaining the activator via a powder method without calcination. A special feature of this method is that it did not include the dissolution of salts in water, that is, it implied a decrease in the energy consumption required to calcinate a composition. Technological scheme of the technique is shown in Fig. 2.

In order to prepare glass ligament-activator No. 1, salts in the assigned ratio (Table 3) were dissolved in a solution of ethyl silicate at constant agitation by an electric stirrer (800 rpm). To accelerate gel-formation, we added an acid catalyst (nitric acid). A colloidal system was formed in 10–60 min., which passed into the gel-like state; the time of gel-formation depended on the amount of the acid catalyst and water (Fig. 3).

The reported results show that an increase in the amount of water and the acid catalyst resulted in a decrease in the period of gel-formation in line with a hyperbolic curve, which agrees with data by author of [4]. In this case, the decisive factors are: the amount of water – the need for its further evaporation is limited, as well as energy consumption, and the amount of nitric acid – limited by its cost.

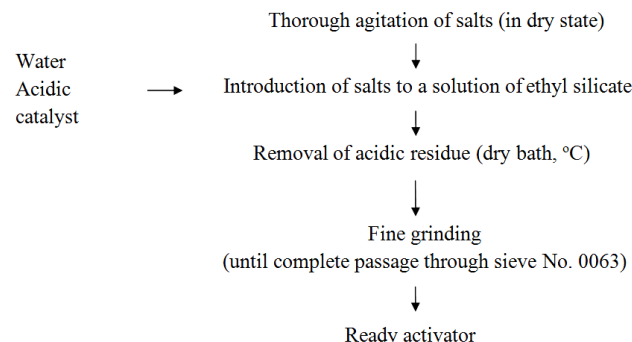


Fig. 2. Technological scheme for obtaining glass ligament-activator No. 1 via a powder method without calcination

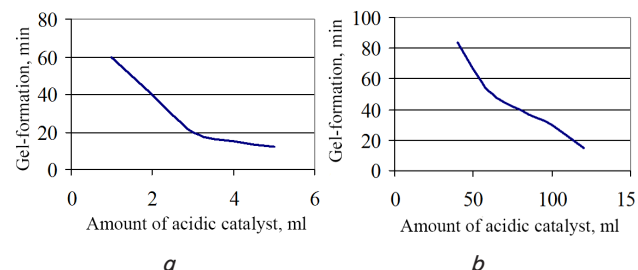


Fig. 3. Influence of quantity of technological factors on gel-formation time of the system: a – acidic catalyst, b – water

Thus, we accepted the parameters at which time of gel-formation was 30 minutes to be optimal (the amount of nitric acid is 2.5 ml; water, 100 ml per 20 g of dry composition).

The resulting gel was dried on a sand bath at a constant temperature of 200 °C. It was assumed that the first to be decomposed at 150 °C had to be aluminum salt, and given

the high activity of components, free aluminum oxide “captures” the nitric component from other salts that also decompose. There occurs a “chain reaction”, which stimulates the decomposition of other salts. An evidence for the release of nitric oxide was a distinctive smell during the progress of the reaction.

In order to determine the phase composition of glass ligament-activator No. 1, we performed its X-ray phase analysis in a dried state, after thermal treatment at a temperature of 200 °C, and in the sintered (at 600 °C) state (Fig. 4).

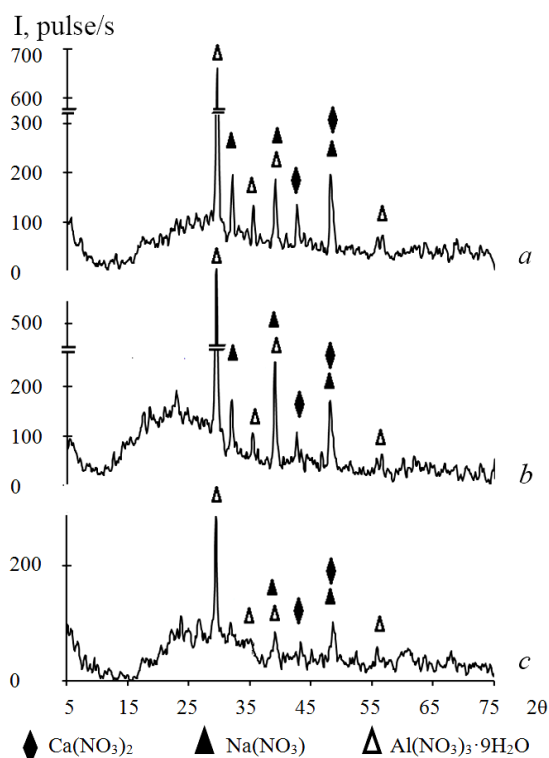


Fig. 4. Radiographs of examined activator No. 1: *a* – in a dried state, *b* – after thermal treatment at 200 °C, *c* – after thermal treatment at 600 °C

