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COMPOSITION AND PROPERTIES STUDY OF GALVANIC SLUDGE HEAT TREATMENT PRODUCTS

The results of investigations of chemical and phase composition and dispersity of precipitates formed in wastewater treatment of galvanic enterprises of the Republic of Belarus are presented. Conditions of modifying precipitates by liquid glass and effect of temperature on phase composition and colors of heat treatment products are investigated. Paint-technical properties of heat treatment products dependence on sludge/liquid glass ratio and heating temperature is shown. Increased opacity and color purity and reduced oil absorption are established. This is due to the change in dispersity of the sludge in the process of liquid glass modifying.

Introduction. Thermal recycling into pigment materials, first of all for building industry, is one of the trends of galvanic sludge disposal. A number of studies [1–4] demonstrate that on the basis of galvanic sludge it is possible to receive pigments, pigment fillers with different shades of brown and red colors, technical features of which being approximately the same as those of natural pigment – iron minium, synthetic red – α-Fe_2O_3, as well as anticorrosive pigment materials in the form of phosphate and ferrite compounds. Analyses of the results of numerous researches in the area of galvanic sludge recycling into pigment materials show that the sludge-based raw material to be treated thermally must meet several requirements, in particular: it must correspond to the prescribed value of iron compounds content in scaling of Fe_2O_3, to the molar ratio of chromophore-containing metal compounds and to the high dispersity. As it is well known the paint-technical properties of pigments (covering and oil absorption) depend on the nature of their porous structure, particles dimension and shape, specific surface. Widely used pigments and pigments-fillers are usually polydisperse materials, and at the same time, most of them have the average particles dimension within the range from 0.2 to 10.0 μm, the value of specific surface makes 60–200 m^2/gr. Particles of pigment materials can have spherical, acicular, plate-like and other shapes. It is demonstrated that for the heat treatment products achieved on the basis of galvanic sludge formed at waste-water treatment by electrocoagulating method or with ferriferrohydrosol, the particles average dimension does not exceed 20 μm and at that the content of the fraction 0–10 micron can make 90%. The particles are usually ball-shaped and the shape factor is within the range of 0.7–0.9. In the series of studies [5, 6] it is mentioned that when reducing the particles average dimensions the color strength and intensity of pigment materials and their covering capacity increase. That's why to increase the pigment characteristics, the adsorption and chemical inoculation of the pigment surfaces is applied. The organic or non-organic silicates of alkaline metals are widely used for chemical inoculation; they are entered on the pigment obtaining stages such as chemical deposition of chromophore-containing compounds, washing, drying.

The present paper deals with the study of phase composition and paint-technical properties of products of the heat treatment of galvanic sludge inoculated with liquid glass. With this purpose the sediments generated during the treatment of waste water of some galvanic factories in the Republic of Belarus were used. The respective characteristics are given in Table 1. According to the table the tested sludge differed in content of chromophore compounds, especially iron, chromium, copper.

Table 1

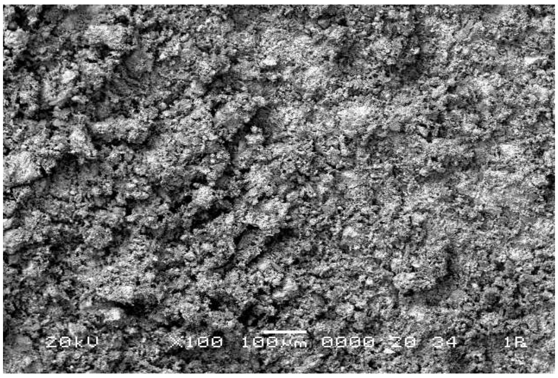
Parameters of galvanic sludge

Number of sludge sample	Place of sampling	Method of treatment	Content of main components in sludge, wt. %				Content of water-soluble substances, wt. %	Mass losses at burning 850°C, wt. %
			Fe_2O_3	ZnO	Cr_2O_3	CuO		
1	RUE Affiliated “ZENIT” Mogilev	Reagent (caustic soda)	45.8	8.9	2.2	26.4	1.76	86.9
2	RUE “MAZ” Minsk	Reagent (caustic soda)	50.1	14.1	3.4	2.4	2.57	87.5
3	JSC “Belelektromontazh” Minsk	Reagent (ferrofer-rihydrosol)	41.5	34.6	4.8	–	1.38	85.8
4	JSC “BelAZ” Baranovichi	Reagent (caustic soda)	55.7	1.3	9.4	1.0	1.36	84.9

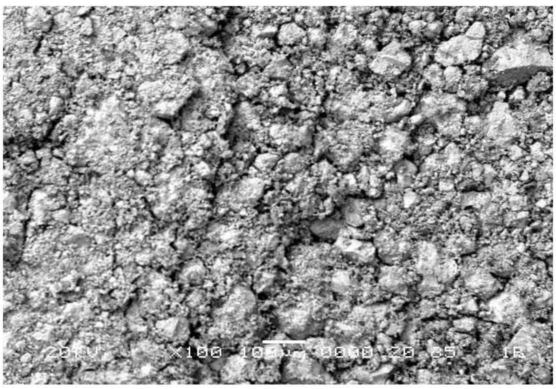
Note. Drying at 100°C up to constant mass.

