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UTILIZATION OF INDUSTRIAL WASTE IN THE TECHNOLOGY OF SYNTHESIS OF INORGANIC PIGMENTS IN DIFFERENT OXIDE SYSTEMS

It was established that industrial waste high-iron Red Sludge, SiC-sludge, medium-temperature STK-1, high Al-containing - spent catalysts AKM, and highly zinc-containing - spent absorber of hydrogen sulfide NIAP-02-05 can be used as a feedstock for synthesis of inorganic pigments of various colors with the equivalent replacement of pure non-ferrous oxides by sludges.

Key words: *Industrial waste, environmental pollutants, pigments, color modifier, charge mineralizer, decor, spinel structures, synthesizing roasting.*

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УТИЛІЗАЦІЯ ПРОМИСЛОВИХ ВІДХОДІВ В ТЕХНОЛОГІЇ СИНТЕЗУ НЕОРГАНІЧНИХ ПІГМЕНТІВ У РІЗНИХ ОКСИДНИХ СИСТЕМАХ

Встановлено, що промислові відходи: високозалізисті Червоний шлам, SiC-шлам, відпрацьовані каталізатори середньотемпературний СТК-1, високоалюмовмісні АКМ, та високоцинковмісний поглинач сірководню - НІАП-02-05 можна використати як вихідну сировину для синтезу неорганічних пігментів різноманітної кольорової гами з еквівалентною заміною чистих оксидів кольороутворюючих металів на відходи.

Ключові слова: *Промислові відходи, полютанти навколишнього середовища, пігменти, модифікатори кольору, мінералізатори шихти, декор, шпінельні структури, синтезуючий обпал.*

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УТИЛИЗАЦИЯ ПРОМЫШЛЕННЫХ ОТХОДОВ В ТЕХНОЛОГИИ СИНТЕЗА НЕОРГАНИЧЕСКИХ ПИГМЕНТОВ В РАЗНЫХ ОКСИДНЫХ СИСТЕМАХ

Установлено, что промышленные отходы высокожелезистые Красный шлам, SiC-шлам, среднетемпературный СТК-1, высокоалюмосодержащие – отработанные катализаторы АКМ, и высокоцинксодержащие – отработанный поглотитель сероводорода НИАП-02-05 можо использовать в качестве исходного сырья для синтеза неорганичных пигментов разнообразной цветовой гаммы с эквивалентной заменой чистых оксидов цветообразующих металлов на отходы.

Ключевые слова: *Примышленные отходы, полютанты окружающей среды, пигменты, модификатор цвета, минерализатор шихты, декор, шпинельные структуры, синтезирующий обжиг.*

Introduction. Industrial waste of various production is the main source of the economy
of the raw, using them in the synthesis of inorganic can reduce the pollution of the atmosphere,soils, underground and surface water during elimination, elimination and preservation. In this aspect, industrial waste can be classified as secondary «deposits» of zinc, chromium (III), ferrum(III), aluminium, vanadium, zircon, titanium, etc. It raises the problem of rational use of secondary mineral resources and deeper processing of raw materials and a reduction wastes of production, and also requires efficient technologies for their utilization.

Currently, as the basis for the production of heat-resistant paints is used the inorganicheat resistant pigments, that were obtained by sintering pure metal oxides during reactions insolid phases. The use of pure oxides makes the price of production higher, that is why the problem of finding alternative sources of pigments and using them instead of pure oxides of zinc, chromium, Ferrum, titanium, vanadium, etc is actual.

Analysis of recent researches and publications. The analysis of literary sources shows that industrial waste from heat and power engineering, chemical, woodworking, textile, metallurgy and other industries is mainly used for the production of building materials [1-5]. But the methods of recycling, that were developed, do not foresee the use of the most valuable specific properties of metal compounds that contain waste. For example, the proximity of their composition to the inorganic pigment charge. It predicts the possibility of replacing pure oxides of metals from chromium (III), ferrum (III), aluminum, titanium, zinc in pigments into industrial waste. The literature also does not systematize the scientific and technological justification for the use of waste as a raw material for the synthesis of pigments. Therefore, it is important to establish the possibility of using different types of waste in the production of pigments of a variety of color schemes.

