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FUNDAMENTAL PATTERNS OF INFLUENCE OF THE STRUCTURE AND COMPOSITION OF THE OXYPHENOL OLIGOMERS ON THE PLASTIFICATION OF CEMENT MIXTURES

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Abstract.

We studied and systematized the plasticizers based on the oxyphenol oligomers of the monomers used for the synthesis, preparation process, structure and plasticizing ability. We synthesized a number of thermoplastic oligomers (novolaks) and thermosetting oligomers (resoles) on the basis of oxyphenols of different functionality. We proved that the oligomers based on the trifunctional phenols have a plasticizing ability. It is found that the preparation of resoles takes place under milder conditions in an alkaline medium, with no need for neutralization of the reaction products, as in the case of the preparation of novolaks, which synthesis usually occurs in an acidic medium. We prepared the rheological characteristics of cement systems with the resole and novolakoligomers based on the trifunctionaloxyphenols. We have a comparative assessment of plasticizing additives based on one-, two-, and triatomic phenols with a knownplasticizing additive S-3. We proved that the thermosetting oligomers are effective in terms of plasticizing ability, while the oxyphenolfurfurol plasticizers liquefy and stabilize the dispersion systems more effectively than the oxyphenolformaldehyde ones. The additive based on phloroglucinolfurfurol oligomers has the highest plasticizing activity, which is due to the maximum number of hydroxy groups in the aromatic links of oligomeric molecules that participate in the adsorption process.

Key words:oxyphenol oligomers, trifunctional phenols, thermosetting oligomers, plasticizers, plasticizing ability, rheological properties.

Introduction. The analysis of well-known plasticizing additives has showed that almost all of them are oligomeric electrolytes based on the organic aromatic compounds. The additives based on the polycondensation products of naphthalene and its compounds became widely used. The most used representative of this class has been and still is the liquefier S-3, which is the condensation product of naphthalenesulfonic acid and formaldehyde, however, its

production and use has faced a number of problems in recent years. Therefore, the works in the field of synthesis of plasticizing additives, their study and application remain relevant and belong to the interdisciplinary tasks [1-6].

For several decades the scientists of the Belgorod State Technological University named after V.G.Shukhov (BSTU) are already engaged in the theory and practice of synthesis of plasticizing and superplasticizing additives for aqueous mineral dispersions used in the production of cement, concrete, construction products and structures based on them [4-14].

It is known that the oligomers of the benzene, naphthalene and polynuclear series with different hydrophilic polar groups have the plasticizing ability. They developed a working hypothesis about the possibility of establishing a range of effective superplasticizing additives on the basis of oxyphenols. The objective of this paper is to identify the fundamental patterns of influence of the spatial structure of oxyphenol oligomers, nature of monomer links, number and position of polar hydrophilic groups in a molecule and other factors on the plasticizing ability of additives.

Method.

Influence of plasticizing additives on the basis oxyphenol oligomers on the rheological properties of cement mixtures was studied in pastes PC-500-D0 of the Belgorod Cement Plant with a surface area of 354 m^2/kg, at the constant water-cement ratio of 0.3. The studies of rheological parameters of the suspensions were performed using a rotational viscosimeter "Reotest-2". The concentration of additives (C_m) was calculated in wt. % on a dry substance from the amount of the dispersed phase. During the study we measured the relationship between the values of shear stress and shear rate. According to the results received we built the rheological curves.

In the medium doses of oligomers we observed a significant increase in the linear part of curves and described their flow by the Bingham's equation $\tau = \tau_0 + \eta_{pv} \cdot \dot{\gamma}$, where $[tau]_0$ – critical shear stress,Pa; $[eta]_{pv}$– plastic viscosity, Pa·s.

With the further increase in the concentration of additives, the curves character showed that the rheological properties of suspensions are close to the rheological properties of fluid-like systems to describe the Newton's equation$\tau = \eta_{pv} \cdot \dot{\gamma}$

To establish the composition and structure of the oligomer molecules we used the liquid chromatography (chromatograph HG-1305 and DIFFERENTALREFRACTOMETERRIDK 101), infrared spectroscopy (IR-Fourier-spectrometer Vertex 70), spectroscopy of a nuclear magnetic resonance (PMR-spectrometer "TESLA BS-476A") and conductometric analysis (conductometer "Expert-002", slide-wire bridge). The molecular weight of synthesized oligomers was determined by the cryoscopy method.

