Advances in Natural and Applied Sciences, 8(5) May 2014, Pages: 373-379

AENSI Journals

Advances in Natural and Applied Sciences

ISSN:1995-0772 EISSN: 1998-1090

Journal home page: www.aensiweb.com/anas/index.html

Plasticizing Additives For Water Mineral Dispersions On The Basis Of Oxyphenol Oligomers

Valentina Anatolievna Poluektova, Nikolai Afanasievich Shapovalov, Mikhail Mikhailovich Kosukhin, Anatoliy Alekseevich Slusar

Belgorod State Technological University named after V.G.Shukhov, Russia, 308012, Belgorod, Kostyukova ,46

ARTICLE INFO

Article history:
Received 20 March 2014
Received in revised form April 2014
Accepted 20 April 2014
Available online 26 May 2014

Keywords:
Aggregate stability, rheological properties, plasticizing ability, modifiers, supersofteners, colloidal and chemical properties of suspensions, oxyphenol oligomer.

ABSTRACT

Softeners on the basis of oxyphenol oligomers were studied; they were used by monomers for synthesis and plasticizing. The study of colloidal and chemical properties of construction dispersions with oxyphenol oligomer was also conducted. The data on rheological, sedimentation and electrokinetic properties of cement and model systems were obtained. The comparative assessment of plasticizing additives on the basis of single - double - and triatomic phenols with a known plasticizing additive of S-3 is given. It is shown that the supersofteners studied are effective from the point of view of their plasticizing ability. The limit dynamic tension of shift falls practically to zero, plastic viscosity considerably decreases. The peptization of the units and increase in aggregate stability of suspensions were observed. The most effective modifiers on plasticizing activity are the modifiers on the basis of oxyphenol furfural oligomers in comparison with plasticizing additives on the basis of oxyphenol formaldehyde oligomer electrolytes. It was proved that supersoftener on the basis of floorglucine and furfural oligomer diluted and stabilized mineral dispersions more effectively than a plasticizing additive based on resorcine and furfural oligomer; that can be explained by the quantity of oxygroups in aromatic links of oligomer molecules.

© 2014 AENSI Publisher All rights reserved.

To Cite This Article: Valentina Anatolievna Poluektova, Nikolai Afanasievich Shapovalov, Mikhail Mikhailovich Kosukhin, Anatoliy Alekseevich Slusar., Plasticizing Additives For Water Mineral Dispersions On The Basis Of Oxyphenol Oligomers. **Adv. in Nat. Appl. Sci.,** *8(5): 373-379, 2014*

INTRODUCTION

The leading role in regulation of rheological properties and aggregate stability of the high-concentrated water mineral suspensions which are used in production of cement, concrete, ceramics, and also in management of structurization processes in construction products and designs is assigned for softeners and supersofteners – the chemical additives, allowing to modify the interface of phases and purposefully to change an mobility of raw mixes and properties of finished products for specific conditions of operation (Kosukhin, M.M., *et al*., 2077; Pivinskii, Yu. E., *et al*., 2003; Shapovalov, N.A., *et al*., 2006; Shapovalov, N.A., *et al*., 2005; Baalbaki, M. and P.C. Aitcin, 1994).

The analysis of the plasticizing additives showed that practically all of them were oligomer electrolytes on the basis of organic aromatic compounds. Wide use was made by additives on the basis of products of polycondensation of naphthalene and its connections. The most used representative of this class is the flux oil of C-3 representing a product of condensation naphthalene sulfur acids and formaldehyde, however its production has recently faced a problem of deficiency of naphthalene and its high cost. Therefore the research in the field of synthesis and application of new plasticizing additives remains topical today (Poluektova, V.A., 2012; Samir Bouharoun, *et al*., 2012).