Previously unsettled problem constituent. Synthesize inorganic pigments with the use of industrial wastes of various manufacturing enterprises, which have clear normative documents of Ukraine (DSTU 2999-95, DSTU 2419-94).

In accordance with the data the aim of this work is the need for selection and passage of spent catalysts and sinks as a raw materials – wastes of the chemical and metallurgical industry, red mud – wastes of alumina production, SiC-sludge, which containing the components of iron oxide, titanium, zinc, aluminum, cobalt, and molybdenum. These wastes give the principle possibility of full or partial replacement of active oxides of metals in charges of inorganic suspect environmental problems and misuse of the target product.

The main material. This work proposes the utilization of industrial waste in the technology of production of inorganic pigments of various oxide systems.

The chemical composition of the samples of industrial waste selected for the study is shown in Table 1.

Table1

Chemical composition of samples of industrial waste used for trial synthesis of inorganic pigments

Components of sludges	The mass fraction of components in the sludge, %.				
	Red slime	SiC- slime	Catalyst AKM	Catalyst NIAP-02-05	Catalyst STK-1
Al_2O_3	18.0		84.0		
Fe_2O_3	55.0	96.47			92.0
ZnO		0.95		90.0	
MgO				10.0	
Cr_2O_3					8.0
TiO_2	6.0				
MoO_3			12.0		
CaO	5.0				
Na_2O	4.0				
CuO		2.56			
SiO_2	8.0				
PbO		0.02			
CoO			4.0		
loss on firing	4.0				

Based on the oxide composition, the wastes used to replace pure oxides in the pigment charge can be classified as high-ferro-content (Red-slime, SiC-slime, medium-temperature catalyst STK-1), high-alumina (activated catalysts AKM) and highly zinc-containing (spent sinks of hydrogen sulfide NIAP - 02-05). High-alumina and highly zinc-compatible - suitable for use in the synthesis of color pigments corresponding to absorption in the long-wavelength spectrum, that is, blue, green, in the oxide system Cr_2O_3- Co_2O_3-ZnO-Al_2O_3, and high-ferro-content - for the short-wave absorption range, respectively, for brown, choristy, terracotta shades in the oxide system - Cr_2O_3- Fe_2O_3-ZnO-Al_2O_3.

In the synthesis of inorganic pigments based on industrial waste, it is necessary to achieve the obtaining of certain coloring and technological properties, and the maximum content of waste in the composition of the charge. Industrial pigments with a mass fraction were selected according to the standard samples by color and technological properties,%: choristy Cr_2O_3 – 16.0, Fe_2O_3 - 15.0, Al_2O_3 - 9.0, ZnO- 60.0; brown Cr_2O_3 – 16.8, Fe_2O_3 - 15.7, Al_2O_3 – 15.1, ZnO- 52.4; blue Cr_2O_3 – 33.0, Co_2O_3 - 13.0, Al_2O_3 - 30.0, ZnO- 20.0, H_3BO_3 – 4.0; green Cr_2O_3 – 50.0, Al_2O_3 - 40.0, H_3BO_3 – 10.0 [6-9].

The quantities of pigments synthesized in the work and their color properties with the use of industrial waste are presented in Table 2

