ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

CHEMISTRY. PHARMACEUTICAL TECHNOLOGIES. BIOMEDICAL ENGINEERING

ХІМІЯ. ФАРМАЦЕВТИЧНІ ТЕХНОЛОГІЇ. БІОМЕДИЧНА ІНЖЕНЕРІЯ

UDC 621.742.4

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SYSTEM ANALYSIS OF MODERN AREAS OF INCREASING ENVIRONMENTAL AND SANITARY HYGIENIC SAFETY OF USING COLD HARDENING MIXTURES IN FOUNDRY

Л.І. Солоненко, С.І. Реп'ях, І.В. Прокопович, К.М. Сухий, Д.О. Дмитренко. **Системний аналіз сучасних напрямків підвищення екологічної і санітарно-гігієнічної безпеки використання холоднотвердіючих сумішей в ливарному виробництві.** На сьогоднішній день Україна є однією з найбільш забруднених техногенними речовинами країн світу, де в промислових регіонах концентрація токсичних і канцерогенних речовин щодня перевищує в два і більше разів їх гранично допустиму концентрацію. Причиною цього є складна екологічна обстановка в Україні. Високий рівень забруднення атмосферного повітря пов'язують з підвищеним вмістом в ньому формальдегіду, фенолу, фтористого водню, аміаку, а також пилу, діоксиду азоту та оксиду вуглецю. Одним з джерел надходження в навколишнє середовище таких речовин є ливарні цехи, які використовують у своїх технологічних процесах синтетичні смоли. Мета роботи: провести вибір найбільш перспективного напрямку розробки сполучного матеріалу і способу виготовлення ливарних форм і стрижнів з точки зору їх екологічної безпеки і відповідності санітарно-гігієнічним нормам виробництва лиття. У ливарних цехах України системи уловлювання, утилізації та переробки газів, що виділяються із залитих форм, як правило, відсутні. Частка токсичних речовин (фенол, бензол, толуол, крезол, формальдегід, аміак та ін.), що виділяються з форм і стрижнів у вигляді газів і конденсату, становить 30...40 % (по масі) всіх викидів ливарного цеху. Крім цього, залишки смоли і затверджувача в відпрацьованої суміші, потрапляють в грунт і грунтові води, збільшуючи показники техногенного забруднення території України. Наведено результати системного аналізу впливу сучасних холодно-твердіючих сполучних матеріалів в ливарному виробництві на екологічну безпеку та санітарно-гігієнічні умови виробництва виливків. Показано, що використання в ливарних цехах в якості сполучних матеріалів синтетичних смол посилює тяжке екологічний стан в Україні. Незаперечні переваги піщано-рідкостекольних сумішей – низька собівартість, матеріали вітчизняного походження, можливість використання відпрацьованої суміші для виробництва рідкого скла в сукупності з вирішенням проблем, пов'язаних з технологічністю цих сумішей дозволять в більшості ливарних цехів України вирішити проблему забруднення навколишнього середовища і різкого поліпшення санітарно-гігієнічних умов виробництва лиття при зниженні витрат на його виробництво. Тому, розробка нових способів формоутворення із застосуванням сполучних матеріалів неорганічного походження, зокрема, рідкого скла, є актуальним завданням сьогодення.
Ключові слова: екологія, сполучна, синтетичні смоли, рідке скло

L. Solonenko, S. Repyakh, I. Prokopovich, K. Sukhoi, D. Dmytrenko. **System analysis of modern areas of increasing environmental and sanitary hygienic safety of using cold hardening mixtures in foundry.** Today, Ukraine is one of the most polluted with technogenic substances of the world, where in industrial regions the concentration of toxic and carcinogenic substances daily exceeds twice or more their maximum permissible concentration. The reason for this is the difficult environmental situation in Ukraine. High levels of air pollution are associated with a high content of formaldehyde, phenol, hydrogen fluoride, ammonia, as well as dust, nitrogen dioxide and carbon monoxide. One of the sources of such substances into the environment is foundries, which use synthetic resins in their technological processes. Objective: to select the most promising areas of development of the binder material and method of manufacturing casting molds and cores

