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# КОМПЛЕКСНЫЙ РАЗЖИЖИТЕЛЬ НА ОСНОВЕ СОДЫ, ЖИДКОГО СТЕКЛА И ОКСИЭТИЛЕНДИФОСФОНОВОЙ КИСЛОТЫ В ТЕХНОЛОГИИ КЕРАМИЧЕСКОГО ЛИТЬЯ

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***Представлены результаты введения оксиэтилендифосфоновой кислоты (OEDPA) и различных добавок в качестве разжижителя для регулирования реологических свойств керамической суспензии. По результатам определения тиксотропии установили, что комплексный разжижитель на основе соды и OEDPA является наиболее эффективным, желательно заменить часть соды жидким стеклом. Методом полного факторного эксперимента установили оптимальный состав компонентов комплексного разжижителя. Предполагаемый разжижитель высокоэффективен в широком диапазоне концентраций OEDPA, соды и жидкого стекла. Полученные суспензии имеют стабильные, высокие структурно-механические свойства. Представлена математическая модель, описывающая влияние состава разжижителя на вязкость и тиксотропные свойства суспензии. Определили влияние действия разжижителя на механические свойства формованных высушенных и обожженных образцов. Добавление OEDPA к разжижителю существенно снижает реологические параметры суспензии, и свойства приближаются к реологическим свойствам ньютоновских систем. Установлено, что OEDPA снижает скорость наращивания массы, которая может быть увеличена за счет снижения содержания влаги в суспензии, что позволяет увеличить плотность образцов после литья и сушки. Введение данной добавки приводит к увеличению гидратной оболочки вокруг глинистой частицы и повышению стабильности суспензии, а увеличение ζ-потенциала по сравнению с заводской добавкой очень небольшое. Предложен механизм действия комплексной добавки, включающий ионообмен, комплексообразование и хемосорбцию. Наблюдается увеличение прочности и плотности высушенных и обожженных образцов, уменьшение усадки и пористости. Комплексная добавка позволила оптимизировать технологию на этапах подготовки отливок и уменьшить количество брака при формовании, сушке и обжиге.***

**Ключевые слова:** оксиэтилендифосфоновая кислота, сода, жидкое стекло, реологические свойства, разжижитель, глинистая суспензия, механизм действия комплексной добавки

# COMPLEX DEFLOCCULENT BASED ON SODA, LIQUID GLASS AND OXYETHYLIDENEDIPHOSPHONIC ACID IN CERAMIC CASTING TECHNOLOGY

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***Here are discussed some results to use oxyethylidenediphosphonic acid (OEDPA) and various additives as a deflocculant composition for controlling the rheological properties of a ceramic suspension. According to the results of determining thixotropy, it was found that a complex thinner based on soda and OEDPA is the most effective. It is desirable to replace a portion of the soda with liquid glass. By the full factorial experiment method, it was established the optimal composition of the components of the complex thinner. The proposed thinner is highly effective***

***in a wide range of OEDPA, soda, and liquid glass concentrations. The resulting suspensions have stable, high structural–mechanical properties. A mathematical model describing the effect of the composition of the thinner on the viscosity and thixotropy of the suspension is presented. The effect of the diluent on the mechanical properties of the molded dried and fired samples was determined. The addition of OEDPA to the thinner significantly lowers the rheological parameters and the rheological properties of the suspensions approach the rheological properties of Newtonian systems. It was found that OEDPA lowers the mass buildup rate, which can be increased by lowering the moisture content in the suspension, which makes it possible to increase the post-casting and -drying density of the samples. The introduction of this additive leads to an increase in the hydrate shell around the clayey particle and an increase in the stability of the suspension, but the increase in the ζ - potential in comparison with the production additive is very small. The mechanism of action of a complex additive is proposed, including ion-exchange, complexation and chemisorption. An increase in the strength and density of dry and calcinated clay samples as well as a decrease in the shrinkage and porosity are observed. The complex additive makes it possible to optimize the technology at the stages of casting slip and to decrease the number of parts rejected during molding, drying and firing.***

**Key words:** oxyethylidenediphosphonic acid, soda, liquid glass, rheological properties, deflocculant, clay suspension, mechanism of action of a complex additive

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## INTRODUCTION

The production of ceramic sanitary wares by casting under pressure makes it possible to obtain a strictly prescribed thickness which is the same over all parts of an article. This eliminates many negative factors associated with the appearance of defects on sites with a thickness differential. Article quality largely depends on how well the technological settings of the casting program conform to the slip parameters. For this reason, the key problem of the technology is to make slips whose properties would conform to the rapid structure formation and strength buildup in fired paste. Thus, the study of the rheological stability of slip and finding effective thinners are especially topical problems [1-3].