The scientists of Belgorod State Technological University have been engaged in the theory and practice of synthesis of supersofteners for the water mineral dispersions applied at production of cement, concrete, ceramics, construction products and designs for a few decades (Shapovalov, N.A., 1999; Poluektova, V.A., 2012; Slyusar, A.A., 2009; Shapovalov, N.A., *et al*., 2001; Kosukhin, M.M., 2006). The conducted study showed that oligomer of benzene, naphthalene and poly nuclear rank with various hydrophilic polar groups possessed plasticizing ability. There was also a working hypothesis concerning the possibility of application of effective plasticizing additives of oligomer on the basis of phenols with different quantity and the arrangement of oxygroups in a molecule. The study of dependence of additive efficiency on the structure of an oligomer molecule, the nature, quantity and position of hydrophilic polar groups in a molecule, the nature of monomeric

Corresponding Author: Valentina Anatolievna Poluektova, Belgorod State Technological University named after V.G.Shukhov, Russia, 308012, Belgorod, Kostyukova, 46

links, oligomer structure and other factors is the purpose of the present work. Detection of dependence of efficiency of additives from a structure of an oligomer molecule, the nature, quantity and position of hydrophilic polar groups in a molecule, the nature of monomeric links, oligomer structure and other factors became the main purpose of this work.

Methodology:

In this work we study the concentrated water mineral suspensions, the choice of which choice was caused by the scale of their application in the construction industry. The influence of plasticizing additives on the basis of oxyphenol oligomer on rheological properties of cement mixes with a specific surface 354 sq.m/kg, at the constant water cement relation equal 0,3 were studied on PTs-500-D0 pastes of the Belgorod cement works. In cement suspensions there is a continuous chemical interaction of the dispersive environment and a disperse phase that leads to continuous change of rheological, adsorptive, electrokinetic and other properties of system. Besides, cement has difficult mineralogical structure that complicates the study of the mechanism of plasticizing action of the developed oligomer. Therefore the main colloidal and chemical research was conducted on the model systems: suspensions of chalk ($CaCO_3$), alumina (Al_2O_3) and silicon dioxide (SiO_2), the structure of which includes the links close to components of cement.

The study of rheological parameters of suspensions was conducted by means of the rotational Reotest-2 viscometer. The concentration of additives (Cm) was counted in mass % on a solid from quantity of the disperse phase. Carrying out this study it became possible to define the dependence between values of the shifting tension and shift speed. Based on the results obtained, the rheological curves were drawn.

At great values of the shift speed of the dependence

$\tau = f(\dot{\gamma})$,

where [tau] – is the shifting tension, Pa; [gamma] – is the shift speed, c^{-1}, is easily approximated by the direct curve (fig. 1).

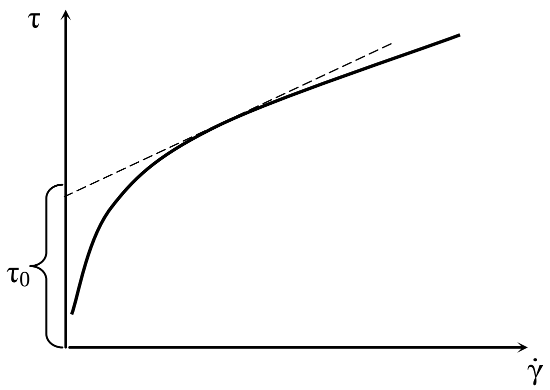


Fig. 1: The rheological curve of the disperse system.

The piece on the axis of the shifting tension is equal to the limit tension of the shift $[tau]_0$. The plastic viscosity $[eta]_{pl}$ was defined as an angle tangent of the straight line inclination to the axis of the shift speed.

The initial suspensions represent typical viscoplastic bodies. For the description of the character of the curves Ostvald's equation can be applied:

$\tau = k \cdot \dot{\gamma}^{n}$,

where [tau] is the shifting tension, Pa; [gamma] – shift speed, c^{-1}; *k* and *n* – the constants characterizing this system.

In the field of the average dosages of oligomer, a significant increase in the linear part of the curves is observed and their currency is described by Bingam's equation:

$\tau = \tau_0 + \eta_{pl} \cdot \dot{\gamma}$,

where $[tau]_0$ is the limit tension of the shift, Pa; $[eta]_{pl}$ – plastic viscosity, Pa·s.

