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BIOCIDAL RESEARCH OF OXYPHENOLIC MODIFIERS FOR FUNGICIDAL PROPERTIES

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Abstract.

Using the biocidal research they revealed the fungicidal properties of plasticizers based on oxyphenols. The additives synthesized from the production of phenol, resorcinol, catechol are the oligomers of different composition, molecular structure, with different number and nature of functional groups. The tests were performed which determined the fungal resistance and the fungicide nature of cement and concrete samples with oxyphenolic additives. The isolates of Aspergillus niger and Penicillium chrisogenum Thom fungi were used as the biological factors of sample destruction. The assessment of resorcinol oligomer fungicidal properties was presented according to 6-point scale (sample/medium). The results of the experiment visual observation for fungal resistance were demonstrated. It was proved that the introduction of oxyphenolic superplasticizers reduces the pH drop over time dramatically due to the presence of resole groups in additives that also shows the manifestation of the fungicidal properties concerning the studied additives. The dependences of cement and concrete samples containing the additives contaminated by spores of molds were studied. The article proved that the additives based on oxyphenolic oligomers are the multifunctional modifiers of concrete, combining some effective plasticizing and fungicidal properties that can be used during the manufacture of building and structure structural elements in biologically active environments.

Keywords: biocorrosion, fungicidal additives, superplasticizers, mushroom mycelium, fungi Aspergillus niger and Penicillium, fungal resistance, polyfunctional modifiers.

Introduction.

Currently, polymer, plaster, gas silicate, cement and concrete materials are widely used in many industrial sectors. They have valuable physical and mechanical properties which make them suitable for harsh environmental

conditions. The operation of architectural and construction objects takes place with the active action of the environment temperature, humidity, chemicals and micro-organisms. The combination of favorable acidity and high humidity results in building material surface colonization by microorganisms and their subsequent microzonal penetration into the material depth, which results into the premature destruction of products. At that it is possible to change the composition and the strength of a material, and the material degradation products of microorganism products can be toxic ones [1].

The need for reliable of anti-corrosive biomaterials is a constant stimulus for production technology improvement concerning building products and materials. The damage caused by biocorrosion reaches billions of dollars per year and continues to increase during the accumulation of materials and products. With a unique enzymatic apparatus fungi are capable to destroy almost all the materials that enter their spores by turning them into simple mineral compounds. Only the presence of enzyme poisons in a substance can stop the destructive action of fungi. There are always the samples of microorganisms in an inactive state on the surface of samples. One of the most common methods of material protection from the biodeterioration of materials is the use of chemical compounds with biocidal activity.

They use antifungal agents widely in order to protect against a fungi impact. Fungicides are applied a material surface or introduce it into the composition during the stage of a material or a product manufacture. However, the use of fungicide additives has significant limitations. Many currently used fungicides introduced into the material composition worsen its physical and mechanical properties. Therefore the problem of finding and the development of new, effective fungicidal additives remains an urgent task today without the deterioration of building material strength characteristics.

During the research they put forward the hypothesis that the superplasticizers synthesized at BSTU named after V.G. Shukhov on the basis of oxyphenolic oligomers [2-9] and derived from the waste products of phenol, resorcinol, catechol, have fungicidal properties. The prerequisites for this assumption is that there is a benzene ring in the structure of this series superplasticizers [10]. Phenol has antibacterial and disinfectant properties. It was used for the first time in medicine as an antiseptic by Lister in 1867. The availability of oxyphenolic groups in SB-2A SB-3, SB 4, SB-5 composition allows to suggest that they will have fungicidal properties.

Methods. The synthesis of additives was carried out in a three-necked flask equipped with a stirrer and a reflux condenser. The temperature was maintained within the accuracy ± 1 °C.

The studies on the evaluation of fungal resistance and fungicide nature was carried out according to GOST 9.048-89 "Technical products. Laboratory test methods for mold resistance". The objects of the study were the samples of heavy concretes with plasticizing additives.