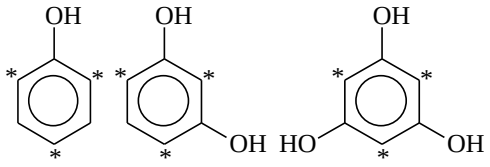
Main part. As monomers for the synthesis of plasticizers we used the oxyphenols shown in Table 1.

Table 1. Monomers used for the synthesis of plasticizing additives.

Technical name	Chemical name	Chemical formula
1	2	3
1	2	3
Phenol	hydroxybenzene	C_6H_5OH
Resorcinol	meta-dihydroxybenzene	$C_6H_4(OH)_2$
Pyrocatechol	ortho-dihydroxybenzene	$C_6H_4(OH)_2$
Hydroquinone	para-dihydroxybenzene	$C_6H_4(OH)_2$
Phloroglucinol	1,3,5-trihydroxybenzene	$C_6H_3(OH)_3$
Pyrogallol	1,2,3-trihydroxybenzene	$C_6H_3(OH)_3$

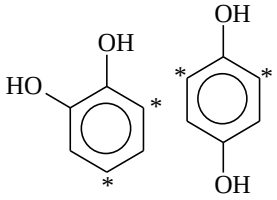
It is known that as a result of condensing interaction of phenol and its derivatives with the aldehydes, it is derived the oligomers andpolymers, which structure depends on the functionality of phenol, aldehyde type, mole ratio of the reactants and pH of the reaction medium. Thus, changing the type or function of the starting monomers, or the synthesis conditions, it is possible to synthesize the linear (may be slightly branched)thermoplastic oligomers (novolaks) or the highly branched thermosetting oligomers (resoles).

The phenols include the reactive hydrogen atoms, which are in the ortho and para positions to the hydroxyl group. Therefore, a monohydric phenol, a dihydric phenol - resorcinol and trihydric phenol - phloroglucinol are the trifunctionaloxyphenol



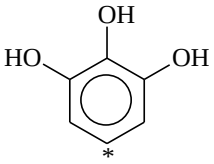
Phenol Resorcinol Phloroglucinol

The oxyphenols with the hydroxogroups in the ortho or para positions - pyrocatechol and hydroquinone - are bifunctional



Pyrocatechol Hydroquinone

The monofunctional include 1,2,3-trihydroxybenzene (pyrogallol)



Pyrogallol

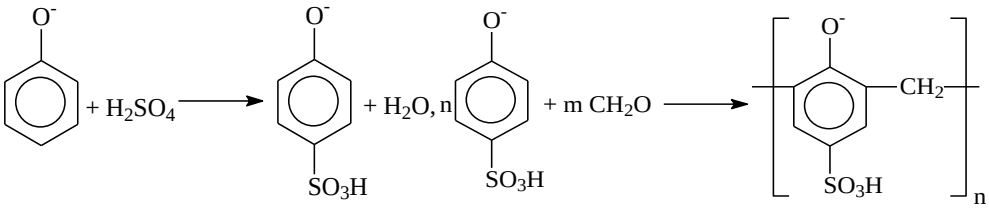
The polycondensation reaction of bifunctional phenol compounds led to the formation of linear polymers, which are soluble and do not cure when heated. The bifunctional phenols form only the thermoplastic oligomers.

By the condensation reaction with the trifunctional phenols (phenol, resorcinol, phloroglucinol) we can prepare the spatial ones - there are firstly formed the meltable and soluble thermosetting oligomers, which are capable to transfer into the insoluble infusible polymer molecules with the spatial structure when heated.

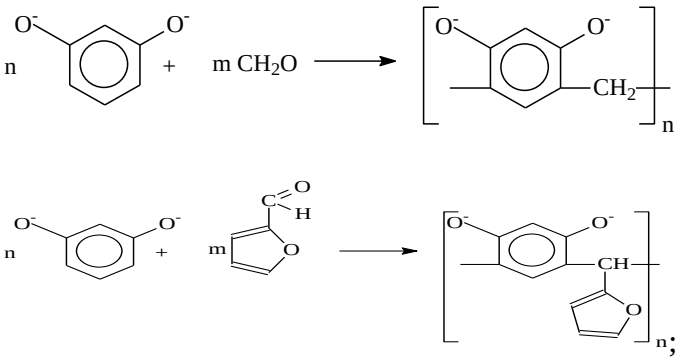
From aldehydes only the formaldehyde and furfurol are capable of forming the thermosetting oligomers at the polycondensation with the trifunctional phenols. Other aldehydes (acetic, butyric, etc.) do not form the thermosetting oligomers due to the reduced chemical reactivity and steric hindrances. At thepolycondensation oftrifunctional phenols with the formaldehyde and furfurol, they can be synthesized both as the thermoplastic and thermosetting oligomers.