In case of further increase in concentration of additives, the character of the curves shows that rheological properties of suspensions come nearer to the rheological properties of liquideous systems and can be described by the Newton's equation:

$\tau = \eta_{pl} \cdot \dot{\gamma}$.

The aggregate stability of cement suspensions was estimated on the basis of the most probable radius of the particles which were formed in the system cement-water by means of the sedimentation analysis.

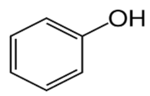
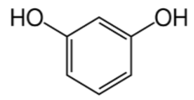
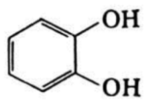
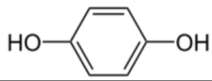
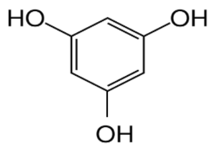
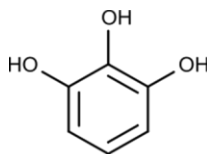
To determine the electrokinetic properties of the surface we used the method of capacity of the current taking into account the superficial conductivity, allowing to define [zeta] – the potential in the concentrated suspensions.

To establish the structure of oligomer molecules we applied a gas-liquid and liquid chromatography, ultra-violet spectroscopy, infrared spectroscopy, spectroscopy of a nuclear magnetic resonance, conductive-and potentiometry. The molecule weight of the synthesized oligomer was determined by the crioscopic method.

The main part:

We used oxyphenols as monomers for synthesis of softeners presented in Table 1.

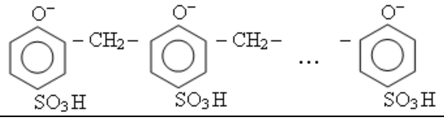
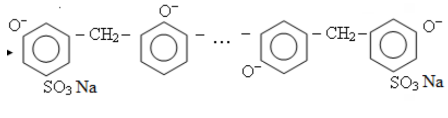
Table 1: Monomers used for synthesis of plasticizing additives.

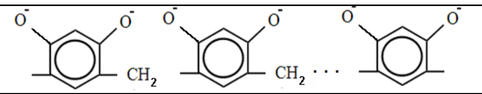
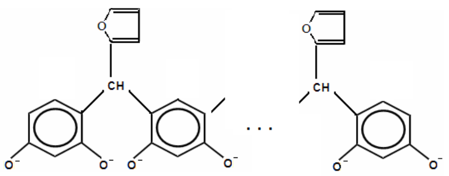
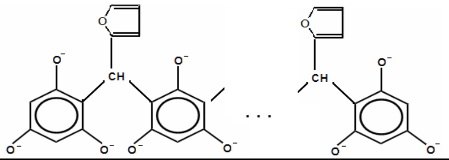
Technical name	Chemical name	Chemical formula	Structure of molecule
Phenol	hydroxybenzol	C_6H_5OH	
Resorcin	meta- dihydrobenzol	$C_6H_4(OH)_2$	
Pyrocatechin	Ortho- dihydrobenzol	$C_6H_4(OH)_2$	
Hydrochynone	Twain dihydrobenzol	$C_6H_4(OH)_2$	
Phloroglucine	1,3,5-trihydrobenzol	$C_6H_3(OH)_3$	
Pyrogallol	1,2,3-trihydrobenzol	$C_6H_3(OH)_3$	

Depending on the monomers used, various technologies of receiving softeners [3, 6] were developed.

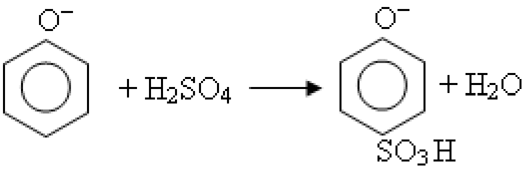
The softeners which were received on the basis of oxyphenol oligomers are systematized and presented in Table 2.

