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A pigment−filler in rubber compounds based on calcium carbonate containing waste

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Abstract. The article presents theoretical background and experimental data on the use of thermally modified waste of the sugar industry – sugar defecate as a black pigment filler in rubber compounds instead of carbon black and chalk. In previous studies, a method for processing calcium carbonate-containing raw material by thermal modification of its surface was suggested. As a result of heat treatment at a temperature of 600°C, a thermolysis sugar defecate TD_{600} - a fine black powder - was obtained. It was established that on the surface a layer of carbon (soot) coating $CaCO_3$ particles is formed. The purpose of this article is to study the possibility of using the thermolysis defecate TD_{600} as a pigment-filler in rubber compounds. To establish the possibil-ity of using the TD_{600} thermolysis defecate as a pigment-filler and an amplifier of polymer compositions, its physicochemical parameters were studied and compared with traditional pig-ments. A comparative analysis of physicochemical properties of fillers used in rubber com-pounds and thermolysis defecate TD_{600} was carried out. Properties of the pigment filler corre-spond to the parameters of materials used in rubber compounds; its oil absorption (80 ml/100g) is similar to that of classic carbon P514. The use of TD_{600} a black pigment-filler will solve two problems: saving raw materials and energy and improving the ecological situation.
Key words: pigments-fillers, thermality defecate TD_{600}, carbon black, carbon black, rubber compound, the Mooney viscosity, the butyl rubbe.

1. Introduction

Analysis of the market for the production and consumption of carbon black and carbon black in the world and Russia showed that the quantity of the product produced in the Russian Federation does not cover demand, and foreign analogues are too expensive. Figure 1 shows the main producers of carbon black in Russia.

A tire tread rubber contains about 45 parts of carbon black per 100 parts of rubber. Today, carbon black consumption is more than 6 800 000 tons. Most of this volume is used in rubber. Only 550 000 tons are used as pigment soot.

About 70% of all manufactured carbon black is used in the production of tires, ~ 20% in the production of rubber products. The remaining amount is used as a black pigment; a plastics anti-degradant; a component that gives plastics special properties (electricity conductivity, absorption of ultraviolet radiation, radiation of radars).

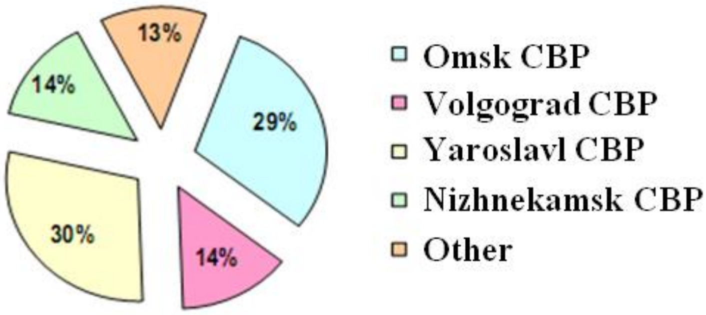

Figure1. Distribution of carbon black production in Russia.

From [1-10], it is known that carbon black is the main dispersed fillers used to strengthen elastomers.

In previous studies [11–17], it was shown that TD_{600} thermolysis defecate is used as a sorbent for purifying wastewater from various organic and inorganic pollutants, a filtration material for cleaning from soluble organic impurities, and a pigment-filler in silicate paints. The thermolysis defecate TD_{600} is used as a black pigment - filler in rubber compounds instead of carbon black and chalk. This paper presents studies of physicochemical properties of the pigment-filler based on TD_{600} and comparative characteristics of the carbon black-based pigments.

2. Materials and Methods

To establish the possibility of using the TD_{600} thermolysis defecate as a pigment-filler and an amplifier of polymer compositions, its physicochemical parameters were investigated and compared with traditional pigments.

The physical and chemical properties of the pigment-filler were determined depending on the temperature, pH of the aqueous suspension according to GOST 21119.3-91; density according to GOST 21119.5-75.

Determination of oil number or oil absorption. Five g of the pre-dried pigment were put into a porcelain cup with a capacity of 50 ml. The content was mixed with a glass rod with a melted (rounded) end; using a microburette with a capacity of 5 ml, 4-5 drops of oil were addedcarefully mixing the mass after each addition; after the formation of non-adherent lumps, the oil was added. To determine the absorption of oil, "Oksol" was used.