In order to produce the samples they used the following materials: cement - PC-500-D0 of Belgorod cement plant with a surface area of 354 m2/kg; The sand from Nizhne-Olshansky quarry with the size module of 1.27, the humidity of 3%, and the density of 1350 kg/m3; Novopavlovsk quarry gravel with the density of 1345 kg/m3, the moisture content of 1,2%, M-I200 and the fractions of 5-20 mm. The indicators of concrete compressive strength was determined in accordance with the GOST 10180-2012 using the press P-50 №1856 GOST 8905-73.

The isolates of Aspergillus niger and Penicillium chrisogenum Thom fungi were used as the biological factors of destruction.

The determination of fungal resistance was conducted according to GOST 9.048-89, method B, which establishes the presence of the material fungicidal properties. The duration of the test at the determination of fungicidal properties makes 14 days at least (in our case up to 28 days). The processing of results was performed to determine the fungicidal properties according to mold development degree within a six-point scale: they consider a material passed the test if there are molds, the intensity of which is estimated at no more than 3 points.

The assessment of studied additive fungicidal properties was performed by isolate sowing method on the surface of a solid and liquid nutrient medium (Czapek-Dox medium) into which various concentrations of fungicides were introduced. They used oxyphenolic superplasticizers as fungicides. The media without fungicides were the control ones. The fungicidal effect was determined visually by the growth of fungi on the surface at the evaluation according to 6-point scale within the GOST 9.048-89:

0 points - spores and conidia were not found by microscope;

1 point - microscopically visible germinating spores and slightly developed mycelium;

2 points - microscopically visible developed mycelia with a possible sporulation;

3 points - mycelia and sporulation are barely visible to an eye, but clearly visible under a microscope;

4 points - a naked eye can clearly see the development of fungi, covering at least 25% of a test surface;

5 points - a naked eye can clearly see the development of fungi, covering more than 25% of a test surface.

Morphological and cultural properties of the test organisms within Aspergillus niger and Penicillium chrisogenum genus were studied using the agar and the liquid nutrient medium, into which various concentrations of fungicides were added. During the process of isolate they observed visually the differences in colony morphology, mycelium

coloring and the onset of sporulation moment. He served as control medium with isolates without making fungicides. The differences of isolate microscopic picture were studied by the microscope MBI-1 and 3-MBI.

Main part. On the basis of oxyphenolic waste production the additives were synthesized in the course of research, which are the oligomers of different composition, molecular structure, with different number and nature of functional groups. The abbreviation of additives, the monomers used for the synthesis and the techniques for the most effective additives according to their plasticizing ability are shown in Table 1.

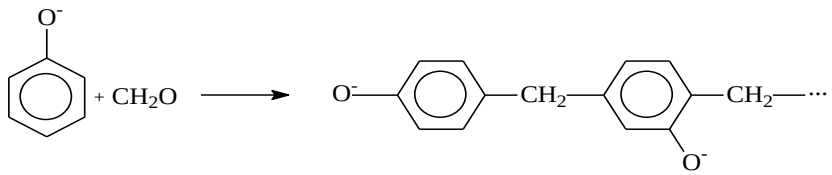
Table1. Plasticizing additives on the basis of chemical industry bottoms.

Additive name	Used monomers		Production technology
	Production waste, wt.(%)	Condensing agent	
СБ-2А	Of phenol (phenol (5-7), α-methylstyrene dimers (up to 29), cumylphenol (25-30), dimethylphenylcarbinol (up to 10), acetophenone (10-17), severe resins (9-25))	Formaldehyde	1. Polycondensation 2 Sulfonation 3. Neutralization
СБ-3	Of resorcinol (monomeric phenols (20-40), dimeric phenols (20-35), trimeric phenols (10-25), resorcinol (2-18))	Formaldehyde	1. Polycondensation 2. Neutralization
СБ-5	Resorcinol (monomeric phenols (20-40), dimeric phenols (20-35), trimeric phenols (10-25), resorcinol (2-18))	Furfural	1. Polycondensation 2. Neutralization
СБ-4	Pyrocatechol (catechol (15-16), resorcinol (2-4), heavy resins (75-80), NaCl (10-15), Na_2SO_4 (10-12))	—	1. Neutralization