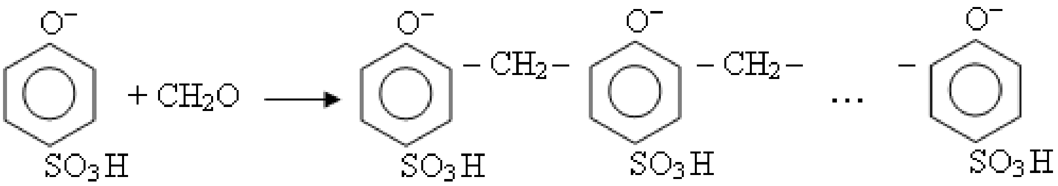
Table 2: Softeners on the basis of oxyphenol oligomers.

Designation	Monomer	Technology of receiving	Structural formula of oligomers	Molecule weight (average)
СБ-1	phenol	1. 1. Sulfate work 2. Polycondensation with formaldehyde in the sour medium; 2. 3. Neutralization		1200
СБ-Ф	phenol	1. Sulfate work 2. Polycondensation with formaldehyde in the sour medium; 3. Neutralization		1000
СБ-Р	resorcin	1.Polycondensation with formaldehyde in alkaline medium		800

				
СБ-РФ	resorcin	1. Polycondensation with furfural in alkaline medium		800
—	Pyrocate-chin	1. Polycondensation with furfural in alkaline medium	—	—
—	Hydrochi-none	1. Polycondensation with furfural in alkaline medium	—	—
СБ-ФФ	Phlorogluci-nol	1.Polycondensation with furfural		950
—	pyrogallol	1. Polycondensation with furfural in alkaline medium	—	—

Softeners on the basis of one-nuclear phenols (СБ-1, СБ-Ф) were produced in the polycondensation way: sulfate work (for introduction of hydrophilic groups), polycondensation with formaldehyde in the sour medium (environment) (for receiving oligomer molecules) and neutralization:

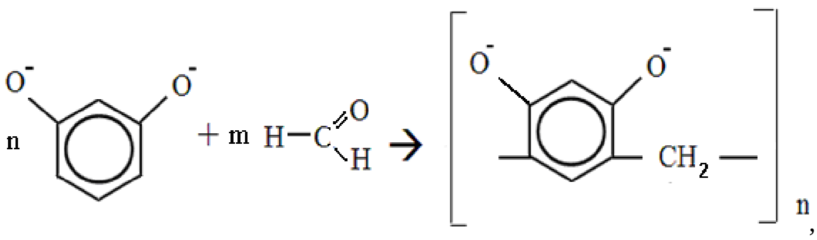




The polystageness of the process of synthesis of oligomer demanded big expenses and involved in increase in prime cost of plasticizing additives.

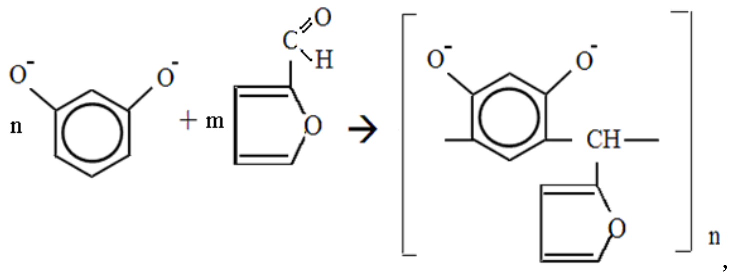
This problem was solved by means of the synthesis of softeners on the basis of two - and triatomic phenols. Single-stage technologies of synthesis of the following oligomer were developed:

1) СБ-Р – product of polycondensation of resorcin in the alkaline medium with formaldehyde:

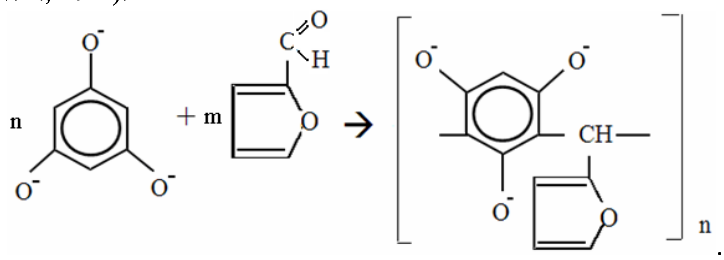


2) СБ-РФ – product of polycondensation of resorcin in the alkaline medium with furfural (Shapovalov, N.A., 1999)

Advances in Natural and Applied Sciences, 8(5) May 2014, Pages: 373-379



3) СБ-ФФ – polycondensation product of phlor glucinum in the alkaline medium with furfural (Poluektova, V.A., 2012):



Oligomera produced on the basis of individual substances of pyrocatechin, hydrochinone and pyrogallol had low plasticizing ability. Therefore, further study was not conducted.