The use of several components in the development of deflocculants with new compositions is due the fact that it is necessary to increase not only the degree of thinning but also the working concentration range of the additives. Since additives of different chemical nature are used, it is important to understand the characteristics of their chemical interaction with clay suspensions and thinning mechanisms [4, 5]. Control of the rheological characteristics makes it possible to decrease the amplitude of the fluctuations of the technological parameters of a ceramic slip and increase the stability of the processes occurring during casting. Specifically, obtaining a denser casting with lower air shrinkage makes it possible to decrease significantly the probability of obtaining rejects and the greater mechanical strength of the intermediate product makes it possible to optimize the rate of the production processes associated with the tooling and transport of an article [6-11]. Important objective is to control the rheological properties of the ceramic slip using a combination of components as the thinner.

Deflocculants such as sodium silicate, carbonate, and tripolyphosphate are conventionally used to adjust the rheological properties and aggregative stability of ceramic slips. Several Russian ceramic companies are also starting to adopt new deflocculating products for ceramic slips for casting in polymer molds under high pressure. For example, Reotan (Lamberti Co.) and Dolapix (Zschimmer&Schwarz) are based on sodium polyacrylate and ammonium polyacrylate, respectively. It is recommended that they be used together with sodium tripolyphosphate [12-17]. However, in ceramic sanitary ware technology sodium tripolyphosphate is not generally used. Typical deflocculent constituents in this case are soda and liquid glass. However, for more pronounced thinning effect their further use in deflocculent composition should be reinforced by additional additives.

As such additional component we propose to use oxyethylidenediphosphonic acid (OEDPA). The introduction of OEDPA is based on the fact that it has been used effectively for preparing casting slips using the conventional ceramic technology [18].

EXPERIMENTAL PART

The following batch composition of a porcelain mix for ceramic slip was used in the present investigation (content, wt.%): Vesko-Granitik clay – 6; Stephan Schmidt 13250 clay – 14; Glukhovetskoe kaolin – 30; Quartz sand – 17; Vishnevogorodskoe feldspar – 24; Scrap of fired articles – 9.

Casting slip is obtained in three steps: 1) preparation of a Stephan Schmidt Clay suspension in a high-speed paddle mixer; 2) preparation of a suspension of inert materials by grinding in a ball mill; 3) mixing a clay suspension with a suspension of inert materials and with kaolin's. Distilled water was used in all the experiments.

Deflocculant is introduced at all steps. The amount and composition of the deflocculant are determined by the properties of the clay suspension used at each step as described above.

RESULTS AND DISCUSSION

At the initial stage of investigation, we focused on the first of the steps indicated above with the aim to study an effect of a complex additive on the structural-mechanical properties of a Stephan Schmidt 13250 clay suspension.

For this purpose, three suspensions were prepared (content, wt.%): N 1 – reference suspension with a factory additive (0.500 soda and 0.072 liquid glass); N 2 – conformance prototype [18] (0.572 soda and 0.572 OEDPA); N 3 – factory prescription modified with OEDPA additive (0.500 soda, 0.072 liquid glass, and 0.572 OEDPA).

Clays were dissolved in a laboratory high-speed paddle mixer. The moisture content of the clay suspension, taken to be the same for all compositions (35%), was checked by the pycnometric method according to the density of the suspension. The temperature of the suspension was maintained at 25.0 ± 0.1 °C. The thixotropy was determined according to the difference between the suspension viscosity and viscosity after 1 or 6 min standing.

The experimental data, including the dissolution time of the clays, are presented in Table 1.

***Table 1***

**Properties of the suspensions N 1 – 3**
***Таблица 1.* Свойства суспензий № 1-3**

| Parameter | Check apparatus | Suspension | | |
|---|---|---|---|---|
| | | N 1 | N 2 | N 3 |
| Dissolution time, h:min | Timer | 6:30 | 5:00 | 3:00 |
| Density, g/cm$^3$ (±0.01) | Pycnometer, scales | 1.61 | 1.61 | 1.61 |
| Viscosity, Pa·sec (±0.001) | Galenkamp viscosimeter | 1.009 | 0.537 | 0.206 |
| Thixotropy (every 1 min of standing), Pa·sec (±0.001) | Galenkamp viscosimeter | 1.733 | 0.288 | 0.000 |
| Thixotropy (every 6 min of standing), Pa·sec (±0.001) | Galenkamp viscosimeter | 6.246 | 1.492 | 0.019 |

As Table 1 shows, the suspension N 2 with complex thinner has unquestionable advantages over a suspension with the factory thinner. The complex thinner in suspension N 3 has an even stronger effect on a clay suspension.