DOI: 10.15276/opu.1.57.2019.11

from the point of view of their environmental safety and compliance with sanitary and hygienic standards for casting production. In foundry shops in Ukraine, systems for capturing, utilization and processing of gases released from the cast forms, as a rule, are absent. The proportion of toxic substances (phenol, benzene, toluene, cresol, formaldehyde, ammonia, etc.) released from the forms and rods in the form of gases and condensate is 30...40 % (by weight) of all emissions from the foundry. In addition, the remnants of the resin and hardener in the waste mixture fall into the soil and groundwater, increasing the indicators of industrial pollution in Ukraine. The results of the system analysis of the influence of modern cold-hardening binder materials in the foundry industry on the environmental safety and sanitary conditions of the production of castings are presented. It is shown that the use of synthetic resins in foundries as binding materials of synthetic resins exacerbates the difficult ecological state in Ukraine. Undeniable advantages of sand-liquid mixtures are their low cost, domestic origin. The possibility of using a mixture of waste for the production of liquid glass in combination with solving the problems associated with the technology of these mixtures will allow most casting plants in Ukraine to solve the problem of environmental pollution. This will contribute to improving the sanitary and hygienic conditions of the production of casting while reducing the cost of its production. Therefore, the development of new methods of forming with the use of binders of inorganic origin, in particular, liquid glass, is an important task of the present time.

Keywords: ecology, binder, synthetic resins, liquid glass

Introduction. Today, Ukraine is one of the most polluted man-made substances of the world. According to the results of environmental studies in industrial regions of Ukraine, the concentration of toxic and carcinogenic substances exceeds their maximum permissible concentration by a factor of 2 or more per day. The reason for this is the complex ecological situation in the country. The high level of air pollution is primarily due to the high content of formaldehyde, phenol, hydrogen fluoride, ammonia, as well as dust, nitrogen dioxide and carbon monoxide in it. One of the sources of such substances into the environment is foundries, which use synthetic resins in their technological processes.

The solution to the problem of improving the ecological safety of foundry production is based on the analysis of three factors [1]:

– technological. It includes the selection of the most optimal, from the point of view of ecology, and efficient, from the point of view of the economy, the method of production of castings;

– economic factor includes the cost of facilities, equipment and its operation for the treatment of emissions, discharges and disposal of solid waste in relation to fees for environmental pollution;

– environmental factor includes the volume of gassing in the cold stage of the process and during pouring, cooling and discharging, the possibility and cost of depositing waste, recycling, etc.

Proceeding as from this, as well as from an economic, technological and environmental point of view, it is expedient to include the development of a new method of forming that would take into account all three stages of solving the problem of the ecological safety of the foundry domestic production where a binder using.

Formulation of the problem. According to the results of research carried out by scientists of the Max Planck Institute for Chemistry (Mainz), now around the world about 3 million people die from diseases caused by air pollution every year [2]. Ukraine for this indicator is one of the three most disadvantaged countries in the world [2, 3].

The reason for this is the difficult ecological situation in Ukraine, as evidenced by, for example, the map of the total chemical and radiation pollution of the environment of Ukraine [4]. In Fig. 1 indices of complex air pollution in some cities of Ukraine in 2018. An average value of exceedances of maximum permissible concentrations (MPC) of toxic and harmful substances in the atmospheric air of cities of Ukraine in the first half of 2018 are given respectively in Table 1 and Table 2 [5].

The high levels of air pollution in these cities the ecologists associate with a high content of formaldehyde, phenol, hydrogen fluoride, ammonia, as well as dust, nitrogen dioxide and carbon monoxide. At the same time, the most ecologically unfavorable cities are located in the eastern and southern parts of Ukraine, that is, in its most technically developed and technologically loaded regions.

Generally accepted that the main sources of emissions of harmful substances into the air are cement, steel, coal mining, petrochemical industries, thermal power plants and transportation. However, today in Ukraine, foundry shops should be attributed to the number of significant sources of emissions of harmful substances into the air.

Analysis of recent research and publications. Products foundry was and remains the basis of most industries economically developed and actively developing countries. Among the producing countries, China currently produces the largest amount of castings, the share of which, for example, in 2016 was 45.2 % in the global production of castings. The foundries of the countries of the European

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

Foundry Association (CAEF – the European Foundry Association) in the same 2016 produced 11.4 million tons of castings, Ukraine – 1.15 million tons of castings [6], which follows from the histogram in Fig. 2.