3. Results and Discussion

Oil absorption (in g/100 g) was calculated by formula: $M^1 = Vp_m/m_n$, where V is the volume of oil consumed, ml; m_n – pigment weighed, g; p_m – oil density; p – 0.778 g/cm^3. The results of experimental calculations are presented in Table. 1. The light resistance of the pigment was 6 months. Preliminary experiments showed the possibility of good dispersibility of TD_{600} in butyl rubber.

The results are presented in Tables 1 and 2.

Table 1. Physical and chemical properties of the defecate depending on the processing temperature.

Temperature, °C	Color of the thermolysis product	Value of the pH water suspension	Density, kg/m^3	Bulk volume, kg/m^3	Average particleradius um	Specific surface area, m^2/g	Oilnumber, ml/100g
105	TDbeige	9.8	2590	1540	2.0	14.08	-
500	TD grey	8.5	2545	1060	0.091	18.6	60
600	TD black	7.1	2530	1040	0.08	22.22	80
650	TD grey	8.4	2500	1050	0.098	23.5	70

Many authors have studied the effects of "binary" rubber-based fillers [8, 18]. We suggest using a ready-made "two in one" pigment - a filler consisting of calcium carbonate with a surface chemically bound layer of carbon black which is formed during heat treatment of the defecate at t = 600 °C.

Table 2. Physical and chemical properties of carbon fillers.

Indicators	Technicalcarbon P514	Naturalfillers			TD_{600}
		Graphite GLS-3	chalk	talc	
Specific adsorption surface m²/g	52	23.0	18.1	12.0	22.22
Density, kg/m³	1860	2130	2650	2750	2530
Oil number mg/100g	89	82.5	48	45	80
pH of water suspension	8.2	9.3	8.7	9.0	7-7.5

Analysis of the physicochemical properties of the pigment TD_{600} showed that it has similar properties as widely used fillers.Its oil absorption property is similar to that of P514 technical carbon.

Thus, the thermolysis defecate t = 600°C ($CaCO_3$ + C_{soot}) can be recommended as a "binary" filler in rubber compounds.

3.1. Analysis of dispersibility of TD600 filler in butyl rubber

Since the main indicator for the composition of rubber mixtures is dispersibility of the filler in rubber, we investigated the dispersion of the pigment TD_{600} in butyl rubber. The method for assessing the degree of dispersion of fillers [18-20] is used to evaluate the quality of rubber mixing,structure parameters and properties of rubber compositions.

It is known that the rate and degree of dispersion of fillers in rubber mixtures depend on the nature of the polymer used, mixing conditions and properties of the filler. Rubber compounds based on industrial butyl rubber containing 50 weight parts of carbon black filler (TU) and TD_{600} thermolysis defecate were used as research objects. The mixture was prepared using a laboratory mixer 320×160 during 8; 10; 12; 16, 20 and 30 minutes of mixing carried out sampling for analysis (Mooney viscosity). The results are presented in Figure 2.

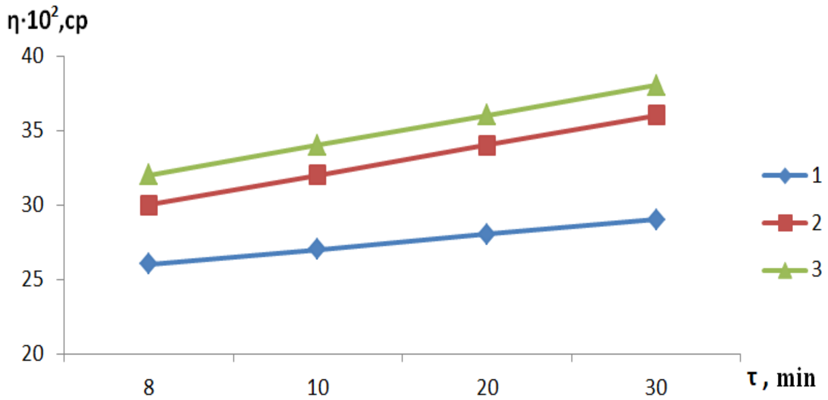

Figure2. The dependence of the Mooney viscosity in TU P514 (1) - based mixtures n; TD600 (2); CAD ground (3) on the duration of mixing.