Depending on the monomers used, we developed the various technologies for the preparation of plasticizers:

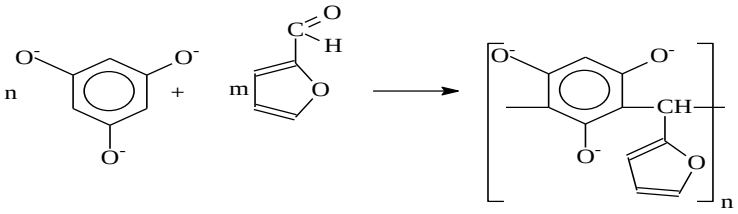
1) according to the well-known polycondensation method: sulfonation (for the introduction of hydrophilic groups), polycondensation with the formaldehyde in the acidic medium (to prepare the oligomeric molecules) and neutralization [3]:



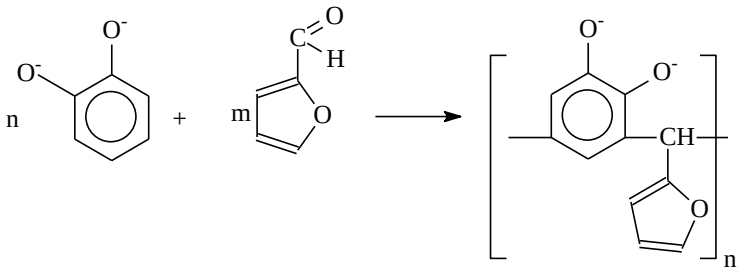
2) by the polycondensation of resorcinol with the formaldehyde and furfurol in an alkaline medium [4, 12,15]:



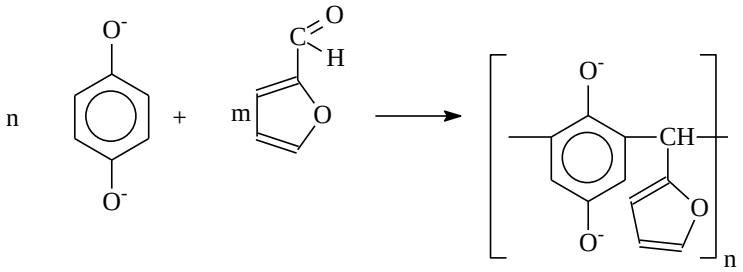
4) by the polycondensation of phloroglucinol with the furfurol in an alkaline medium [1,4,15]:



5) by the polycondensation of pyrocatechol with the formaldehyde and furfurol in an alkaline medium:



6) by the polycondensation of hydroquinone with the furfurol in an alkaline medium:



The synthesis products based on the pyrocatechol and hydroquinone had a low plasticizing ability and the oligomers based on the pyrogallol were failed to be prepared due to the monofunctional nature of this oxyphenol. Therefore the further studies with the pyrocatechol, pyrogallol and hydroquinone were not conducted in this paper.

The studies showed that at the polycondensation of oxyphenols with the formaldehyde or furfurol, it could be synthesized both thethermoplastic and thermosetting oligomers.

The thermoplastic (novolak) oligomers are formed in the following cases:

– at the ratio of phenol : formaldehyde 1 : 0.78-0.86 (excess of phenol) in the acidic medium;

– at the ratio of phenol : formaldehyde 1 : 2-2.5 (large excess of formaldehyde in the presence of acidic catalysts (strongly acidic medium);

The thermosetting (resole) oligomers are formed in the following cases:

– at the polycondensation of a trifunctional phenol, taken in excess, with the formaldehyde in an alkaline medium (basic catalysts). But it should be noted that the resole oligomers are prepared even after repeated excess of phenol that remains in the reaction products in a dissolved form;;

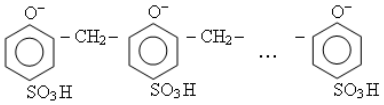
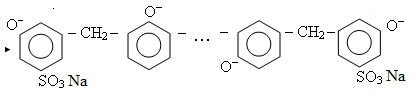
– at the amount of formaldehyde, taken in slight excess, both in the acidic and in alkaline mediums.