The above radiographs show that the result of synthesis is the formed glass-crystalline substance. The radiograph of the dried material demonstrates diffraction maxima, characteristic of $\text{Na}(\text{NO}_3)$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and to a lesser extent of $\text{Ca}(\text{NO}_3)_2$.

The latter partially correlates with temperatures of substance decomposition (Table 2), since the lowest temperature is demonstrated by the compound $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ – 153 °C, which is why during thermal treatment even at 200 °C Fig. 4, *b* shows small (residual) peaks, characteristic of this substance. After heat treatment at 600 °C, the diffraction maxima for these compounds significantly reduce; the substance acquires an amorphous state. Therefore, according to the derived radiographs, it is possible to obtain a glass-like ligament using technique No. 1.

To determine the character of melting, glass ligament-activator No. 1, together with the conventionally melted glass, was exposed to thermal treatment at temperatures of 800 and 1,000 °C (Fig. 5).

The above figure shows that a powder of the basic glass at 800 °C takes a well sintered, but not melted, form. Following the heat treatment at 1000 °C, the glass molten, but, due to

the high surface tension of the melt, the sample is “assembled” in the form of a large drop. The examined powder at 800 °C also demonstrates a sintered, not melted, form. The black color of the powder is due to the residual products of decomposition of salts. At 1,000 °C, there are signs of swelling in the composition.

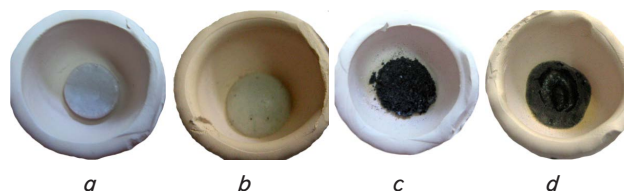


Fig. 5. Character of glass ligament melting: *a* – basic glass at 800 °C; *b* – basic glass at 1,000 °C; *c* – examined glass ligaments-activator No. 1 at 800 °C; *d* – glass ligament-activator No. 1 at 1,000 °C

Thus, the resulting binder, obtained via a sol-gel method, which melts at temperatures below 1,000 °C, could be used in compositions of ceramic masses or engobe coatings in order to intensify their sintering. A limitation relates to dark coloration of the powder.

II. Obtaining the activator using a method for preparing solutions of salts. This method has the following advantages: at the onset of synthesis, high homogeneity of the composition is achieved, while solutions of salts bring additional water to stimulate the hydrolysis. However, the drawback that should be noted is that the increased amount of water predetermines a longer-lasting drying of gel.

In order to obtain glass ligament-activator No. 2, the starting components were also taken in the assigned ratio (Table 3). Technological scheme of the technique is given in Fig. 6.

The metered amount of ethyl silicate was mixed at an electrical stirrer (800 rpm) with water to initiate the process of hydrolysis; HNO_3 was added as a catalyst in the amount of 2.5 ml per 20 g of dry matter. The resulting system, during agitation process, at the expense of an exothermic reaction, was heated to 50–55 °C, which contributed to a more active progress of hydrolysis.

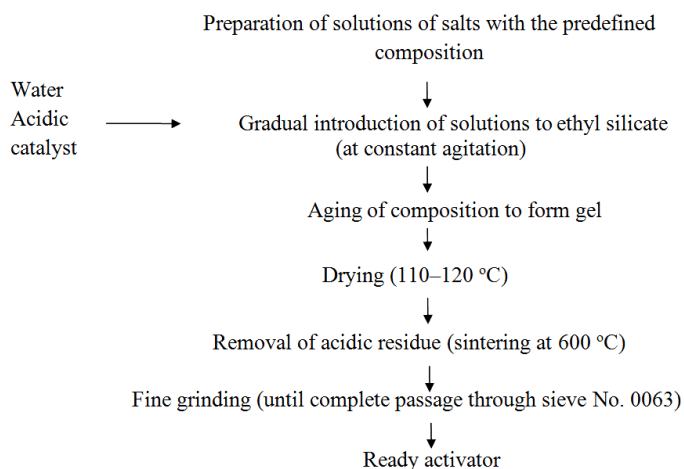


Fig. 6. Technological scheme for obtaining glass ligament-activator No. 2 via a method for preparing the solutions of salts