The mixing time for the formation of a homogeneous compositionat which filler particles in rubber are distributed evenly turned out to be the same for all fillers (20-30 min). Mooney viscosity is inter-

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mediate between technical carbon and powdered CAD ground; however, a high degree of dispersion was observed for TD_{600} (95%). In fact, a chemical bond is formed between the polymer and the filler, and homogeneous floccules are formed during solidification which contributes to the thermo-mechanical high stability of the rubber mixture.

The advantage of the material is that if ordinary soot and black cannot be used to form suspensions due to low bulk density (100 ÷ 890 kg/m^3), they float on the surface of the dispersion medium (water or oil) when preparing suspensions. Pigment filler TD_{600} lacks this disadvantage. The indicators obtained on the basis of the defecate pigment compared with soot are presented in Table 3.

Table 3. Comparative indicators of pigment TD_{600} with carbon black.

T of firing, °C	Pigmentcolor	Typeofdestruction Colorchange	Bulkdensity, kg/m ^{3}
550	Dark grey	Barely noticeable	1060
600	saturated black	missing	1040
650	Gray	hardly visible	1030
Soot	black	invisible	100-500
black	black	inconspicuous	850-890

Analysis of the data shows that the black pigment corresponds to the typical sample of carbon black oby color, but it has 1.5-2 times higher bulk density which makes it possible to produce both aqueous and oily suspensions and use the pigment-filler for producing building materials and paints.

The study of the chemical composition of soot on the surface of $CaCO_3$ showed that its main component is carbon – 99.65%; hydrogen – 0.28%; oxygen – 0.08%; inorganic substances (ash) – 0.01%. Oxygen and hydrogen are present in soot due to adsorption of combustion products of carbohydrates on soot particles. Therefore, carbon can be presented as crystallites (C_xO_y).

The soot on the surface of the defecate is highly resistant to acids, alkalis, and light. The true density of the black pigment ranges from 2545 to 2590 kg/m^3. The bulk density of the pigment is: 1040-1060 kg/m^3. According to microscopic studies, each crystal consists of 3-7 parallel flat carbon lattices (Figure 3).

The presence of C_xO_y systems has a great influence on the surface properties. In cases where the amount of soot on the surface is not large, the solution becomes neutral (pH = 7.1); loss due to ignition at t = 600 ºC is equal to 18.25%.

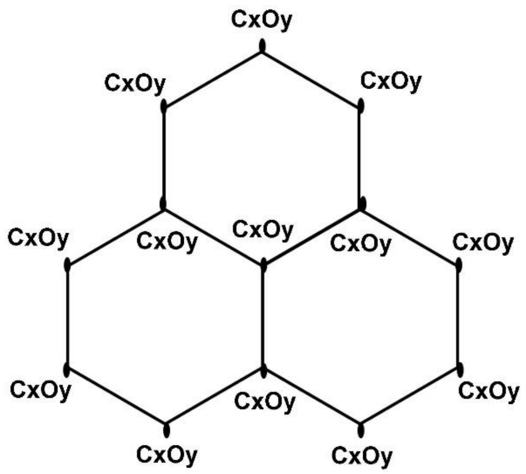

Figure3. The structure of inertness, TD_{600} can be recommended as a pigment-filler in rubber mixtures.

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Rubber is a multi-component system consisting of a polymer base (rubbers) and various chemical additives. To produce rubber, high molecular weight polymers with a low boiling point (room) and high elasticity are used. We used butyl rubber (polyisobutylene) with the formula:[-C(CH_3)$_2$- CH_2-]n-[-CH_2C(CH_3)=CH-CH,-]m, with the following parameters: ρ=910-930 kg/m^3; $t_{fluxing}$=100 °Catμ=70000–225000 (molecular mass).

When mixing, the solid phase of the pigment is evenly distributed in the dispersion medium (rubber). TD_{600} particles form hydrogen bonds with the hydrogen of the isoprene group of butyl rubber. The binding energy determined by the calorimetric method for the heat of wetting in benzene was 35–40 kJ/mol, and the length of the hydrogen bond was 0.17–0.14 nm [21–23].

As a result, the mixing process is uniform and stable, the sludge suspension is zero. Thanks to this “crosslinking”, the bond of the polymer and pigment particles TD_{600} is stable. Soot particles on the surface of $CaCO_3$ have a spherical shape which is in compliance with literature data [7].