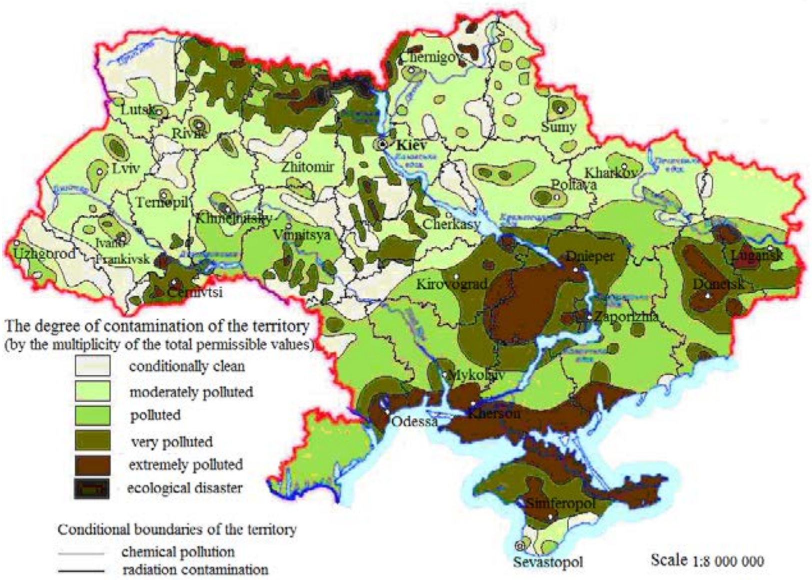

Fig. 1. Map of the total chemical and radiation pollution of the environment of Ukraine [5]

Table 1

Indices of complex air pollution in 10 the most polluted cities of Ukraine in 2018

№	City	ICAP*
1	Mariupol	13.6
2	Odessa	13.1
3	Lutsk	12.2
4	Kamenskoe	11.9
5	Dnepr	11.8
6	Kiev	10.0
7	Nikolaev	9.9
8	Slavyansk	9.0
9	Krivoy Rog	8.8
10	Kramatorsk	8.6

Table 2

The coefficients of the average excess of the MPC of toxic and harmful substances in the air of Ukrainian cities in the first half of 2018

City	Toxic and harmful substances									
	Formaldehyde	Phenol	Nitrogen Dioxide	Nitric Oxide	Hydrogen Fluoride	Hydrogen Chloride	Ammonia	Hydrogen Sulfide	Dust	Soot
Kiev			3.3	1.3		2.0				
Dnepr	3.3		3.0						2.1	
Odessa	4.7				1.4			+		1.2
Kamenskoye		2.3					1.3	+	2.3	
Mariupol	5.0									
Nikolaev	4.7									
Lutsk	3.7		2.8							
Rovno					1.6					
Zaporizhia								+		
Kramatorsk		3.0								

* Indices of complex air pollution (ICAP) are calculated by specialists of the Central Geophysical Observatory (CGO) named after B. Sreznevsky according to the results of the determination of 22 pollutants in the air, including eight heavy metals

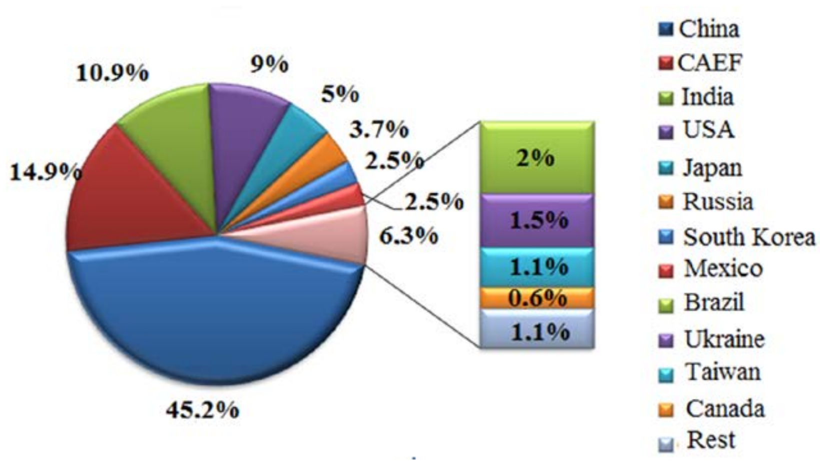

Fig. 2. The proportion of countries in the global release of casting

Despite the relatively small amount of casting, due to a temporary economic downturn, Ukraine remains among the leading countries producing cast parts. In 2016, the largest share in Ukraine consisted of castings from steel (44.34 %) and cast iron (47.81 %). At the same time, the share of castings from gray and alloyed iron amounted to 36.9 %, from ductile iron – 6.51 %, from NCI – 4.4 %.