Table 2

Composition and characteristics of pigments of various oxide systems

Index of pigment	Components of the charge, %					Characteristics of pigment		
	Sludge	Cr_2O_3	Fe_2O_3	ZnO	Al_2O_3	Color	Colorful decor properties	
							porcelain	faience
1	2	3	4	5	6	7	8	9
Raw – SiC-slime. Color – ocher Oxide system: **Cr_2O_3- Fe_2O_3-ZnO-Al_2O_3**								
Industrial	-	16,0	15,0	60,0	9,0	Ocher-brown	Brown light	Brown-ocher
B1	58.0	6.0	-	27.0	9.0	Ocher-brown dark	Brown	Ocher
B2	53.0	7.0	-	31.0	9.0	Dark ocher with a brown undertone	Brown	Ocher-brown
B3	50.0	8.0	-	33.0	9.0	Ocher dark	Brown	Red-ocher
B4	43.0	9.0	-	43.0	5.0	Ocher	Ocher-brown	Ocher dark
B5	40.0	9.0	-	46.0	5.0	Ocher	Ocher-brown	Brown-ocher
B6	40.0	9.0	-	41.0	10.0	Ocher with a brown undertone	Brown	Ocher
B7	50.0	7.0	-	36.0	7.0	Ocher saturated	Ocher	Ocher dark
B8	50.0	7.0	-	38.0	5.0	Ocher dark	Ocher	Ocher dark
Raw material - NIAP 02-05 / STK-1. Color - brownish-green Oxide system: **Cr_2O_3- Fe_2O_3-ZnO**								
Industrial	-	16.8	15.7	52.4	15.1	Brown	Chocolate brown saturated	Brown
1	2	3	4	5	6	7	8	9
K1	90.0/10.0	-	-	-	-	Light Brown	Brown	Brown
K2	30.0/30.	40.0	-	-	-	Brown saturated	Brown	Brown
K3	25.0/30.	45.0	-	-	-	Brown	Light Brown	Light Brown
K4	20.0/-	50.0	30.0	-	-	Brown	Brownish green	Brownish green
K5	15.0/-	55.0	30.0	-	-	Light Brown	Brownish green	Brownish green
K6	10.0/30.	60.0	-	-	-	Green-brown	Green-brown	Green-brown
K7	5.0/30.0	65.0	-	-	-	Dark olive	Olive	Olive
Raw material-AKM. Color blue-sky-blue Oxide system **Cr_2O_3- Co_2O_3-ZnO-Al_2O_3**								
Industrial	H_3BO_3-4.0	33.0	Co_2O_3-13.0	20.0	30.0	Blue	Blue	Blue

C1	90.0	-	TiO_2-10.0	-	-	Grey	Grey light	Grey
C2	90.0	-	MgO-10.0			Sky-blue	Blue light	Sky-blue
C3	80.0	-	CaO-10.0	10.0	-	Sky-blue	Intensively blue	Sky-blue
C4	97.5	-	Co_2O_3-2.5	-	-	Blue	Blue light	Blue
C5	70.0	MgO 10.0	Co_2O_3-12.0	8.0	-	Blue	Intensively blue	Intensively blue
C6	88.5	1.5	MgO 10.0	-	-	Sky-blue	Sky-blue dark	Sky-blue
C7	95.0	5.0	-			Grey	Grey	Grey
Raw material - Red slime. Color -brown Oxide system **Cr_2O_3- Fe_2O_3-ZnO-Al_2O_3**								
Industrial	-	16.8	15.7	52.4	15.1	Brown	Chocolate saturated	Brown
Ч1	55.0	25.0	-	20.0	-	Brown	Chocolate-brown	Chocolate-brown
Ч2	50.0	18.0	TiO_2-3.0	23.0	-	Brown	Coffee-brown	Light brown
Ч3	70.0	10.0	-	20.0	-	Brown dark	Black-browm	Brown dark
Ч4	63.0	18.0	-	19.0	-	Brown dark	Red-Brown	Brown dark
Ч5	50.0	25.0	-	25.0	-	Brown	Brown saturated	Brown saturated
Ч6	47.0	25.0	-	28.0	-	Brown	Brown saturated	Brown
Ч7	45.0	25.0	-	30.0	-	Ligh brown	Ligh brown	Ligh brown

Grinding and mixing components in pigments (waste and pure metal oxides) were carried out wet, rubbing the charged mixture for 30 minutes. The temperature of the burning in the manufacture of pigments should not be lower than the temperature of decorative burning products [10]. Thus, the temperature of the synthesis of choristy and brown pigments is usually 1550 K, and the blue and turquoise pigments are 1620 K. The pigment bonds were burned for 14-15 hours in accordance with the set temperature curve: preliminary heating at a rate of 4 K / min to 900 K; the main heating at which the spinel-chromophores are formed, at a rate of 2 K / min in the range of 900 ÷ 1620 K or 900-1500 K, depending on the charge composition of the synthesized pigment. Exposure at a maximum temperature of 20-30 minutes and cooling of synthesized pigments 5-6 hours in the furnace environment. The uniformity of the temperature field in the synthesis of roughness is ensured by the optimum loading thickness of the charge.