The rubber contains various ingredients: vulcanizing agents, accelerators and vulcanization activators, plasticizers, fillers, antioxidants and other components that give it specific properties. The main components of rubber products (RTI) are pigments - carbon black fillers and inorganic fillers (chalk, clay, etc.).

We have suggested using the TD_{600} thermolysis defecate instead of chalk and soot which will make it possible to reduce the price of rubber products and recycle 80% of waste of the sugar industry improving improve the environmental situation.

Preliminary experiments showed good dispersibility of TD_{600} in butyl rubber. Comparative physicochemical properties of pigment-fillers (Table 2) showed that TD_{600} have properties similar to those of traditional. Itsoil absorption (80 ml/100g) is similar to that of classic carbon P 514.

Physical and mechanical properties of the rubber compound (butyl rubber –100 w.f.; pigment filler ($CaCO_3$ +C_{soot}) – 55-56 w.f.; sulfur - powder –2 w.f.) are presented in table 4.

Table 4. Physical and mechanical properties of the rubber compound

Brand TU	Conditional stress during elongation of 300%, kgf/cm^2		Conditionaltensile strength, ^{kg}·s/cm^2		Relativeextension, %	
	min	max	min	max	min	max
TD_{600}	92	97	170	194	510	586
P 514	84	96	174	190	530	559

P 514 was used as a reference filler. Table 4 shows that physicomechanical indicators of our products are the same level as those of rubber containing P 514. At the same time, carbon chemically bound to particles of calcium carbonate improves compatibility of fillers with other hydrocarbon ingredients of the rubber mixture.

Thus, the combined effect of these factors contributes to a more uniform distribution of the pigment in the rubber mixture increasing its density and uniformity.This was confirmed by the data of microscopic analysis of rubber mixtures.

The great advantage of using the pigment ($CaCO_3$ + C_{soot}) is hydrophobicity of the surface which helps reduce the cracking of rubber compounds in the vulcanization process and reduce the amount of scrap due to a decrease in the physical and mechanical strength of mixtures and products.

In order to establish the uniform distribution of the TD_{600} in rubber and the shape and size of particles of mixture components, optical studies of the microstructure of samples were carried out using a BIOLAM optical microscope. The scale of the photograph is equal to the total increase in the system of applied objects and eyepieces. An eyepiece 10×, a lens 9×0.2, and an objective micrometer with a division value equal to 10 µm = 0.01 mm were used.

An increase in micrographs was determined by dividing the size of a crystal by the true size of the same crystal previously measured under the microscope. The magnification was 200. Figure 4 shows

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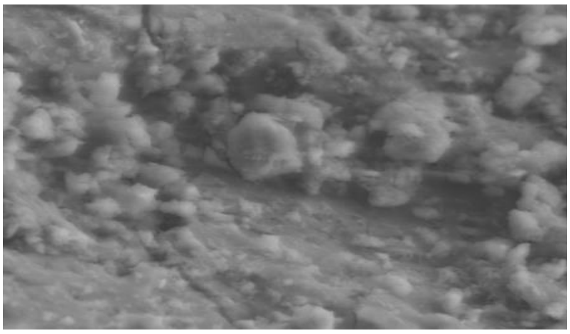
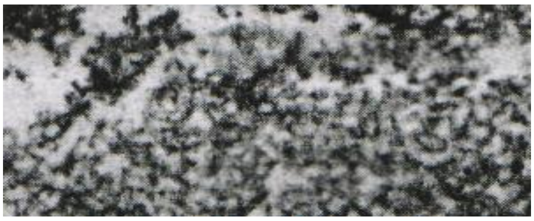
micrographs of the initial defecate and the TD_{600} pigment which is black with structural networks of soot particles.



a

b

Figure 4. Photomicrographs of samples (×200): initial defecate (a); dry pigment ($CaCO_3$ + C_{soot}) (b).



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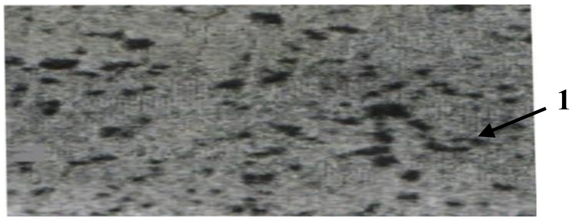

b

Figure 5. Pigment ($CaCO_3$ +C_{soot}) inthewater drop, ×200 (a); the mixture product in butyl rubber1 - ($CaCO_3$+ C_{soot}) particle, ×200 (b).