The overwhelming number of such castings are made in forms where organic (synthetic) resins are used as a binder, curing under the action of either temperature or gaseous hardeners, enveloping the inorganic ingredients of the mixture and forming three-dimensional cross-linked polymer matrices in the process of structuring a mixture (CHM-s). In a much smaller amount (up to 4 %), steel and cast iron castings are made in CHM forms based on inorganic binding materials, as well as in sandy-clay forms, ceramic shell forms, etc.

High durability and manufacturability of the manufactured forms and cores, convenience and speed of manufacture, ease of knocking, etc. promoted the widespread use of CHM-s. However, the use of CHM-s has a significant drawback. This is the toxicity of the binder and the catalyst substance. This circumstance dramatically worsens the sanitary and hygienic conditions of casting production, creates a serious environmental hazard and can cause people to develop chronic diseases and poisoning, even to death [7, 8].

Objective. To select the most promising areas of development of the binder material and the method of manufacturing casting molds and cores from the point of view of their environmental safety and compliance with the sanitary and hygienic standards for casting production.

Research materials. The characteristics of any binder composition (binder with a catalyst for its curing) and the technological process of manufacturing casting molds and cores based on it, as well as recycling from an environmental safety point of view, include the following elements:

Safety regulations for storage, transportation, work with components of the mixture and auxiliary materials;

– release of toxic gases into the atmosphere during the mixing and filling of equipment, aging in equipment before the mold is assembled and filled with metal (“cold stage”);

– release of toxic gases, accumulation of condensate during the pouring of the mold by metal, solidification and cooling of the casting in the mold, knockout of the casting (“hot stage”);

– completeness, material and energy intensity of regeneration;

– release of toxic gases, solid wastes and dust, as well as the release of chemicals into the aquatic environment during regeneration;

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

– release of toxic gases and the entry of toxic substances into the soil and groundwater from waste mixtures and waste in dumps, their impact on the environment and the state of water resources [9, 10, 11].

Among the known binding materials in the foundry industry, the requirements for synthetic resins and mixtures based on them in terms of environmental safety and sanitary conditions of production are the highest and most numerous.

Among the known binding materials in the foundry industry, the requirements for synthetic resins and mixtures based on them in terms of environmental safety and sanitary conditions of production are the highest and most numerous. This is due not only to their high toxicity and carcinogenicity, but to fire and explosion hazards also. Moreover, these shortcomings are inherent in all types of processes of forming with synthetic resins, which follows from the data Table 3.

Table 3

Process, type of CHM and gases emitted from the cast forms and rods

Process, type CHM	Excreted toxic substances
CHM with a binder of organic origin	
Pep-set, Alfa-set (α-set), Beta-set (β-set) or Cold-box-MF, Resol-CO_2, Epoxy-SO_2, Cold-box-amine	carbon monoxide, methanol, formaldehyde, phenol, xylene, toluene, benzene, methanol, furfural, furyl alcohol, sulfuric anhydride, isoacetate, epichlorohydrin, diphenylolpropane, acrylic acid, isopropyl benzene hydroperoxide, trimethylolpropane, etc.
CHM with a binder of inorganic origin	
Based on phosphates, metal phosphates, liquid silicate glasses	Water
Based on ethyl silicate	Ethyl alcohol, water

At the same time, according to [9], the approximate shares of the amount of gas evolution from CHM-s are: 6...8 % – when pouring molds with metal; 85...90 % – when cooling the cast forms; 2...8 % – when knocking out castings.

The average composition of some degradation products, as well as the volume of air containing these substances at the level of their maximum permissible concentration (MPC) released from the filled forms when using the Alfa-set and Beta-set processes per 1 ton of CHM-s are given in Table 4.