Compared with the factory suspension N 1 it does decreases the following: the dissolution time by more than a factor of 2, the viscosity by 0.8 Pa·s, the thixotropy to minimal values.

Thus, the first part of these studies showed that, first, a complex thinner based on soda and OEDPA is effective and, second, it is desirable to replace a portion of the soda with liquid glass.

The second part of these studies consisted of finding the optimal composition of the components of a complex thinner. To accelerate the search process, we used the full factorial experiment method (FFE). The FFE matrix was constructed so that the previous studies performed for suspension N 3 entered into it as a point with the coordinates +1, +1, +1. A thinner composition containing 0.472% OEDPA, 0.400% soda, and 0.057% liquid glass was chosen as the center of the plan. The ranges of variation of the OEPDA and soda concentrations were $\Delta x_1$ = 0.100% and $\Delta x_3$ = = 0.015%, respectively. Two experiments were performed at each point of the plan. The results of the FFE plan implementation are presented in Table 2 as average values of the quantities studied.

The data in Table 2 confirm that the proposed thinner is highly effective in a wide range of OEDPA, soda, and liquid glass concentrations. Eight of the nine suspensions have stable, high structural-mechanical properties which are close in magnitude. The parameters of the suspension N 8 with the minimum content of OEDPA, soda, and liquid glass (0.372, 0.300, and 0.042%, respectively) are somewhat worse. However, the properties of even this suspension are much higher than for the suspension with the factory additive (N 1, Table 1).

***Table 2***

**Results of full factorial experiment implementation**

***Таблица 2.* Результаты полного факторного эксперимента**

| Experiment N | Dissolution time, h:min | Viscosity, Pa·sec | Thixotropy, Pa sec | |
|---|---|---|---|---|
| | | | after 1 min | after 6 min |
| 1 | 3:00 | 0.206 | 0.000 | 0.019 |
| 2 | 2:30 | 0.193 | 0.000 | 0.007 |
| 3 | 3:40 | 0.174 | 0.019 | 0.055 |
| 4 | 2:40 | 0.168 | 0.006 | 0.019 |
| 5 | 2:50 | 0.200 | 0.000 | 0.000 |
| 6 | 3:00 | 0.174 | 0.019 | 0.068 |
| 7 | 2:40 | 0.238 | 0.000 | 0.008 |
| 8 | 4:30 | 0.314 | 0.045 | 0.154 |
| Experiment at plan center | | | | |
| 9 | 3:10 | 0.215 | 0.012 | 0.040 |

Analysis of the results of FFE plan implementation (Table 2) shows that within the limits of the measurement error the variation of the composition and the amount of complex thinner affects the values of the viscosity of the slip as well as the values of the thixotropy of the suspension after 6 min of standing. These indicators were taken into account in the development of the mathematical model used to obtain the regression equations describing the effect of the composition of the thinner on the viscosity and thixotropy of the suspension.

First, the FFE results for the values of the viscosity of the clay suspension were analyzed statistically. The regression equation expressing the dependence of the viscosity η (Pa·sec) of the clay suspension on the quantity and composition of the thinner has the form

$$\eta = 0.209 - 0.004X_1 - 0.015X_2 - 0.023X_3 + 0.014X_1X_2 + 0.009X_1X_3 + 0.029X_2X_3 - 0.019X_1X_2X_3 \quad (1)$$

The following equation was obtained from a similar analysis of the dependence of the thixotropy $T_6$ (Pa sec) after 6 min of standing of the suspension on the amount and composition of the thinner:

$$T_6 = 0.041 - 0.021X_1 - 0.018X_2 - 0.016X_3 + 0.007X_1X_2 + 0.033X_1X_3 + 0.006X_2X_3 - 0.013X_1X_2X_3 \quad (2)$$

It should be noted that, for all practical purposes, the compositions N 2 and 5 have no thixotropic properties after 6 min of standing (Table 2). These are the thinner compositions that are proposed for obtaining a clay suspension in the technology of sanitary ware and building articles.

Thus, the complex thinner OEDPA – soda greatly increases the structural–mechanical properties of a Stephan Schmidt clay suspension: the viscosity of the suspension and the thixotropy decrease with decreasing dissolution time. Adding a small amount of liquid glass to the composition of the complex thinner intensifies the effect of the thinner.