Main part. Sludge inoculation was made on the basis of mass ratios liquid ”glass : sludge” (on a dry basis) = 1.5 : 100 (pH = 9); 2.5 : 100 (pH = 10); 5.0 : 100 (pH = 11.5). Suspension at mass ratio “water – sludge” being equal to 1.5 was mixed with water glass, then carefully mixed up and held at the temperature 60–80°C during 3–4 hours at full volume. After filtration the sediment was dried at 100°C up to the constant mass and studied, then it was heat-treated at preset temperatures to obtain pigment materials. The particles dimensions and shape have been determined by electron-microscopic method using “Jeol JSM – 5610LV” scanning electron microscope and “Analysette 22” laser microanalyzer of particle distribution under dimensions; the phase composition has been detected using 08 Advance diffractometer manufactured by the company “Bruker AXS” (Germany). Paint-technical properties, in particular covering capacity and oil absorption, have been determined under standard procedures.

According to the electron-microscopic researches it was found out that the sludge inoculation with the liquid glass results in the significant changes of the sludge dispersity, which is confirmed by the data of electron microscopy of inoculated and non-inoculated sludge (Fig. 1).



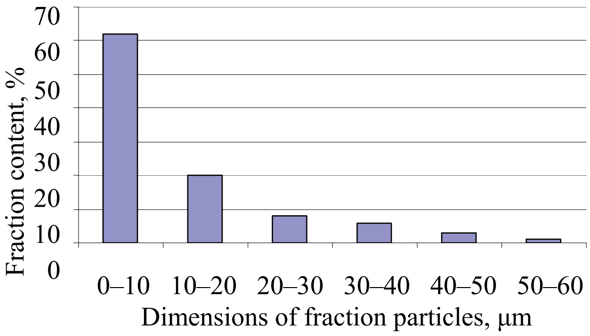
No. 4



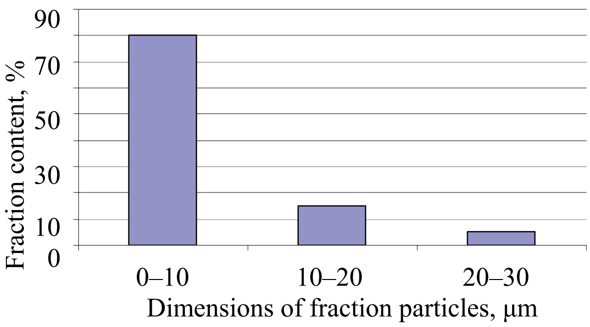
No. 1

Fig. 1. Electron microphotography of No. 4 and 1 sludge samples inoculated by liquid glass

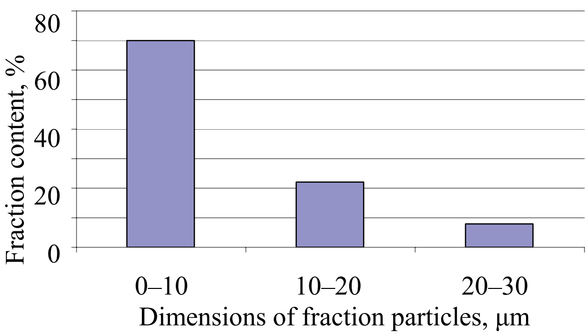
The inoculated samples consist of irregular shape particles having the dimension varying from 1 to 30 μm. Small particles are characterized by the shape close to ball-shape and at the sam time there are small non-isometric particles. The analysis of histograms shows that the inoculated sludges have rather close distribution of the particles by dimensions. The particle with dimensions from 0 up to 10 μm make 95.0 wt % of fraction while the non-inoculated initial sludge exceeds 65.0 wt. % (Fig. 2).



a



b



c

Fig. 2. Distribution of the particles by dimensions for the following sludge samples: *a* – non-inoculated sludge No. 4; *b* – inoculated sludge No. 4; *c* – inoculated sludge No. 1

The provided data indicate the increase of the studied samples dispersity, which is probably connected with peptizing action of liquid glass solution onto the sediment during its inoculation.