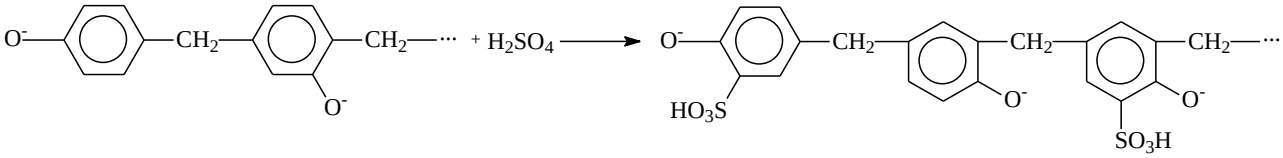
The polycondensation of resole molecules takes place during the synthesis. The result of it the binding of oxyphenolic nuclei by methylene groups or ether links. Phenolic hydroxyl groups are not involved in the formation. These conclusions are based on the studies of phenolic resin curing with a stable hydrogen isotope in the hydroxyl group [11].

The scheme of superplasticizer SB-2A obtaining can be represented as follows:

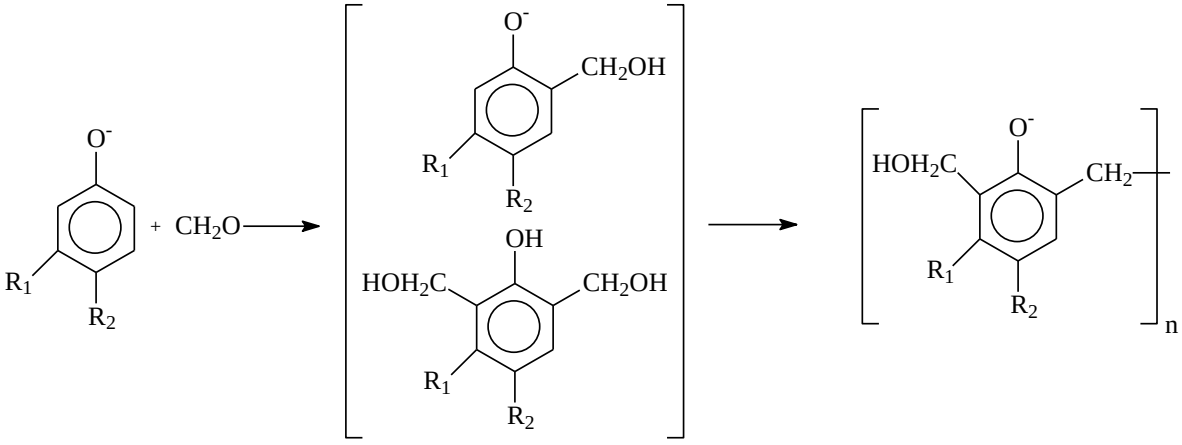
1) Polycondensation stage:



2) Sulfonation stage:

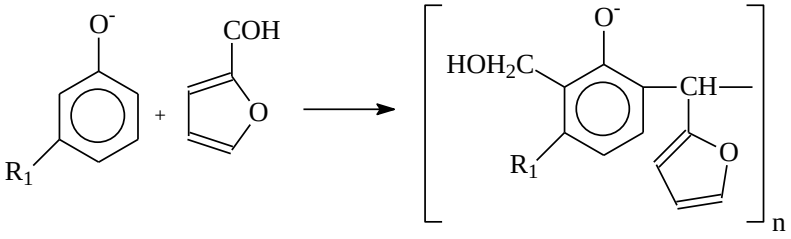


The scheme for superplasticizer СБ-3 obtaining will be presented as follows:

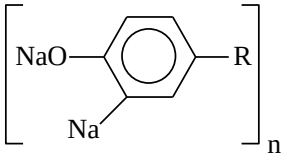


where n=3÷6, R_1, R_2= –OH,–ONa, $–OCH_3$, $–CH_3$ etc.

The scheme for superplasticizer СБ-5 obtaining will be presented as follows:



Instead, of СБ-4 superplasticizer scheme obtaining we will present only the empirical formula, because synthesis is possible without condensation stage.



All obtained oxyphenolic supplements are the plasticizing ones in accordance with the GOST 24211-2008. СБ-2А and СБ-4 are related to plasticizers, and СБ-3 СБ-5 are related to superplasticizers [2,3]. They are not inferior to well-known domestic and foreign counterparts according to plasticizing activity.