The studies performed using the mathematical planning method established that the thinning effect of the complex additive OEDPA – soda – liquid glass is observed in a wide range of concentrations. This makes it possible to confidently regulate the clay dissolution process under production conditions and to obtain suspensions with stable properties.

The optimal compositions (%) of the complex thinner OEDPA:soda:liquid glass are proposed on the basis of the implementation of a full factorial experiment: 1) 39.4:53.0:7.6 (total amount of thinner 0,944%) and 2) 51.3:44.9:3.8 (total amount of thinner 1.114%).

As next we studied the physical-chemical aspects of the action of the complex addition on the rheological and casting properties of the Stephan Schmidt 13250 clay suspension and on the mechanical properties of the molded dried and fired samples obtained from the suspensions studied and to determine the mechanism of the action of the additive.

Thinning additives with the compositions presented in Table 3 were prepared to study the rheological properties of the clay suspensions. We note that the two-component composition N 1 is currently used in production and we recommended the compositions N 2 and 3.

***Table 3***

**Compositions of the thinning additive and rheological characteristics of suspensions**

***Таблица 3*. Состав разжижающей добавки и реологические характеристики суспензий**

| Additive | Composition of thinning additive, wt.% | | |
|---|---|---|---|
| | N 1 | N 2 | N 3 |
| Soda | 0.500 | 0.500 | 0.500 |
| Liquid glass | 0.072 | 0.042 | 0.072 |
| OEDPA | - | 0.572 | 0.372 |
| Parameter | Rheological characteristics | | |
| Plastic viscosity η, Pa·sec | 0.110± ±0.006 | 0.093± ±0.002 | 0.074± ±0.004 |
| Maximum shear stress $\tau_0$, Pa | 5.3 ± 0.6 | 4.4 ± 0.2 | 2.9 ± 0.4 |

The measurements were performed in a RHEOTEST RN rotational viscometer and with the same moisture content (35%) of the clay suspension and constant temperature 25 °C. The results, which were fit by the Bingham–Shvedov equation

$$(\tau = \tau_0 + \eta\gamma), \quad (3)$$

where $\tau$ – the shear stress, $\tau_0$ – the maximum shear stress, $\eta$ – the plastic viscosity, $\gamma$ – the shear rate), are displayed in Fig. 1.

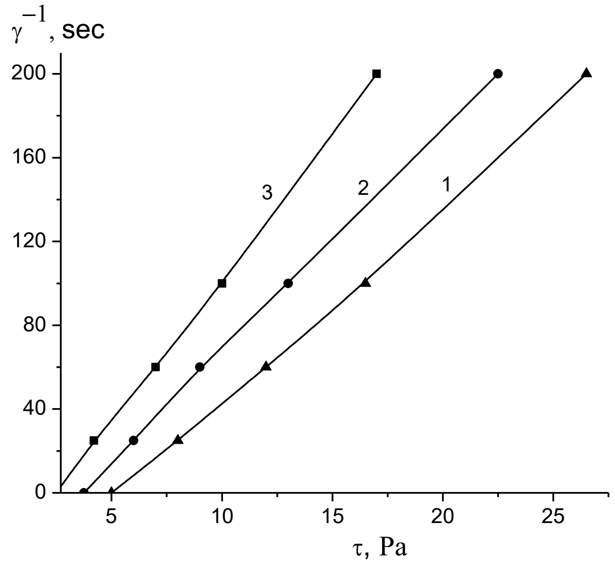


Fig. 1. Rheological curves for suspensions with additives: 1) N 1; 2) N 2; 3) N 3

Рис. 1. Реологические кривые для суспензий с добавками: 1) № 1; 2) № 2; 3) № 3

It is evident from Table 3 that the addition of OEDPA to the thinner significantly lowers the rheological parameters and the rheological properties of the suspensions approach the rheological properties of Newtonian systems. Specifically, a reduction of $\tau_0$ shows that the character of the flow changes from typical for structured systems to typical for free-disperse systems.

The rate of mass buildup was determined by a procedure using gypsum rods [10]. Since it was determined that the N 2 suspension with additive is more stable against aggregation than the N 3 suspension with additive, suspensions with additive N 1 and 2 were chosen for these studies. The average values of the mass buildup rate for the suspensions N 1 and 2 (with constant moisture content $W$ = 35%) were 0.43 ± ±0.01 and 0.37 ± 0.02 g/(cm$^2$/min), respectively.

It is evident that OEDPA lowers the mass buildup rate. The mass buildup rate can be increased by lowering the moisture content of the suspension, which makes it possible to increase the post-casting and -drying density of the samples. For this, it was established by adjusting the fluidity of the suspension using a Ford cup that the N 2 suspension with additive and $W$ = 33% has the same viscosity and thixotropy as the N 1 suspension with $W$ = 35%. The mass buildup rate measured for the N 2 suspension with moisture content 33% was 0.43 ± 0.02 g/(cm$^2$/min).