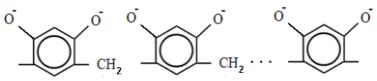
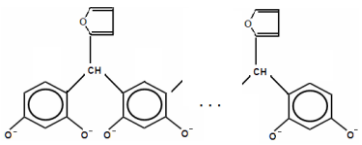
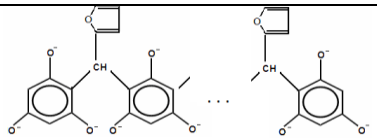
Thus, the preparation of thermoplastic oligomers is usually possible in the presence of acidic catalysts, which necessitates the neutralization of the reaction products for their use as the plasticizing additives. The synthesis of thermosetting oligomer is possible only at the polycondensation of trifunctional phenol and proceeds at milder conditions in the presence of basic catalysts.

In the course of this study we synthesized a number of resole and novolak oligomers based on the trifunctional phenols. We used phenol, resorcinol and phloroglucinol as the monomers for synthesis. It is known that the latter have higher reactivity as compared with the phenol due to the combined effect of two (three) hydroxyl groups. As the condensing agent we used both the formaldehyde, which is widely used for the synthesis of plasticizing additives, and furfurol. To prepare the thermoplastic or thermosetting oligomers, the synthesis was conducted respectively in the presence of acidic or basic catalysts.

The study of synthesis features, the establishment of composition and structure of the oligomers were performed by the methods of IR, PMR-spectroscopy, liquid chromatography and conductivity measurement [15]. The average molecular weight of synthesized oligomers was determined by the cryoscopy method. The results are summarized and presented in Table 2.

Table 2. Plasticizers based on the oxyphenol oligomers.

Plasticizer	Monomer	Preparation technology	Structural formula of oligomers	Molecular weight (average)
SB-1	phenol	1. Sulfonation; 2. Polycondensation with the formaldehyde in an acidic medium; 3. Neutralization		1200
SB-F	phenol	1. Sulfonation; 2. Polycondensation with the formaldehyde in an acidic medium; 3. Neutralization		1000

SB-R	resorcinol	1. Polycondensation with the formaldehyde in an alkaline medium		800
SB-RF	resorcinol	1. Polycondensation with the furfurol in an alkaline medium		800
SB-FF	phloroglucinol	1. Polycondensation with the furfurol		950

The molecules SB-1 and SB-F have a linear structure, that is, they are thermoplastic oligomers. The molecules SB-R, SB-RF, SB-FF have a spatial structure. The soluble and fusible thermosetting oligomers, which become insoluble infusible polymer molecules with the spatial structure when heated, have been formed during synthesis.

Then we studied the plasticizing ability and the rheological properties of synthesized oligomers. With increasing the concentration of additives, the value of critical shear stress was sharply decreased and the pace of its reduction slowed down; and with achieving the optimal dosage it reaches almost zero. The plastic viscosity is also sharply reduced as the beginning, but then reaches a certain minimum value. During the research we carried out the comparative characteristic with the famous domestic analogue - fluxing agent S-3. Dependencies of the critical dynamic shear stress and plastic viscosity of the cement suspensions on the concentration of plasticizers are shown in Fig. 2, 3.