The dependences of limit dynamic tension of shift and plastic viscosity of cement suspensions based on the concentration of modifiers are presented in Fig. 2. The comparative description, using domestic analog – C-3 flux oil was provided.

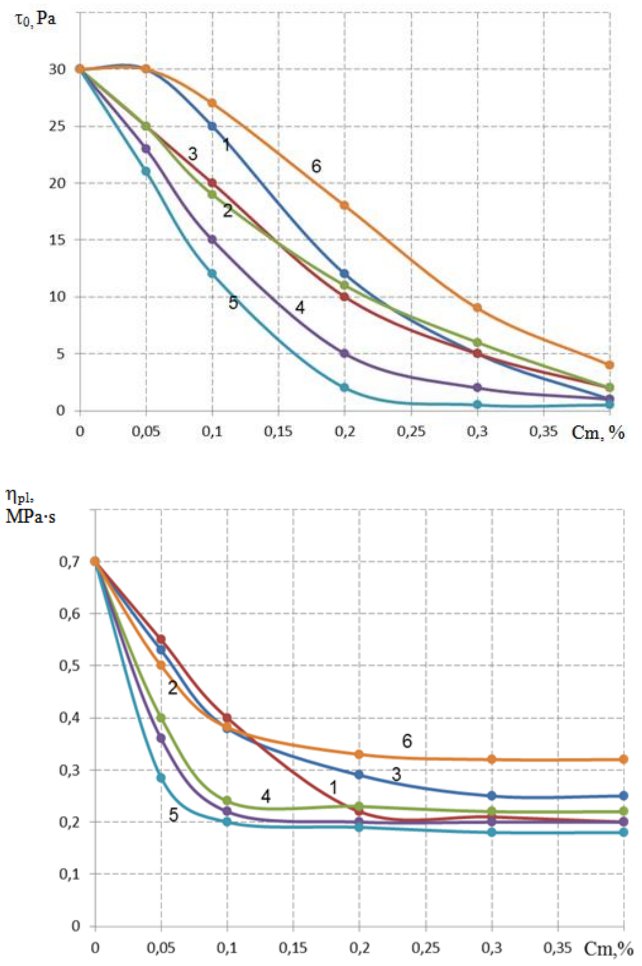


Fig. 2: Dependence of limit tension of shift (a) and plastic viscosity (б) of cement suspensions on the basis of The Belgorod ПЦ-500 Д0 from concentration of additives:

1 – СБ-1, 2 – СБ-Ф, 3 – СБ-Р, 4 – СБ-РФ, 5 – СБ-ФФ, 6 – С-3

In case of the increase in the concentration of additives, the limit tension of shift at first decreases sharply, then the rate of its decrease slows down and, achieving the optimum dosage, it tends to zero. The plastic viscosity also decreases sharply in the beginning, but then it reaches a certain minimum value.

The reduction $[tau]_0$ practically to zero at optimum dosages of additives is caused by the decrease in the durability of individual contact to values, comparable with thermal movement energy [13, 14]. The reduction in plastic viscosity is connected, first of all, with release of the immobilized water and with the increase, in this regard, in the relative of the dispersive medium. The increase in thickness of water layers between particles leads to the friction reduction between moving layers and to the decrease in plastic viscosity.

The influence of oxyphenol oligomer electrolytes on aggregate stability of suspensions was estimated on the most probable radius of the particles formed in the model systems by means of the sedimentation analysis. The study showed that the increase in the concentration of modifiers led to the reduction in the radius of particles and plasticization of the systems. In Fig. 3 there are curve dependences of the most probable radius of particles (r) on the concentration (Cm) of the modifier having the highest plasticizing activity СБ-ФФ.