It can be concluded from the results of physical-mechanical tests (Table 4) that OEDPA addition to the thinner com- position increases strength for dry and fired samples. Samples with additive N 2 show smaller shrinkage compared with samples with additive N 1.

***Table 4***

**Mechanical properties of air-dry and fired samples**

***Таблица 4.* Механические свойства образцов после воздушной сушки и обжига**

| Parameter | Additive | |
|---|---|---|
| | N 1 | N 2 |
| Air linear shrinkage, % | 8.1 ± 0.5 | 8.5 ± 0.5 |
| Strength of dry samples, MPa | 2.8 ± 0.2 | 4.3 ± 0.2 |
| Fire linear shrinkage, % | 6.2 ± 0.6 | 4.2 ± 0.6 |
| Total linear shrinkage, % | 14.3 ± 0.9 | 12.5 ± 0.9 |
| Strength of fired samples at 1050 °C, MPa | 19 ± 2 | 28 ± 2 |
| Water absorption, % | 9 ± 1 | 8 ± 1 |
| Bulk mass of fired samples, kg/m$^3$ | 1780 ± 80 | 1900 ± 80 |

The results of the investigation of the granulometric composition and ξ-potential of clay particles for all suspensions studied (Zetasizer Nano Laser Analyzer, Malvern Instruments) are presented in Figs. 2 and 3, respectively. The data presented in Fig. 2 show that the OEDPA addition to a complex additive has no effect on the granulometric composition.

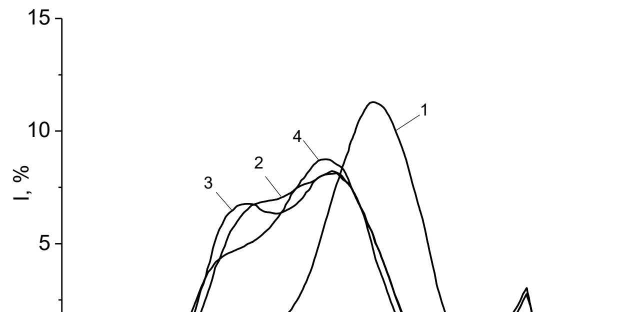


Fig. 2. Data of granulometric analysis of clay suspensions: 1) no additives; 2) with additive N 1; 3) with additive N 2; 4) with additive N 3

Рис. 2 Данные гранулометрического анализа глинистых суспензий: 1) без добавок; 2) с добавкой № 1; 3) с добавкой № 2; 4) с добавкой № 3

It follows from Fig. 3 that positively charged particles are present in a suspension of pure clay. After the production additive is introduced, they completely vanish and the ξ-potential increases in modulus. Therefore, the hydrate shell around a clayey particle increases and the stability of the suspension increases. The introduction of OEDPA increases the ξ-potential very little compared with the production additive. The average values of the ξ-potential (mV) for all the suspensions studied are as follows: -17.5 – no additive; 47.9 – with additive N 1; 53.2 – with additive N 2; 53.3 – with additive N 3.

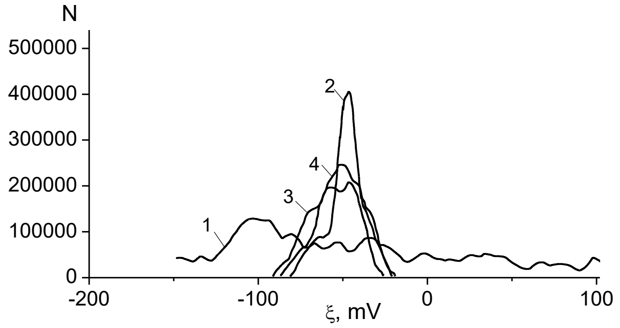


Fig. 3. Distribution of the ξ-potential in clay suspensions: 1) no additives; 2) with additive N 1; 3) with additive N 2; 4) with additive N 3

Рис. 3. Распределение ξ- потенциала в глинистых суспензиях: 1) без добавок; 2) с добавкой № 1; 3) с добавкой № 2; 4) с добавкой № 3

In summary, it is our opinion that ion-exchange and chemosorption determine the effect of a complex additive consisting of soda, liquid glass and oxyethylidenediphosphonic acid on the rheological properties of a clay suspension. When these components are mixed the complexonate $Na_2OEDP$ is formed, and in solution it dissociates into the anion $[OEDP]^{2-}$ and the cations $Na^+$ [19].