Table 4

Average mass composition and air volume with degradation products for Alfa-set and Beta-set processes[*]

Substance	MPL, g/m^3	Average values of gas emission from 1 ton of mixture			
		from forms		from rods	
		by weight, g/t	by air volume, m^3/t	by weight, g/t	by air volume, m^3/t
Carbon monoxide	0.02000	610	30500	360	18000
Phenol	0.00010	34	340000	20	200000
Formaldehyde	0.00005	17	340000	10	200000

We assume that the mass of castings that produced by the Alfa-set and Beta-set processes is 40000 tons. The ratio of the mass of the molding mixture to the degraded resin and the mass of the casting produced is 1. Then the annual air volume emitted from the foundry with the maximum allowable the content of phenol and formaldehyde, will be:

$$340000 \cdot 40000 = 13\,600\,000\,000 \text{ m}^3.$$

[*] The air volume is calculated using data from the table and the MPL values of substances [12]

The resulting value of 13.6 billion cubic meters is approximate. However, for Ukraine, taking into account the technogenic and radiation contamination of its territory, the level of automation and culture of foundry, etc., it is not only undesirable, but also unacceptably high.

The main factors that determined the use of organic resins for the manufacture of casting molds and cores were:

– the possibility of pre-production and long-term storage of binder compositions for casting molds and cores;

– satisfactory technological and strength characteristics of structured mixtures;

– quick and time controlled curing of mixtures.

The use of organic binders has contributed to significant progress in the manufacture of foundry products. However, steadily increasing requirements for environmental protection today require a global review of the technologies and materials used. Saving energy and reducing emissions of harmful substances into the environment while maintaining production efficiency are two main challenges facing scientists around the world. Realizing the seriousness of the problems arising from emissions of toxic substances, the global community has developed initiatives aimed at improving the environmental situation (Montreal and Kyoto Protocols). As a result, a huge amount of organic compounds fell under a complete ban or limited use, which, in turn, stimulated the development of so-called "green" technologies.

The problem of using organic resins in the production of casting molds is related to their thermal decomposition during the production of molded products, since the onset temperature of decomposition of most organic compounds, as a rule, does not exceed 350...400 °C, which is significantly lower than the melting point of metals and alloys used to manufacture cast products. Based on the analysis of literature data and the review of the market of organic resins for foundry compositions, polycondensation resins (phenol-formaldehyde, phenol-urethane, epoxy, acrylic, epoxy-acrylate, epoxy-urethane) are the most used at present.

The curing mechanism of such resins with the formation of a three-dimensional cross-linked polymer structure in the process of structuring the mixture suggests the presence of one of the following or a set of factors, namely:

– input of hardener (hardener in addition to chemical reagents for a number of resins can be air moisture and carbon dioxide),

– raising the temperature of the structured mixture, at which the decomposition of the polymerization initiator can occur with the formation of a radical pair, initiating the polymerization process.

Given the volume of consumption of organic resins, their cost and commercial availability, today the most used are phenol-formaldehyde resins and their modified analogues, which are 2 times cheaper than acrylic and 3...4 times cheaper than epoxy, but the decomposition products of which (phenol , formaldehyde and their derivatives) are extremely toxic.

Currently, to solve environmental problems in the technology of manufacturing molded products associated with the decomposition of organic resins during heating, there are four main areas:

1 – reducing of the level of toxicity of using phenol-formaldehyde resins and their decomposition products. In the context of the present invention, it is promising to reduce the content of phenol and formaldehyde in resins at the stage of resin synthesis. This reduces (until completely removed) the resin content of the non-reactive solvent component by reducing the polymerization of resins. As a result, the viscosity decreases, less toxic solvents are used based on raw materials of vegetable origin, the efficiency of the resins increases and, accordingly, their content in the mixture decreases;

2 – improvement of equipment and technological processes aimed at the capture and disposal of decomposition products;

3 – search for commercially available and environmentally friendly organic resins;

4 – the use of inorganic binders [12].

Considering the prospects for solving the environmental problem of using synthetic resins in the foundry industry, should be noted that the implementation of paragraphs 1 – 3 does not solve it, although if successful, it can reduce the amount of toxic emissions into the environment.