According to the X-ray phase analysis, the iron compounds and compounds of other chromophore metals in the dried sludge are in the X-ray amorphous state. Sludge sample No. 1 (Table 1) is light-brown. After the heat treatment at 300°C the color changes to black-brown. Such a color is caused by the high quantity of copper hydroxide contained in the sludge, and the temperature increase provokes its dehydration followed by generation of copper oxide having the black color. Further increasing of temperature up to 600°C does not influence the color, however at 800°C the sample is dark-brown. The same color is typical also for the products of heat treatment of sludge No.4 at 800°C. According to the X-ray phase analysis, the products of the mentioned sludges heat treatment include two crystalline phases, i.e. hematite and maghemite, the main of which is maghemite.

Presence of maghemite (his structural formula is $Fe^{3+}[□_{1/3}Fe_{5/3}^{3+}]O_4^{-2}$, where "□" is cation vacancy) can be caused by the filling of cation vacancy with the atoms of copper, chromium and nickel and thus its structure stabilization, at the same time the spinel with ferrite structure can be created. In this connection the transformation of maghemite into hematite is complicated and is carried out at higher temperatures.

Iron-and-zinc containing sludge (samples No. 2, 3) is characterized by the significantly higher content of ZnO and CaO. At the temperature of 100°C the sludges have dirty-reddish tint. The temperature rising to 300°C, the color changes to light-orange (sample of sludge No. 3), and the sample of sludge No. 2 – to dirty-red color. The samples color remains unchangeable up to the temperature of 600°C. Sludge No. 2 (heat treated at 800°C) has the red color that is connected with hematite crystallization, and sludge No. 3 is light-red because of the formation of both hematite and zincite having the white color.

Despite the fact that the hematite α-Fe_2O_3 is the basic crystalline phase, based on the sludges chemical composition, the heat treatment products contain the ferrites generated through the following reactions:

$$CaCO_3 + Fe_2O_3 = CaFe_2O_4 + CO_2;$$

$$ZnO + Fe_2O_3 = ZnFe_2O_4;$$

$$CuO + Fe_2O_3 = CuFe_2O_4;$$

$$ZnO + Cr_2O_3 = ZnCr_2O_4.$$

Paint-technical properties of tested sludge samples, heat-treated at different temperatures, are shown in Table 2. According to the results obtained the parameter of the covering capacity of the heat treatment products of tested sludges changes within the wide limits depending on temperature of the sludge heat treatment and on the conditions of their inoculation by liquid glass. On the basis of the data from Table 2 it becomes evident that increasing of the samples treatment temperature results in the significant increase of the covering capacity of generated pigment materials and in the reducing of its oil absorption.

Thus, the temperature rising from 600 up to 800°C, the oil absorption reduces approximately from 80 to 49 g/100 g practically in all the samples. At the same time the values of covering capacity are lowered from 50–26 down to 25–10 gr/m^2. The research results show that the inoculation of sludges with liquid glass and their further heat treatment result in covering capacity reduction, i.e. to the increase of pigment materials opacity. It is to be mentioned that the heat treatment products of sludges No. 3 and 4 have the minimum values of covering capacity at the temperature of 800°C. The mass ratio "liquid glass : sludge (dry)" = 1.25–2.5 : 00 (pH = 9–10) is the most optimal in respect to the paint-technical properties of pigment materials. At such a ratio the heat treatment products have more intense color and better paint-technical properties. At the ration "liquid glass : sludge" = 1.25 : 100 (pH = 9) the content of water-soluble substances in the samples (for all the samples) is at the same level as their content in pigment.

Table 2

Paint-technical properties of heat-treated samples

Number of sludge sample	Temperature of heat treatment, °C	Covering capacity, gr/m^2				Oil absorption, g/100 g				Content of water-soluble substances, wt %
		Water glass : sludge ratio, wt %								
		0	1.25:1	2.5:1	5.0:1	0	1.25:1	2.5:1	5.0:1	
1	600	35.9	24.7	25.5	36.8	87.3	75.5	73.7	8.2	1.12
2	600	27.5	24.9	25.9	48.9	62.7	52.1	54.3	59.8	1.10
	800	22.2	20.0	25.9	35.8	49.2	48.3	51.6	57.6	1.10
3	600	22.7	21.3	25.1	32.7	66.1	60.1	62.6	69.2	1.67
	800	18.4	12.6	18.5	23.5	54.8	69.3	65.3	62.2	1.67
4	600	22.7	20.7	24.6	32.5	68.2	64.1	67.3	62.3	1.8
	800	11.4	10.0	22.3	26.5	53.8	52.7	60.3	64.16	1.8

Note. 100 gr of dry sludge are considered as a unit of sludge.

Increasing of ratio liquid glass : sludge (on a dry basis)" over 2.5 : 100 (pH = 10) results in the decrease of paint-technical properties as well as of color purity and intensity.

Conclusion. Surface inoculation by liquid glass, through heating sludge suspension containing liquid glass results in the reduction of sludge dispersity and formation of products with color and paint-technical properties corresponding to those of synthetic iron-containing pigments. This allows to consider galvanic sludges promising raw materials for the production of pigment materials having the combination of required characteristics.

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