For a thinner based on soda and liquid glass the mechanism of ion-exchange with the participation of $Na^+$ and $Ca^{2+}$ ions in the volume of the suspension and on the surface of clay particles is presented in the literature [20, 21]. In the complex additive, in view of the much higher stability of the complexes Ca[OEDP] compared with $Na_2OEDP$ [19], the anion $[OEDP]^{2-}$ interacts with the cation $Ca^{2+}$ on the surface of a clay particle (Fig. 4), as a result of which the surface charge of clay particles becomes more negative (the ξ-potential increases in modulus).

Owing to the chelation effect the anion $[OEDP]^{2-}$ forms in the volume of the suspension undissociated compounds with calcium ions. These suppositions are confirmed by the observed reduction of the viscosity of suspensions on introduction of OEDPA.

The increase in the strength of dry samples when complex thinner is introduced into the slip composition can be explained by the fact that Ca[OEDP] undergoes polymerization during the drying process [19]. However, the increase in strength of the samples after firing is explained by the fluxing action of calcium phosphate compounds.

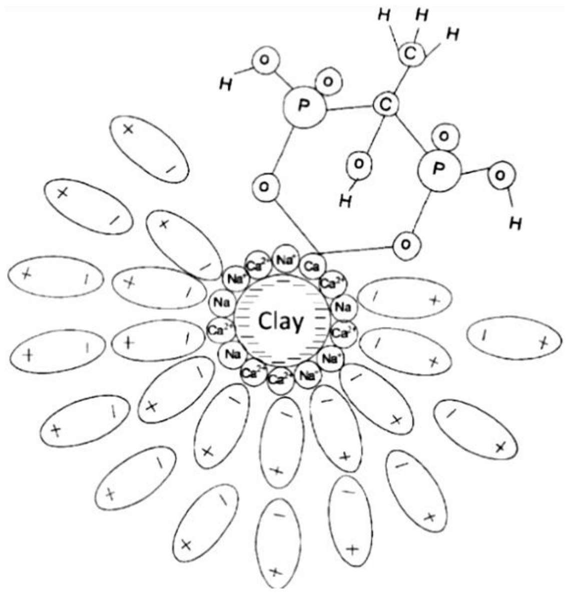


Fig. 4. Schematic representation of the chemosorption of OEDPA on clay particles

Рис. 4. Схематическое изображение хемосорбции OEDPA на глинистые частицы

At this stage of studies it was concluded that the action of a complex defflocculent based on soda, liquid glass and oxyethylidenediphosphonic acid in the technology for the production ceramic articles by casting is effective: the clay dissolution time decreases and the viscosity and thixotropy of the suspension decrease to minimal values. To explain the changes in the structural-mechanical properties of the suspensions a mechanism was proposed for the action of the complex additive that includes ion exchange, complex formation and chemosorption. It was determined that the complex additive makes it possible to decrease the moisture content of the suspension by 2% while preserving the working parameters of the suspension. An increase in the strength and density of dry and fired clay samples as well as a decrease in the shrinkage and porosity are observed. In summary, the complex additive makes it possible to optimize the technology at the stages of preparation of the casting slip and to decrease the number of parts rejected during molding, drying and firing.

The final aim of this work was to study the technological properties (rheological, casting, drying, and firing) of ceramic casting slip under high pressure using a complex deflocculent based on OEDPA in combination with soda and liquid glass as compared with the conventional thinner (liquid glass and soda) as well as the deflocculent Reotan (Lamberti Co.) actively used in production.

To determine the efficacy of the new complex additive which we are proposing it is best to compare it with the conventional two-component deflocculent based on soda and liquid glass as well as with the deflocculent Reotan SL which is gaining popularity. Information on the composition of the deflocculents studied in the present work is presented in Table 5.

It should be noted that at the second stage during the milling of the non-plastic materials in a ball mill a decision was made to reject the use of the deflocculent OEDPA because it was found that the milling time in this case increases by 25% on average. In our view this occurs because the hydrate shells of the particles of the clay mineral decrease in size, which diminishes the role of the clay as a milling additive. Therefore, at this stage we used conventional thinner (soda and liquid glass).