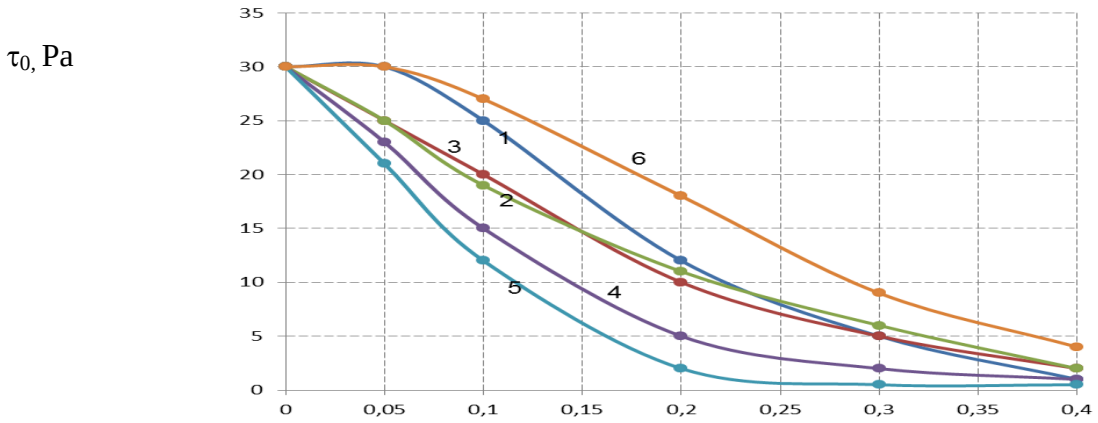


Fig. 2.Dependence of the critical shear stress of the cement suspension on the concentration of additives:1 – SB-1, 2 – SB-F, 3 – SB-R, 4 – SB-RF, 5 – SB-FF, 6 – S-3

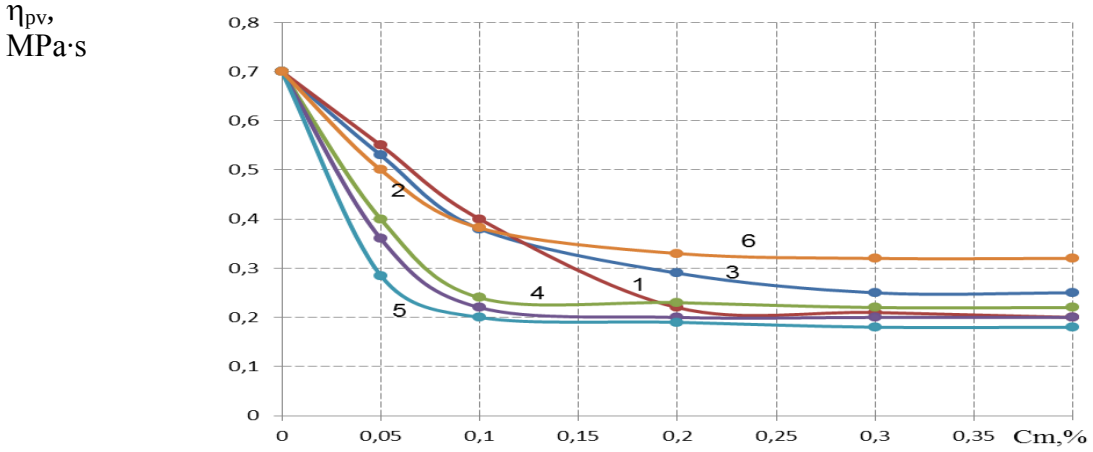


Fig. 2. Dependence of the plastic viscosity of the cement suspension on the concentration of additives: 1 – SB-1, 2 – SB-F, 3 – SB-R, 4 – SB-RF, 5 – SB-FF, 6 – S-3

The theoretical calculations enabled to explain an decrease in $[tau]_0$ to almost zero at the optimum dosages of additives by the strength decrease in the individual contact to values comparable with the energy of thermal motion [1]. And a decrease in the plastic viscosity relates primarily to the release of immobilized water and therefore, an increase in the relative content of dispersion medium. An increase in the thickness of water layers between the particles reduces friction between the moving layers and a decrease in plastic viscosity. This explains the observed plasticizing of the system by the introduction of synthetic oligomers and is due to the surface modification of the disperse phase particles by the adsorbed oligomers.

Summary. The thermosetting oligomers have the highest plasticizing ability, while the oxyphenolfurfurol plasticizers liquefy and stabilize the dispersion systems more effectively than the oxyphenolformaldehyde ones. The additive based on phloroglucinolfurfurol oligomers has the highest plasticizing activity, which is due to the maximum number of hydroxy groups in the aromatic links of oligomeric molecules that participate in the adsorption process.

Conclusion. The research conducted has proved that as a result of condensing interaction of phenol and its derivatives with the aldehydes, it is derived the oligomers andpolymers, which structure depends on the functionality of phenol, aldehyde type; and the structure of prepared oligomers makes influence on the plasticizing ability of additives. The scope of research conducted enabled to obtain the fundamental patterns of influence of the structure and composition of the oxyphenol oligomers on the plastification of cement mixtures. We have proved the possibility of using the oxyphenol resoles based on the trifunctional phenols for the cement suspensions as the effective superplasticizing additives, which are not inferior to the well-known liquifier S-3.