These additives can adjust the properties of concrete mixtures and the properties of a hardened concrete in heavy small grain and light concretes. They are designed to improve the technological properties of a concrete compound

(installation comfort increase); the loss of a compound motility regulation in time; the reduction of concrete heat treatment duration; strength increase; frost, concrete and reinforced concrete resistance increase in different harsh environments; the increase of concrete protective properties towards steel reinforcement; the reduction of cement consumption; the saving of fuel and energy resources [4-6].

The aim of this work was to determine the fungicidal properties of oxyphenolic oligomers by biocidal research. They performed the studies to determine the fungicidal nature and the fungal resistance of cement and concrete samples with the obtained additives, as well as for the comparison with the known superplasticizer C-3 (supplement based on sodium salts of naphthalenesulfonic acid and formaldehyde condensation products) and a complex plasticizing LMG additive.

The last additive is the concrete hardening accelerator and an effective plasticizer of the 2-nd group with air suction and a reinforcement corrosion inhibitor.

The studies showed that the resistance to mold impact in the test samples with the additives based on oxyphenols is quite high. Being typical heterotrophs, Aspergillus niger and Penicillium does not use the concretes with oxyphenolic additives as a food source for its development and functioning. All tested cement samples with the additives of СБ series have a fungal resistance and are fungicidal ones, unlike the analogue - LMG additive which is a favorable environment for mold development.

At the presence of essential nutrients in the environment, molds may colonize the studied samples actively, which do not have the ability to suppress or inhibit the growth of microbial communities (Fig. 1).

Aspergillus niger and Penicillium fungi colony

The growth of molds on the samples with СБ-3 additive

The growth of molds on the samples with LMG additive

Fig. 1. The influence of additives on fungal resistance and fungicide nature

The visual observations of fungal resistance experiment showed that the samples produced with the superplasticizers of СБ series are not overgrown with fungi mycelium. Due to the adsorption of superplasticizers on mineral particles, the process of interaction with acids is difficult.

These acids are the products of fungi life activity. Thus, it was proved experimentally that oxyphenolic oligomers reduce the growth of molds.

At that the estimate according to a 6-point scale (a sample/a medium) for LMG makes 4 / 4-5 points, and for oxyphenolic oligomers it makes 0/0 points using СБ-3 examples (0.35%) (Table 2) [12-15].

Table 2. Determination of fungal resistance and fungicide nature of cement samples with СБ-3, С-3 and LMG additives.

Additive (type)	Amount, %	W/C	Estimation according to 6 point scale (sample/environment) in points
Control	0	0,3	2 / 3
LMG	0,3	0,3	4 / 4-5
С-3	0,4	0,3	0 / 2-3, lateral surface. 1-2 points
С-3	0,6	0,3	0 / 1-3, lateral side 1 point
С-3	0,4	0,255	1(separate figures) / 1-2
С-3	0,6	0,255	0-1 / 1-2
СБ-3	0,1	0,3	0 / 0-1
СБ-3	0,2	0,255	0 / 1
СБ-3	0,35	0,255	0 / 0

Cement specimen durability change contaminated with mold spores in time with different additives is presented on fig. 2.

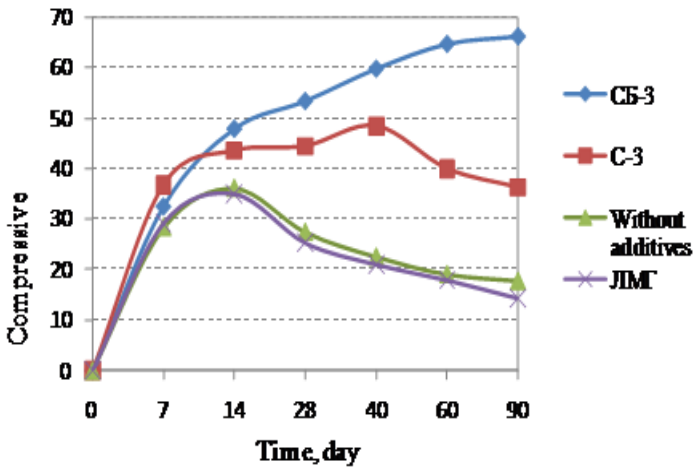


Fig. 2. Cement specimen durability change in time with various additives (samples were contaminated with mold spores).