Next, we added to the system the saturated aqueous solutions of salts, and stirred it until obtaining homogeneous sols, which in 30–35 min. after the onset of synthesis passed

into gels. The latter were exposed to natural drying to a humidity of 2–3 %. Next, the mixtures obtained underwent thermal treatment at 600 °C in order to decompose and remove nitrogen oxides.

Petrographic study of the obtained powders was conducted in the passing light using an optical microscope (Fig. 7); it revealed that the average particle size was less than 1 μm, which were in the aggregate state.

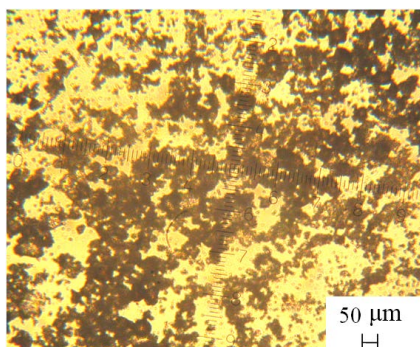


Fig. 7. Aggregated particles in glass ligament-activator No. 2

The average size of aggregates was 40–70 μm, which is why the received compositions were additionally grounded at a ball mill until their complete passage through sieve No. 0063. The X-ray phase analysis of glass ligament-activator No. 2 is shown in Fig. 8.

It demonstrates that a glass-crystalline substance forms even after drying. Fig. 8a shows diffraction maxima, characteristic of all salts, which were used to obtain the composition – Ca(NO₃)₂; NaNO₃; Al(NO₃)₃·9H₂O and SiO₂, but, because salts, due to the proposed technology, are averaged at the molecular level, the diffraction maxima are of low intensity even prior to heat treatment. After the heat treatment, the radiographs of the composition demonstrate clearly expressed X-ray amorphous halo that testifies to the amorphous state of the matter.

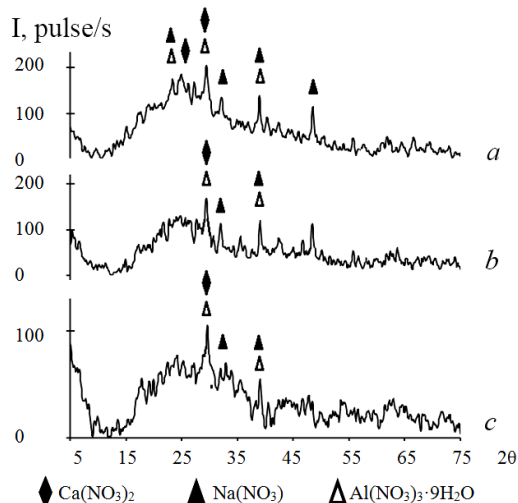


Fig. 8. Radiographs of the examined activator No. 2: a – dried state, b – after thermal treatment at 200 °C, c – after thermal treatment at 600 °C

To determine the activity of glass ligament-activator No. 2, it was exposed to heat treatment at 800 and 1,000 °C (Fig. 9). The examined powder at 800 °C also demonstrates

a sintered, slightly melted, form. At 1,000 °C, the character of melting is different from that of the basic glass (Fig. 5) – the examined glass melt is well distributed across the entire bottom of the crucible, not “assembled” as a drop, which indicates the better wetting capacity of its crystalline particles at annealing of ceramic products or coatings.



Fig. 9. Character of melting of a glass ligament-activator No. 2: a – at 800 °C; b – at 1,000 °C

Thus, our study has shown that this technique makes it possible to obtain glass-binding-activators with better spreading and wetting capacities in comparison with the basic glass, while the high degree of purity implies a possibility to apply these activators for coatings with high whiteness.

III. Obtaining the activator via a powder method with salt melting. This technique implies a thorough mixing of salts at the ratio given in Table 3, as well as their pre-melting at a temperature of 150–170 °C (Fig. 10).