The micrograph of the pigment TD**600** (Figure 5b) shows that it is evenly distributed in the polymer base throughout the entire volume of the dispersion medium. Soot particles are visible on the $CaCO_3$surface. Due to its high lightfastness, structure, high specific surface area and inertness, the pigment was recommended and tested as a pigment-filler produced byKurskrezinotehnik. According to the laboratory data, the physico-technical indicators of the rubber product meet the federal standards. Mooney viscosity at 100 °C is 25-35 s.u.; conditional elongation at the 300% elongation is 45 kg.s./cm^2; conditional tensile strength is 45 cm; Shore hardness is 63, humidity is 0.2%.

Rubber mixtures were manufactured on laboratory rollers according to the regimes adopted for serial mixtures; there were no complications in technological processes and mixing parameters were not adjusted. TD_{600} was well distributed in the rubber matrix, without forming a mixture of foreign inclusions.

4. Conclusion

Comparative analysis of physicochemical properties of fillers used in rubber mixtures and a TD_{600} thermolysis defecatewas carried out. Properties of the pigment-filler correspond to the parameters of materials used in rubber compounds;its oil absorption (80 ml/100g) is similar to that of classic carbon P514.

Analysis of dispersion and mixing in butyl rubber was carried out. Mooney viscosity was determined (25-30 units). It meets the requirements of GOST for rubber compounds pigments. The TD_{600} can be recommended as a "dual-binary" filler in rubber compounds.

Comparative analysis of properties of the pigment-filler and traditional carbon black pigments made it possible to establish that the TD_{600} pigment corresponds to a typical soot sample, but has 1.5-2 times higher bulk density and will not float in the volume polymer base when mixed. It can improve homogenization of the mixture.

The assessment of stability of quality indicators and properties of TD_{600} rubber compounds in the Central laboratory of Kursk plant "Rezinotekhnik" showed that their indicators correspond to the P514 pigment.

The main consumer of carbon black and chalk is the rubber industry which uses more than 80% of world soot products. The use of the developed pigmentwill allow for 80% utilization of calcium carbonate-containing waste and improvement of the ecological situation.

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References

[1] Treboganova V M 1979 *Primenenie texugleroda v promy`shlennosti RTI* [The use of carbon black in the industry of rubber products] (Moscow: TsNIITEneftekhim) [In Russian]
[2] Pechkovskaya K A 1968 Sazha kak usilitel` kauchuka [Soot as an amplifier rubber] (Moscow: Himiya) [In Russian]
[3] Kraus G 1966 *Reinforcement of elastomers* (New York: John Wiley & Sons Inc)
[4] Orekhov S V 1973 Perexod shinnoj promy`shlennosti na ispol`zovanie texugleroda v sootvetstvii s nomenklaturoj i trebovaniyami mezhdunarodny`x standartov [The transition of the tire industry to the use of carbon black in accordance with the nomenclature and international standards] *Sy`r`e i materialy` dlya rezinovoj promy`shlennosti* [*Raw materials and materials for the rubber industry*] (Moscow: GUPNIISHIP) pp 89-91 [In Russian]
[5] Verbas V V 2002 Osobennosti primeneniya novy`x marok texnicheskogo ugleroda v shinny`x rezinax [Features of the use of new grades of carbon black in tire rubber] *Voprosy` ximii i ximicheskoj texnologii* [Chemistry and chemical technology issues] **5** 50-6 [In Russian]
[6] Belozerov I V 1964 *Texnologiya reziny`* [Rubber technology] (Moscow: Himiya) [In Russian]
[7] Koshelev F F, Kornev A E and Bukanov A M 1978 *Obshhaya texnologiya reziny`* [General technology of rubber] (Moscow: Himiya) [In Russian]
[8] Goncharov V M and Khodov V V 1988 Vliyanie sostava i sposoby` polucheniya binarny`x napolnitelej na osnove texnicheskogo ugleroda i svojstva rezin [The influence of the composition and methods of production of binary fillers based on carbon black and properties of rubbers] *Kauchuk i rezina* [*Rubber*] **7** 30-4 [In Russian]
[9] Yashunskaya F I et al 1974 *Spravochnik rezinshhika* [Handbook of the rubber producer] ed P A Zaxarchenko et al (Moscow: Himiya) [In Russian]
[10] Estrin R I and Pesin O Yu 1994 Vzaimosvyaz` mezhdu strukturny`mi pokazatelyami texnicheskogo ugleroda i svojstvami rezinovy`x smesej i vulkanizatorov [The relationship between structural indicators of carbon black and properties of rubber compounds and vulcanizers] *Kauchuk i rezina* [*Rubber*] **4** 12-6 [In Russian]
[11] Lupandina N S, Sapronova Z A and Lesovik V S 2014 Copper and nickel substances extraction from water mediums by waste of disaccharide production *J. of Eng. and Appl. Sci.* **9(8)** 310-5
[12] Starostina I V, Sverguzova S V, Ovcharova I V and Pendurin E A 2015 Recycling of microbiological industry waste with the obtaining of foaming agents for building industry *Int. J. of Applied Eng. Res.* **10(21)** 42701-6
[13] Sverguzova S V, Starostina I V, Tarasova G I and Fomina E V 2015 Using Ferruginous Quartzite Tailings In Dry Building Mixes *Int. J. of Applied Eng. Res.* **10(24)** 45082-90
[14] Sverguzova S V, Tarasova G I, Starostina I V and Fedorina M Y 2015 Composite pigment-filler on the basis of sludge of heat power plant and tails of engichment of ferruterousquartzites *Res. J. of Appl. Sci.* **10(12)** 827-31