***Table 5***

**Composition of the deflocculent**
***Таблица 5.* Состав дефлокулянта**

| Clay component | Deflocculent | Component content, wt.% | | | |
|---|---|---|---|---|---|
| | | Sodium silicate | Sodium carbonate | OEDPA | Reotan SL |
| Vesko-Granitik clay | Conventional | 1.15 | - | - | - |
| Stephan Schmidt 13250 clay | | 0.30 | 0.05 | - | - |
| Glukhovetskoe kaolin | | 0.23 | - | - | - |
| Vesko-Granitik clay | Based on Reotan SL | 0.575 | - | - | 0.575 |
| Stephan Schmidt 13250 clay | | 0.175 | - | - | 0.175 |
| Glukhovetskoe kaolin | | 0.115 | - | - | 0.115 |
| Vesko-Granitik clay | Based on OEDPA | 0.77 | - | 0.77 | - |
| Stephan Schmidt 13250 clay | | 0.30 | 0.03 | 0.23 | - |
| Glukhovetskoe kaolin | | 0.15 | - | 0.15 | - |

The suspensions were prepared under identical conditions and were brought to the same moisture content (based on the density of the suspensions).

Subsequently, the experiment studying the technological properties of the slip was performed in two stages. First, a freshly prepared or ‘primary’ slip obtained immediately after the third step of the preparation process by mixing all components of the slips was investigated. Second, the ‘technological’ (or casting) slip was obtained; for this, the primary slip was allowed to stand, with mixing, for five days in order to maximize the interaction of the deflocculent with the particles of the clay minerals and average their compositions. This makes it possible to minimize the deviations of the viscosity of the slips, which is especially important for forming articles by casing under high pressure.

The conditions of fabrication and the structure and mechanical properties of the primary slip are presented in Table 6. The viscosity was measured with a Galenkamp rotational-type viscometer. It is evident from the data in Table 6 that the viscosity of suspension N 1 increases with time (from 1.48 to 7.93 Pa·sec in 6 min), which indicates that the thixotropy of this slip composition is high. On the other hand the compositions N 2 and 3 show the rheological parameters to be stable in time in a state of rest, which is the most favorable factor for the coagulation interaction of the clay particles. The thixotropy of the composition N 3 is lower than that of N 2.

To adequately compare the casting properties of slips prior to the casting tests the standard production procedure of adjusting the viscosity of the slips by changing the moisture content was applied. Specifically, in view of the excessive deviation of the viscosity of the composition N1 its moisture content was increased by 2% until comparable parameters in terms of viscosity and thixotropy were obtained with the N 2 and 3. The properties of the technological slip are presented in Table 6.

Comparing the data for primary and technological slips it is evident that the viscosity and thixotropy of the compositions N 2 and 3 did not change as much as that of the composition N 1 during the standing period, which shows that their rheological behavior was more stable. The composition N 1 has the lowest viscosity, but since the thixotropy is too high its viscosity increases by more than a factor of 2 in 1 min. During an investigation of the structural and mechanical properties it was established that for the composition N 2 the viscosity of the suspension increases by 27% (standing time 1 min) and by 114% (after 6 min) and for composition N 3 by 35 and 103%, respectively. The highest values in terms of the thixotropy were obtained for the composition N 1: the viscosity increases by 112% in 1 min and 414% in 6 min.

*Table 6*

**Primary and technological slips**

***Таблица 6.* Первичный и технологический шликера**

| Parameter | Slip composition | | |
|---|---|---|---|
| | N 1 (con- ventional) | N 2 (based on Reotan SL) | N 3 (based OEDPA) |
| Primary Slip | | | |
| Preparation conditions | | | |
| Mixing time, h | 12 | 12 | 12 |
| Moisture content, % (±0.5) | 28 | 28 | 28 |
| Density, g/cm$^3$ (±0.001) | 1.815 | 1.815 | 1.815 |
| Structural and mechanical properties | | | |
| Viscosity, Pa·sec (±0,01) | 1.48 | 0.75 | 0.68 |
| Viscosity after 1 min, Pa·sec (±0,01) | 2.99 | 1.01 | 0.90 |
| Viscosity after 6 min, Pa·sec (±0,01) | 7.93 | 1.58 | 1.34 |
| Technological Slip | | | |
| Preparation conditions | | | |
| Holding time, days | 5 | 5 | 5 |
| Moisture content, % (±0.5) | 30 | 28 | 28 |
| Density, g/cm$^3$ (±0.001) | 1.772 | 1.815 | 1.815 |
| Structural and mechanical properties | | | |
| Viscosity, Pa·sec (±0.01) | 0.68 | 0.83 | 0.72 |
| Viscosity after 1 min, Pa·sec (±0.01) | 1.44 | 1.05 | 0.97 |
| Viscosity after 6 min, Pa·sec (±0.01) | 3.47 | 1.78 | 1.46 |
| Casting properties | | | |
| Mass of moist casting, g (±0.1) | 174.8 | 168.9 | 199.8 |
| Mass of dry casting, g (±0.1) | 142.5 | 140.2 | 166.2 |
| Moisture content of casting, g (±0.1) | 18.5 | 17.0 | 17.2 |
| Filtrate volume, ml (±0.5) | 24 | 26 | 24 |

The casting properties of slips were studied by determining the mass of the residue formed on the filtering barrier of the Baroid apparatus under pressure 0.5 MPa in the initial moist state and in state obtained by drying at 100 °C.