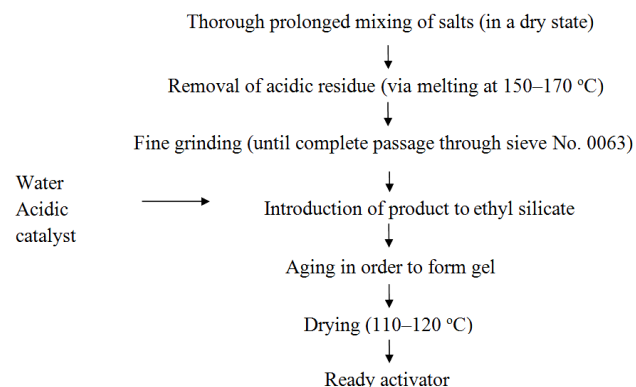


Fig. 10. Technological scheme for preparing glass ligament-activator No. 3 via a powder method with melting of salts

Aluminum salt (with a melting temperature of 73 °C), when melted, dissolves other components, thereby forming a homogeneous melt. When heated to 150 °C, the decomposition of aluminum salt took place, with a release of nitric oxide, which was indicated by a brown smoke of characteristic smell.

Upon the termination of decomposition and hardening of the mixture, it was fine-grounded until the complete passage through sieve No. 0063, and introduced to ethyl silicate solution at constant stirring (800 rpm) in the presence of an acidic catalyst (2.5 ml per 20 g of dry matter). It should be noted that there was no gel-formation within 30 minutes, while the composition, despite careful agitation, was constantly stratified, that is, there was no averaging of the composition in ethyl silicate. After increasing the amount of acidic catalyst to 10 ml and prolonging the duration of mixing to 2.5 hours, a gel-like semi-finished product was formed, although it took the form of a mechanical mixture, evenly distributed throughout the entire volume of the gel.

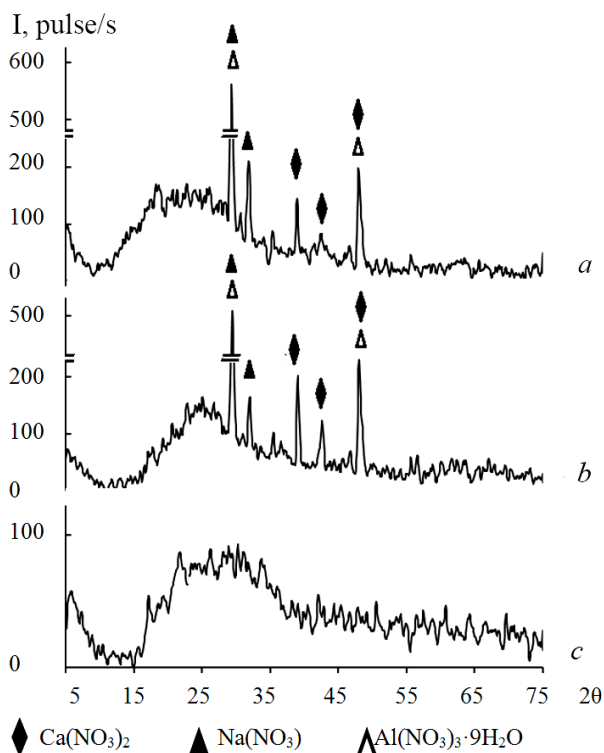


Fig. 11. Radiographs of examined activator No. 3: *a* – dried state, *b* – after thermal treatment at 200 °C, *c* – after thermal treatment at 600 °C

An X-ray phase analysis of the obtained materials revealed (Fig. 11) that the composition, after drying under natural conditions and at 200 °C, contains the residues of salts that were introduced to ethyl silicate. After sintering at 600 °C, the composition becomes completely amorphous: diffraction maxima of the specified salts disappear (Fig. 11, *c*). The result is the obtained glass ligament-activator, which melts at a subsequent heat treatment at $t=800-1,000$ °C (Fig. 12).