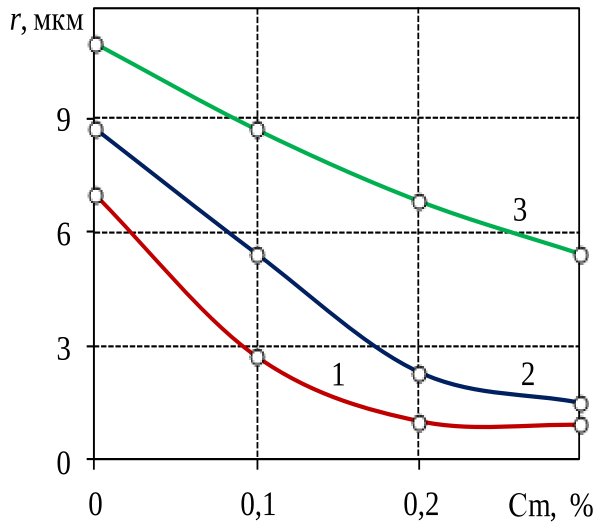


Fig. 3: Influence of the СБ-ФФ modifier on the relative size of units:
1 – chalk; 2 – alumina; 3 – silicon

The peptization of coagulants is only possible in the case of reversible nature of coagulation of particles in suspension. Therefore, the increase in aggregate and sedimentation stability of suspensions is connected with prevention from distant aggregation of particles. It should be noted that the greatest change in the particle radius is observed within smaller extents of filling the adsorptive layer than suspension transition from a tyxotrophe current to the Newtonian character according to rheology (Slyusar, A.A., 2008).

The peptization under the influence of supersofteners leads to the increase in the volume of the dispersive medium being in the untied condition.

The change in the rheological parameters and aggregate stability of mineral suspensions is caused by modifying of the surface of the disperse phase. The study of the adsorption isotherms showed that adsorption of additives on chalk was of a monomolecular character.

The study of electrokinetic [zeta] potential of the chalk particles showed that the surface of unmodified chalk had an insignificant excess negative charge. It is demonstrated by the small negative value [zeta] – of the potential. The increase in dosages of supersoftener leads to the change of absolute values [zeta] – the negative potential from □5 to □40 of mV that is explained by the existence of anion active groups in molecules of the modifiers studied. Their oligomer molecules are adsorbed on the surface of the disperse phase.

Comparing the data on adsorption, values of electrokinetic potential and rheological properties of cretaceous suspension, it should be noted that the concentration of additives, at which there is a completion of the monolayer formation on the surfaces of chalk particles and achievement of the maximum value [zeta] of the potential, corresponds to the release of limit tension of the shift practically on a zero value.

Conclusions:

The study conducted allows drawing the following conclusions. Molecules of additives on the basis of oxyphenol oligomer are adsorbed on the surface of particles, forming a monomolecular layer. The adsorption on the surface of particles is provided with dispersive forces of the interaction between the system of aromatic rings of an additive and the surface of the particles. Thus, as additives are anion active substances, the charge of the surface of particles becomes more negative that leads to the increase in the forces of pushing away by the particles. It is possible to get the same formation of hydrant layers round particles owing to the existence of hydrophilic groups in supersoftener molecules. As a result of pushing away, the forces prevail over molecular forces of attraction that leads to the decrease in the energy of coagulative contact to values, comparable with the energy of thermal movement. The thyxotropic caused by the interaction of particles, practically disappears. The limit tension of the shift falls practically to zero, the plastic viscosity considerably decreases. The peptization of units and the increase of aggregate stability of suspensions can be observed.