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

The fact is that the use of synthetic resins, including those modified, using advanced systems for the capture and utilization of gaseous products of the destruction of resin from forms, ranging from their burning to the use of a specially selected strain of destructor microorganisms immobilized on an inert fiber carrier (packaging), is possible only reduce the amount of harmful substances emitted into the atmosphere [4, 5, 9]. But the cost of foundry production is substantially increased and this does not solve the problem as a whole

In the foundries of Ukraine, to reduce the cost of casting production, a system for capturing, utilization and processing of gases released from the cast forms, as a rule, are absent. As a result, the proportion of toxic substances (phenol, benzene, toluene, cresol, formaldehyde, ammonia, etc.) released from the forms and rods in the form of gases and condensate is 30...40 % (by weight) of all emissions from the foundry [12]. In addition, the resin residues, condensed products of its evaporation and destruction, as well as the hardener in the spent mixture, get into the soil and groundwater, increasing the indicators of man-made pollution of the territory of Ukraine. For this reason, no synthetic resin, including modified, cannot be environmentally friendly. In this regard, the statements of the developers of the resins about the absolute ecological purity of their next development [13, 14] are nothing more than an advertising move in the market of foundry materials.

It should also be noted some of the technological features of the application of widely advertised HTS-s. For successful use of CHM–s used quartz sand should have a certain grain composition and a limited amount of impurity ions, a strictly defined pH-level, a certain temperature and humidity up to 0.1...0.5 % (by weight). The negative technological features of CHM-s should also include the low duration of storage of forms and rods, significant gas evolution from them and a sharp irritating odor, the need to use sealed containers and pipelines, etc. In this regard, the question of technical efficiency in the foundry industry, economic feasibility and environmental safety of the use of synthetic resins is of particular importance.

Research results. The above data indicate the need for a fundamental change in the approach to technology and materials used in foundries in Ukraine. The way out of this situation is the replacement of synthetic resins with alternative materials of inorganic origin or the development of new methods for manufacturing forms with known or new binding materials of inorganic origin (orthophosphoric acid – CHM-f, liquid glass – CHM-g).

At all stages of production and storage of CHM–s with a binder of inorganic origin, only water vapors emit into the atmosphere and are indeed environmentally friendly materials. However, this type of HTS has its significant drawbacks. In particular, waste dumps of CHM-f lead to the pollution of groundwater by phosphorus compounds – phosphates. Entering phosphates into a reservoir leads to its eutrophication – a sharp decrease in dissolved oxygen in water due to the active growth of blue-green algae, which absorb large amounts of oxygen in water, respectively, the extinction of fish in the reservoir and its transformation into a swamp. Remaining in the ground, phosphates can cause contamination of the drinking water of aquifers, wells, etc.

Casting molds and cores based on CHM-f and CHM-g are characterized by high gas-making ability and crumbling, low processability, brittleness. In addition, any CES are characterized by the complexity and power consumption of regeneration, which increases the cost of the production process of casting.

The indisputable advantages of sand-liquid mixtures is low cost, the materials of domestic origin, the ability to use the waste mixture for the production of liquid glass in conjunction with solving problems related to the technological effectiveness of CHM-g. It will allow in most of the foundries of Ukraine to solve the problem of environmental pollution on hygienic conditions of production of casting while reducing the cost of its production.

Conclusion. Today, Ukraine is one of the most polluted with technogenic substances of the world, where in industrial regions the concentration of toxic and carcinogenic substances daily exceeds twice or more their maximum permissible concentration.

One of the sources of toxic and carcinogenic substances into the environment is foundries, which use synthetic resins in their technological processes.

No synthetic resin, including modified resin, can be environmentally safe in foundries in Ukraine.

Further use or expansion of the use of synthetic resins for the production of casting in Ukraine without radical reconstruction and reorganization of the technological process and equipment, as well without the use of highly efficient waste gas collection systems and thermal regeneration of waste mixtures is a dead end direction from the environmental and sanitary points of view.

To date, for foundries of Ukraine, only binding materials of inorganic origin are ecologically and sanitary-hygienically safe. In this regard, promising areas of work on the CHM can be considered:

– development of new methods of forming using domestic binding materials of inorganic origin;

– improving the composition of the binder compositions and mixtures based on liquid silicate glasses;

– development of new domestic binding materials of inorganic origin.

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Received January 15, 2019

Accepted February 15, 2019