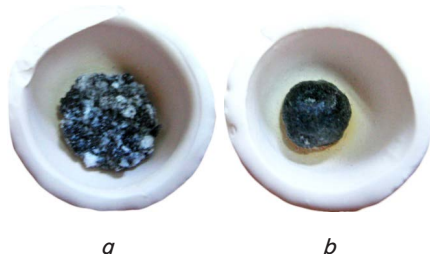


Fig. 12. Character of melting of a glass ligament-activator No. 3: *a* – at 800 °C; *b* – at 1,000 °C

The examined powder at 800 °C has a sintered, but not melted, form. At 1,000 °C, the character of melting resembles basic glass, that is, there is a high surface tension of the melt (glass is “assembled” in the form of a ball). The dark coloration indicates the presence of residual products from salt decomposition in the mixture.

Thus, we have obtained the composition via a sol-gel method by introducing pre-sintered salts to ethyl silicate. Despite the difficulties related to obtaining a homogeneous composition at the mixing stage, it demonstrated the signs of melting at 1,000 °C.

5. 3. Studying the influence of sintering activators on the technological properties and quality characteristics of engobe coatings

The cullet and glass ligaments-activators No. 1, No. 2, and No. 3 were thinly ground until their complete passage through sieve No. 0063. These activators in the amount of 3 and 5 % by weight were introduced to the composition of engobe [20]. The prepared engobe ceramic slurry was applied to the dried ceramic samples that were exposed to annealing at 1,170 °C.

An analysis of the results of visual evaluation and the properties of engobe coatings revealed a significant effect of the technique to synthesize a glass ligament on rheological characteristics of ceramic slurry and the properties of engobes (Table 4). The results show that, based on the value for water absorption of engobes, the most appropriate are the compositions for glass ligaments-activators No. 1 and No. 2 – they contribute to a decrease in this indicator by 4–5 times. This, in turn, indicates the more intensive sintering of a ceramic material with the addition of the examined glass ligaments compared to a conventional glass additive (for such an engobe, water absorption is 0.43–0.67 %). Introducing to the composition of engobe the glass ligament No. 3 leads to an increase in the water absorption of engobe, which can be caused by the composition swelling.

Table 4

Visual evaluation and properties of engobe coatings

Indicator	Type, number, content of glass ligament (sintering activator)							
	cullet		No. 1		No. 2		No. 3	
	3 %	5 %	3 %	5 %	3 %	5 %	3 %	5 %
Ceramic slurry fluidity, s	21	19	50	65	20	19	20	17
Coating water absorption, %	0.67	0.43	0.14	0.17	0	0.03	1.51	1.32
Coefficient of diffuse reflection, CDR, %	84.0	83.2	78.5	77.5	87.2	88.3	73.22	76.2
Visual estimation	Without defects, coating of white color		Without defects, light gray color, black «flies» at the surface		Without defects, coating of white color		Without defects, coating of gray color, with an insignificant number of black «flies»	

5. 4. Determining the most rational technique for obtaining the glass-like activator

By comparing the results of studying the effect of the activator, obtained by the conventional glass melting, and the activators, received using the sol-gel methods, we can conclude that the sol-gel techniques make it possible to obtain more active glass ligaments, which manifests itself in the intensification of the liquid-phase sintering of coatings. That contributes to improving such characteristics as durability, resistance of engobes to mechanical and corrosive environmental influences, etc. [15].

When comparing the glass ligaments-activators, obtained by three techniques, the data derived testify to the expediency of introduction to the composition of engobe of glass ligament No. 2 in the amount of 5 % by weight, which is obtained via the method for the preparation of solutions of salts. It is this glass ligament that promotes the formation of

the dense structure of a coating with low water absorption (0–0.3 %) and high whiteness of the surface (87.2–88.3 %).

cus on reducing the time required to obtain glass ligaments via a sol-gel method.

6. Discussion of research results

The advantages of our study are in the fact that the developed technology for obtaining the glass ligaments-activators for engobe coatings is new and promising. Compared to cullet, the proposed glass ligament No. 2 requires less energy to manufacture, it is clean and more active, which contributes to improving the quality of engobe coatings. The drawback of the design is that the technology for production engobes coating is supplemented with a new technological operation – glass ligament preparation.

The study conducted is useful and could be applied in the production of building materials, specifically engobe ceramic bricks. Introduction of glass ligaments-sintering activators to the composition of engobes could significantly strengthen their adhesion to a ceramic base and obtain a high-quality densely-sintered layer at the surface of products. That, in turn, makes it possible to expand the range of building products and improve their competitiveness.