The introduction of LMG additive provides some concrete strength reduction over time as compared to the control composition. The samples with С-3 addition show higher strength as compared with control samples, although the

sample strength is reduced in time with the addition of C-3. At the same time, the samples with the additives based on oxyphenols demonstrate a steady increase of concrete strength over time.

The comparative analysis of control sample strength containing additives and similar samples infested by fungi is shown in Table 3.

Table 3. The effect of fungi on sample strength.

Additive (type)	Amo unt, %	W/C	Specimen durability without fungi Rсж, MPa	Specimen durability with fungi Rсж, MPa
Control	0	0,3	59,3	59,0
LMG	0,3	0,3	43,7	23,1
С-3	0,4	0,3	66,5	63,5
С-3	0,6	0,3	66,3	56,3
С-3	0,4	0,255	60,3	59,0
С-3	0,6	0,255	73,0	68,0
СБ-3	0,1	0,3	28,8	41,3
СБ-3	0,2	0,255	54,0	51,8
СБ-3	0,35	0,255	59,8	66,9

According to numerous experimental data, they concluded the following: synthetic additives based on oxyphenolic oligomers have fungicidal properties and can be recommended as fungicides, and also allow to obtain the concretes with increased strength characteristics.

An important indicator of concrete biological stability is pH change of the aqueous extract from concretes over time, as most part of fungi leads to the decrease in pH values by spreading. In the course of life activity the biocorrosion products stand out which also lead to the decrease in pH values. The dependence of aqueous extract pH change from concrete contaminated by fungi showed (Fig. 3) that the introduction of superplasticizer C-3 resulted in a slight increase of pH, compared to a control sample.

The introduction of LMG reduces the biocidal properties of concrete, significantly reducing pH value. This is due to the fact that the foundation of LMG supplement structure is lignosulfonates, which serve as a nutrient medium for the growth of molds. At the same time, the introduction of superplasticizer СБ-3 reduces the pH drop over time drastically conditioned by the presence of resole groups in this additive. This change of pH leads to the conclusion about the manifestation of an additive fungicidal properties.

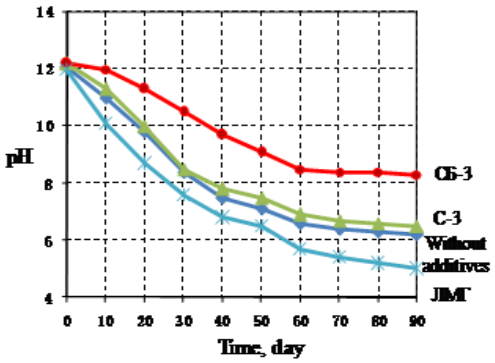


Fig. 3. Aqueous concrete extract pH change dependence over time.

The change of cement sample strength over time with various additives (samples were infected with fungi spores) showed that the introduction of СБ-3 additive demonstrates a steady growth of concrete strength in time, due to less exposure of biological corrosion on concretes with СБ-3 and is consistent with the presented fungal resistance data.

Thus, the use of oxyphenolic fungicidal additives allows to eliminate the impact of mold on concrete and to increase the biological stability of concrete. The obtained modifiers-biocides are designed to improve the processing properties and the protection of building materials. They satisfy the toxicological, sanitary requirements and have similar efficiency as the conventional additives in concrete, and even more efficient than some of them.

Summary. At the moment a large amount of by-products and intermediates is developed along with the main products of petrochemical synthesis. These products are hardly applied and are often regarded as waste. In this regard it is necessary to search for the ways of waste output reduction and the methods of their processing into valuable commercial products that will improve the environment. Therefore, the development of new technologies and technological processes of secondary raw materials processing is a critical issue of industrial ecology. The difficulties of search for some ways of industrial waste use and the byproducts of organic and petrochemical synthesis are usually explained by the fact that they all consist of a mixture of hydrocarbons which differ by their composition, structure and reactivity. Often the separation of this compound on the individual compounds is a very complex production and technical task that requires great technical and economic costs. Therefore, the synthesis of additives based on oxyphenol production waste without their separation into individual components is a promising use of hazardous chemical product waste. On the other hand it was proved that oxyphenolic supplements have a number of positive properties: they have a plasticizing effect, water-reducing, anti-corrosion, fungicidal properties. They improve the strength characteristics, etc. Thus oxyphenolic polyfunctional oligomers have a polyfunctional effect, and they be attributed to the polyfunctional modifiers of concrete.