[15] Sapronova Z A and Starostina I V 2016 Disposal of Synthetic Surfactants-Containing Wastewater Treatment Sludge in the Ceramik Brick Production *Procedia Eng.* **150** 1610–6

[16] Tarasova G I and Starostina I V 2016 Special features of processing siliceous rocks *Int. J. of Pharmacy and Technology* **8(4)** 24770-80

[17] Sukhanov E V, Sapronova Z A and Fomina E V 2017 Nekotory`e osobennosti koagulyacionnoj ochistki vody` s pomoshh`yu py`li e`lektrostaleplavil`nogo proizvodstva [Some features of coagulative water purification with the help of electric steelmaking dust] *E`kologiya i Promy`shlennost` Rossii* [*Ecology and industry of Russia*] **21(1)** 24-9 [In Russian]

[18] Harris E V, Jones F E and Church F C 1976 *Carbon blacks in a variety of elastomers. Cabot Corp. Technical Report RG-130* (Alpharetta: Cabot Corp.)

[19] Dmitrenkov AI, Shumilin YF 2002 Analiz dispergirovaniya napolnitelej v kauchukax [Analysis of dispersion of fillers in rubbers] *Voprosy` ximii i ximicheskoj texnologii* [*Chemistry and chemical technology issues*] **5** 111-6 [In Russian]

[20] Grishin O I 1980 Ocenka stepeni dispergirovaniya [Estimation of the degree of dispersion] *Kauchuk i rezina* [Rubber] **10** 24-7 [In Russian]

[21] Epstein L M and Shubina E S 2003 Mnogolikaya vodorodnaya svyaz` [Multi-sided hydrogen bond] *Priroda* **6** 40-5 [In Russian]

[22] Maes G and Smets J 1993 Cooperative hydrogen bond. Quantitative study using IR Fourier spectroscopy of matrix isolation *J. Phys. Chem.* **97(9)** 1818-25

[23] Tarasova G I 2018 Razrabotka sostavov silikatny`x krasok na osnove termoliznogo transporterno-moechnogo osadka - otxoda saxarnoj promy`shlennosti [The development of compositions of silicate-based paints thermalizing conveyor-washing sediment – waste of the sugar industry] *Stroitel`ny`e materialy` i izdeliya* [*Construction Materials and Products*] **1(1)** 21–31 [In Russian]

[24] Tarasova G I 2012 Racional`ny`j sposob polucheniya pigmentov-napolnitelej iz metallosoderzhashhix promy`shlenny`x otxodov [Rational method of producing pigments – fillers from metal-containing industrial waste] *Vestnik BGTU im V G Shukhova* [*Bulletin of BSTU named after V G Shukhov*] **2** 128-32 [In Russian]