The results were obtained while investigating the rate of mass buildup in casting a sample from the experimental suspensions:

- the buildup rate for composition N 3 is higher than for compositions N 1 and 2 by 14 and 16%, respectively;
- the buildup rate difference between the compositions N 1 and 2 is small, 1.4%;
- the maximum moisture content obtains in composition N 1 (it is 8% higher than for N 2 and 7% for N 3);
- the minimum moisture content of a casting obtains for composition N 2, and the difference of the moisture content of castings obtained using the compositions N 2 and 3 is 1%.

Finally, we studied the physical and chemical properties of cast samples. The cast samples were molded by the standard method of pouring into gypsum molds. The results are presented in Table 7.

The reduction of the air shrinkage of the samples with the composition N 3 by 0.8 and 0.6% as compared with the compositions N 1 and 2, respectively, significantly decreases the internal stresses of the cast samples on drying and therefore also the probability of cracking.

*Table 7*

**Properties of dried and calcined samples**

***Таблица 7.* Свойства высушенных и обожженных образцов**

| Sample | Shrinkage, % (±0.1) | | Ultimate strength in bending, MPa (±0.1) | | Water absorption, % (±0.01) | |
|---|---|---|---|---|---|---|
| | Air | Firing | After drying | After firing | Boiling method | Vacuum method |
| N 1 | 2.1 | 8.8 | 5.3 | 46.9 | 0.87 | 0.18 |
| N 2 | 2.3 | 8.6 | 7.0 | 54.8 | 0.82 | 0.18 |
| N 3 | 1.3 | 8.0 | 7.3 | 55.7 | 0.82 | 0.18 |

The lowest ultimate strength in bending after drying obtained for samples with the composition N 1. The highest values were obtained in the samples with the composition N 3: the strength of these samples was 1% greater than that of the samples with composition N 2 and 27% greater than for N 1.

The shrinkage of the samples with the composition N 3 during firing is 0.8 and 1% smaller than for the compositions N 2 and 1, respectively.

The mechanical strength of the samples with the composition N 3 after firing is somewhat higher than for the composition N 2 (by 1.6%) and significantly higher (by 15.8%) than for N 1.

The water absorption in all three samples is at the lowest level.

In summary, overall the shrinkage of the samples with the composition N 3 is almost 15% smaller than for the compositions N 1 and 2. This undoubtedly has a favorable effect on the mechanical strength, whose ultimate value for the samples with the composition N 3 is higher in the dry and fired states.

## CONCLUSIONS

It has been clearly shown that the OEDPA-based deflocculent in combination with liquid glass and soda is effective according to the results of the studies the effect of the composition of different deflocculents on the rheological properties of a suspension of ceramic slip. It makes it possible to reduce considerably the thixotropy of the slip not only compared with the conventionally combined components (soda and liquid glass) but also compared with the increasingly more popular deflocculent Reotan SL.

In the work with deflocculents the buildup rate of a casting decreases with the thixotropy of the slip, which results in loss of productivity, especially when casting under pressure, where the cycle time is 20-30 min. Our investigations showed that the reduction of thixotropy achieved by using a complex deflocculent based on OEDPA makes it possible to retain a high buildup rate of the casting upon reaching the minimum thixotropy. In turn, the minimal thixotropy with the required viscosity of the ceramic slip makes it possible to eliminate one of the weakest points in slip casting technology (especially at high pressure) – the formation of a flocculation line in the casting, which forms a bounding zone between slip flows with different viscosity as the casting mold is filled. In most cases this technological problem, which arises at the molding stage, is discovered only after drying and leads to 100% rejection of articles.

The production of castings with lower moisture content led to a reduction of the shrinkage during drying and firing, which when combined with the branching structure of OEDPA on the surfaces of clay particles gives higher mechanical strength of the intermediate product in the dried state, which also promotes a significant reduction of the rejection rate upon tooling and mechanical transport of the dried intermediate product.

In summary, the use of a complex OEDPA-based deflocculent improves the structure properties of the slip and the physical-chemical properties of the cast parts.

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