In contrast to a still existing opinion on that obtaining materials via a sol-gel method is irrelevant for large-tonnage technologies, in this paper we have demonstrated the feasibility of replacing conventional glass with a glass ligament, obtained using a sol-gel method with the preparation of solutions of salts. It is proposed to receive not the entire engobe applying a sol-gel technology, but only an activating additive to it, which is introduced in the amount of 5 % by weight. Moreover, given the high cost of energy, reducing the temperature for obtaining a glass ligament by more than 500 °C is a very important factor. Further research might fo-

7. Conclusions

1. In the oxide system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ we have synthesized the glass-like sintering activators for engobe coatings applying a powder method without sintering, by the method for preparing the solutions of salts, and a powder method with the melting of salts. Underlying these methods are the sol-gel processes, however, they were different in the sequence of mixing and thermal treatment of components and, as a result, by the phase composition and the character of melting. Thus, the most amorphous state after heat treatment at 600 °C was demonstrated by compositions No. 2 and No. 3. However, based on the wetting capacity of ceramic base and the distribution of glass melt at the surface of ceramics, the most expedient was glass ligament-activator No. 2.

2. We have established the effect of glass ligaments-activators on fluidity of the engobe ceramic slurry and such engobe coating characteristics as water absorption, coefficient of diffuse reflectance, and a color tone. In comparison with the coatings based on the conventional glass ligament, whose water absorption is 0.43–0.67 %, we have obtained the engobe coating with a significantly lower water absorption, 0–0.03 %, as a result of introduction to the composition of engobe of glass ligament-activator No. 2.

3. The study conducted has shown that the most effective is the activator, which was obtained using technique No. 2. It enables the formation of the densest structure of engobe after annealing at 1,170 °C with an insignificant water absorption (not larger than 0.05 % C) and high whiteness of the surface (8–88 %).

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В роботі проаналізовані існуючі методи оцінки придатності глинистої сировини для виробництва архітектурно-будівельної кераміки та обґрунтована необхідність їх удосконалення в напрямку розроблення показника, заснованого на аналізі мінерального складу глин. З використанням композицій системи «каолінит – монтморилоніт – гідрослюда – кварц», які моделюють склад полімінеральних глин, встановлений вплив глиноутворюючих мінералів і домішок кварцу на властивості клінкерних керамічних матеріалів. Визначено, що позитивний вплив на водопоглинання матеріалів чинить монтморилонітові складова композицій, а на механічну міцність і морозостійкість – каолінова. Збільшення вмісту кварцу у складі композицій від 30 % до 50 % приводить до зростання водопоглинання матеріалів, зниження їх механічної міцності і морозостійкості до рівня, неприйняттого для керамічного клінкеру. Встановлено, що для отримання клінкерної кераміки вміст кварцу в композиціях не може перевищувати 40 %.

Розроблена діаграма мінерального складу, яка наочно ілюструє співвідношення основних породоутворюючих мінералів у глинах із вмістом в них 30 % і 40 % кварцу, допустимі для отримання сучасної клінкерної продукції. На діаграмі виділені області мінерального складу глин, придатних для виробництва фасадного, тротуарного і дорожнього клінкеру марок М200–300, а також дорожнього клінкеру марки М400 за температури випалу 1100 °С. Діаграма мінерального складу доповнює існуючі показники придатності глинистої сировини для виробництва архітектурно-будівельної кераміки і може служити додатковим критерієм їх технологічної якості. Діаграма може застосовуватися для аналізу придатності глинистої сировини для виробництва керамічного клінкеру за умови визначення лише мінерального складу глин без встановлення їх хімічного і гранулометричного складу

Ключові слова: архітектурно-будівельна кераміка, клінкерні матеріали, полімінеральні глини, критерії технологічної якості, промислове використання

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AN IMPROVEMENT OF CRITERIA FOR ASSESSING THE QUALITY OF CLAY RAW MATERIAL FOR ARCHITECTURAL AND CONSTRUCTION CERAMICS

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1. Introduction

The construction materials industry is an important component of any economy, which significantly affects the rate of development of other industries. The modern con-

struction materials industry is a complex area that includes many independent subsectors, one of which is the production of construction ceramics. The most widespread types of construction ceramics, which are widely used in modern construction technologies, are ordinary brick, large-size