Conclusions:

The most effective modifiers in terms of plasticizing activity are the ones modifiers on the basis of oxy phenol and furfural oligomer (СБ-РФ и СБ-ФФ) in comparison with plasticizing additives on the basis of oxyformaldehyde oligomer electrolytes (СБ-1, СБ-Ф, СБ-Р). The colloidal and chemical study showed that СБ-ФФ supersoftener in comparison with СБ-РФ reduced extremely dynamic tension of the shift, it reduced more the superficial tension on the border of solution - firm body (Poluektova, V.A., 2012), it considerably increased the absolute value of electro kinetic potential, it increased aggregate stability of water mineral suspensions. It is connected with the fact that in СБ-ФФ molecules there are more oxygroups in aromatic links in comparison with СБ-РФ supersoftener molecules. The increase in oxygroups in a supersoftener molecule on the basis of phlorglucid and furfural oligomer promotes to the best stabilization of mineral dispersions and improves the plasticizing activity in comparison with a plasticizing additive on the basis of rezorcin and furfural oligomer.

The study conducted proved the possibility of the use of oxyphenol oligomer for water mineral suspensions as the effective plasticizing additives which were not worse than well- known C-3 flux oil being applied in construction now.

REFERENCES

Baalbaki, M. and P.C. Aitcin, 1994. Cement / Superplasticizer / Air-Entraining Agent Compatibility ACI Special Publication, 148: 47-62.

Kosukhin, M.M., 2006. Vibropressed concrete with a superpastifikator on the basis of resorcinol formaldehyde oligomer / M.M. Kosukhin, N.A. Shapovalov, Y.V. Denisova, A.V. Popova, S.I. Leschev, N.D. Komarova // Building materials., pp: 32-33.

Kosukhin, M.M., N.A. Shapovalov, Y.V. Denisova, 2007. The vibropressed concrete with various types of plasticizing additives // Izvestiya vuzov. Stroitelstvo,# 6. pp: 26-29.

Kosukhin, M.M., Theoretical aspects of action mechanism of superplastificators/ M.M. Kosukhin, N.A. Shapovalov // Concrete and Бетон иreinforced concrete., pp: 25-27.

Pivinskii, Yu. E., N. Ermak Yu., A.V. Cherevatova, N.A. Shapovalov, 2003. The effect of thinning agents on rheological and technological properties of the bauxite hcbs system. Refractories and Industrial Ceramics, 44 (3): 169-174.

Poluektova, V.A., 2012. Adsorption of oxyphenol and furfurol oligomer on disperse materials / V.A. Poluektova, N.A. Sharypina, L.N. Balyatinskaya // Fundamental researches. 6: 1470-1474.

Poluektova, V.A., 2012. Supersoftener on the basis of floor glucine and furfurol oligomer for water mineral suspensions: monograph / V.A. Poluektova, A.A. Slyusar, N.A. Shapovalov. – Belgorod: BSTU publishment. 12: 108.

Samir Bouharoun, Yannick Vanhove, Chafika Djelal, Pascale De Caro, Isabelle Dubois, 2012. Interactions between Superplasticizer and Release Agents at the Concrete / Formwork Interface. Materials Sciences and Applications, 3: 384-389.

Shapovalov, N.A., A.A. Slyusar', O.A. Slyusar', 2006. The effect of oligomeric electrolytes on the aggregative stability and rheological properties of aqueous mineral suspensions. Colloid Journal, 68(3): 350-356.

Shapovalov, N.A., A.A. Slyusar, V.A. Poluektova, O.A. Slyusar, 2005. Dilution of ceramic slip using complex additives. Glass and Ceramics, 62(7-8): 253-254.

Shapovalov, N.A., V.A. Lomachenko, M.M. Latypova, 2001. Plasticizing additives synthesized from by-products (bottoms) in the production of resorcinol. Наука – производству, 3: 20.

Shapovalov, N.A., 1999. Regulation of aggregate stability of mineral suspensions by oligomer aromatic electrolytes: abstract– Belgorod: BSTU publishment. p: 32.

Slyusar, A.A., 2008. Colloidal and chemical aspects of plasticization of mineral suspensions by oxyphenol and furfurol oligomer / A.A. Slyusar, V.A. Poluektova, V.D. Mukhacheva // Science and theoretical magazine Vestnik BGTU. pp: 66-69.

Slyusar, A.A., 2009. Concrete of the basis of knitting low water requirement and the modifier СБ-ФФ / A.A.Slyusar, V.A. Poluektova, V.D. Mukhacheva // Building materials. pp: 65-66.