Conclusions. The results of this work show that the additives based on oxyphenolic oligomers are the modifiers, combining effective plasticizing and fungicidal properties that can be used in the manufacture of building and structure structural elements in biologically active media [1].

Laboratory studies showed, that the introduction of polyfunctional modifiers in concrete composition at the amount of 0.1-0.25% from the weight of cement, completely inhibits the growth of fungi isolated from the surface of similar unprotected concrete samples. The strength characteristics of a cement stone with the studied additives during the infection with fungi spores are not decreased, but are increase somewhat due to the increased mobility of the cement paste, reducing the water/cement ratio, reducing the cracks in a concrete body and in the seal of its structure.

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References

1. Denisova Y.V., 2015. To the issue of fungicide additives use against the bio-corrosion of composite compounds. Bulletin of science and education of the North-West of Russia: e-magazine, 1 (1). URL: http://vestnik-nauki.ru/wp-content/uploads/2015/10/2015-№1-Денисова.pdf.
2. 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.
3. 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.
4. 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.
5. Slyusar A.A., V.D. Mukhacheva, 2005. Complex additive for cement-based mixture based on C-3 and СБ-5 superplasticizer. Bulletin of the Belgorod State Technological University named after V.G. Shukhov, 10: 273-275.
6. Shapovalov, N.A., A.A. Slyusar, V.A. Poluektova and O.A. Slyusar, 2005. Dilution of ceramic slip using complex additives. Glass and Ceramics, 62(7-8): 253-254.
7. Poluektova V.A., N.A. Shapovalova and A.A. Slyusar, 2012. Superplasticizer based phloro-glucinol-furfural

oligomers for aqueous mineral suspensions. Belgorod: Publishing House of the BSTU, p. 108.

8. Poluektova, V.A., Z.V. Stolyarova, S.M. Lomachenko and R.O. Chernikov, 2015. Adsorption of domestic wastes-based modifier of resorcinol on the surface of mineral particles. Міжнародний науковий журнал, 4: 45-46.
9. Poluektova V.A., V.A. Lomachenko, Z.V. Stolyarova, S.M. Lomachenko and V.M. Malinovker, 2014. Colloid-chemical properties of chalk and marble aqueous dispersions. Fundamental research, 9 (6): 1205-1209.
10. Poluektova V.A., N.A. Shapovalov and L.N. Balyatinskaya, 2013. The synthesis and the structure of superplasticizers based on oxyphenolic oligomers. Fundamental Research, 11 (6): 1136-1141.
11. Schwartz A.G. and B.N. Dinzburg, 1972. The combination of rubber with plastics and synthetic resins. M.: Publishing House of Chemistry, p. 224
12. Shapovalov I.V., L.Y. Ogrel, M.M. Kosukhin, V.I. Pavlenko, Yu.V. Popova, N.A. Shapovalov and A.A. Slyusar, 2002. Fungicidal modifier of mineral building compositions. Patent 2235695 Russian Federation. Publ. on 10/07/02. p. 6.
13. Kosukhin M.M., N.A. Shapovalov and Y.V. Denisova, 2007. Vibro pressed concretes with different types of plasticizers. Proceedings of the universities. Construction, 6: 26-29.
14. Shapovalov I.V., L.Y. Ogrel, M.M. Kosukhin, V.I. Pavlenko, Yu.V Popova, N.A. Shapovalov and A.A. Slyusar, 2006. Fungicidal modifier of mineral building compositions. Ecological systems and devices, 4: 50-51.
15. Kosukhin M.M., V.A. Poluektova, V.M. Malinovker and N.A. Shapovalov, 2013. Multifunctional superplasticizer for concretes based on catechol waste. Fundamental Research, 1 (3): 718-722.