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References

1. Poluektova V.A., N.A. Shapovalov and A.A. Slyusar, 2012. Superplasticizer Based on the Phloroglucinolfurfurol Oligomers for the Aqueous Mineral Suspensions. Belgorod: Publiching House of the Belgorod State Technological University, p.: 108.
2. Samir Bouharoun, YannickVanhove, ChafikaDjelal, Pascale De Caro, Isabelle Dubois, 2012. Interactions between Superplasticizer and Release Agents at the Concrete / Formwork Interface. Materials Sciences and Applications, 3: 384-389.
3. ShapovalovN.A.Regulation of Aggregate Stability of Mineral Suspensions by the Oligomeric Aromatic Electrolytes: Thesis Abstract.Belgorod: Publiching House of the Belgorod State Technological University. 1999. 32 p.
4. Poluektova, V.A., N.A. Shapovalov, M.M. Kosukhin and A.A. Slusar, 2014. Plasticizing Additives For Water Mineral Dispersions On The Basis Of Oxyphenol Oligomers. Advances in Natural and Applied Sciences, 8(5): 373-379.
5. Poluektova, V.A., N.A. Shapovalov and A.I. Gorodov, 2015. Modifiers On The Base Of Oxyphenol Chemical Production Waste For The Industrial Mineral Suspensions. International journal of applied engineering research, 10(21): 42654-42657.
6. Poluektova V.A.N.A. Shapovalov, L.N. Balyatinskaya, 2012. Adsorption of Oxyphenolfurfurol Oligomers on the Disperse Materials. FundamentalnyeIssledovaniya (Fundamental Researches), 11(6): 1470-1474.
7. Poluektova V.A., 2006. Regulation of Rheological Properties and Aggregate Stability of the Aqueous Mineral Suspensions by the Superplasticizer Based on the Phloroglucinolfurfurol Oligomers: Thesis of the Candidate of Technical Sciences. Belgorod State Technological University, Belgorod.
8. Slyusar, A.A., V.A. Poluektova and V.D. Mukhacheva, 2008. Colloid-chemical aspects of plastifying mineral suspensions with oxyphenol-furfural oligomers. Scientific theory journal Bulletin of BSTU named after V.G. Shukhov, 2: 66-69.
9. ShapovalovN.A., V.A. Poluektova, 2015. Nanomodifier for the Cement and Concrete Mixtures. Herald of the Belgorod State Technological University named after V.G. Shukhov, 5: 72-76.

10. SlyusarA.A., V.A. Poluektova and N.M. Zdorenko, 2006. Superplasticizer SB-FF as an Additive for the Cement and Concrete Mixtures. IzvastiyaVysshykhUchebnykhZavedeniy (News of the Higher Education Institutions). Construction, 10: 16-20.
11. SlyusarA.A., N.A. Shapovalov and V.A. Poluektova, 2008. Regulation of the Rheological Properties of Cement and Concrete Mixtures by the Additives Based on theOxyphenolfurfurol Oligomers. StroitalnyeMaterialy (Construction Materials), 7: 42-43.
12. Poluektova V.A., Z.V. Stolyarova, S.M. Lomachenko and R.O. Chernikov, 2015. Adsorption of Domestic Modifier Based on the Resorcinol Production Wastes on the Surface of Mineral Particles. MizhnarodnyNaukovyZhurnal (International Scientific Journal), 4: 42-44.
13. Poluektova V.A. V.A. Lomachenko, Z.V. Stolyarova, S.M. Lomachenko and V.M. Malinovker, 2014. Colloid and Chemical Properties of the Aqueous Dispersions of Chalk and Marble. FundamentalnyeIssledovaniya (Fundamental Researches), 9(6): 1205-1209.
14. Poluektova, V.A., I.S. Makushchenko and R.O. Chernikov, 2015. Comparative analysis of the effectiveness hyper - and superplasticizers in mineral suspensions. Science, technology and Higher Education Materials of the IX International Research and Practice conference: 185-192.
15. Poluektova V.A., N.A. Shapovalov, L.N. Balyatinskaya, 2013. Synthesis and Structure of Superplasticizers Based on the Oxyphenol Oligomers. Fundamental nye Issledovaniya(Fundamental Researches), 11(6): 1136-1141.