A weakly-containing medium (carbon monoxide (II) oxide content in the gas environment ≈ 1.2%, air excess coefficient ‹ = 0.98) is used for the spillage of pigments with high content of chromium (III) oxide (more than 30%). For the spillage of pigments containing ferrum (III), cobalt (III) oxides use an oxidizing medium (excess air ratio ‹ = 1.2).

Regarding the degree of shredding of charge materials, in order to provide the necessary contact surface of phases in the solid phase synthesis of pigments at specified temperatures, the initial mixture of components, after grinding, must pass without a residue through a sieve with a grid of 0315 (100 hole/cm^2).

As can be seen from Table 2, as a result of synthesis, pigments with given color characteristics - blue, green, coral and brown-coffee corresponding to DSTU 2999-95, DSTU 2419-94 - were obtained as a result of synthesis.

The cobalt (III) oxide, chromium (III) oxide, aluminum (III) oxide, titanium, nickel and manganese oxides were used as modifiers in the system based on spent catalyst such as NIAP and AKM, Red-slime as modifiers.

Synthetic pigments of different colors - from blue-violet, violet to red-brown and olive-green. In the main pigments are obtained loose structure, the decorative surface on porcelain and earthenware corresponds to the current standards for shine, the contour of the figure is clear.

The analysis of the results indicated the promising use of NIAP-02-05, the main component of which is zinc oxide, and STK-1, as a source of ferrum (III) oxide. But the negative point is that the spent sinks of hydrogen sulfide NIAP-02-05 contain about 20% of sulfur, because in the methane conversion and purification of natural gas from sulfur compounds absorption of hydrogen sulfide occurs by the reaction: $ZnO + H_2S = ZnS + H_2O$. Before using the spent NIAP-02-05 as raw material in pigment charge, it is necessary to remove the sulfur compounds by preliminary burning it at a temperature of 1073-1273 K in an oxidizing medium: $2ZnS + 3O_2 = 2ZnO + 2SO_2$.

At simuдфк use of high-iron catalyst STK-1 and high-zinc-containing NIAP-02-05 and modifiers of chromium (III), aluminum (III) oxides pigment of brown scale is obtained. This achieves practically 100% saving of pure oxides of ferrum (III) and zinc. Color of decor from chocolate brown (samples К1, К2) to green-brown (samples К4-К7). STK-1 and NIAP-02-05 contain up to 92% iron (III) oxide and 8% chromium (III) oxide, 90% zinc oxide and 10% magnesium oxide. This amount of iron (III), chromium (III), zinc and magnesium oxides is sufficient for the formation of spinelide-chromophore on the basis of iron (III), chromium (III) $Zn_{1-x}Fe_y[Zn_xFe_{2-y}]$, $Zn_{1-x}Cr_y[Zn_xCr_{2-y}]$ and magnesium spinelite based magnesium compounds $Mg_{1-x-y}Zn_{n-y}Fe_{x+y}[Fe_{2-x-y}Mg_xZn_y]O_4$ that provide saturation to the shades of brown pigments. Insufficient amount of chromium (III) oxide, necessary for the formation of zinc-iron-chrome dyed spinel, can be offset by pure chromium (III) oxide.

Non-traditional raw materials for the synthesis of blue-and-blue pigments are spent cobalt-containing catalysts of hydrogenation type AKM, which are used in the processes of hydro-purification of natural gas and petroleum products from sulfur compounds in the technological processes of ammonia production and oil refining.

The catalyst of AKM in the main technological processes practically does not undergo changes, but it can adsorb organic compounds on its surface, which did not enter the main reaction. Therefore, the preliminary heat treatment of the alumina-cobalt-molybdenum activated catalyst at a temperature of 1000-1300K will ensure the full suitability of the catalyst for the synthesis of pigments.

Aluminum and chromium (III) oxides were used as modifiers and mineralizers for the blue-and-blue series of pigments. Soft pink blue powders were obtained, which are technological in manufacturing. The decorating swindle gives the porcelain and faience surface colors from light gray, blue to blue.

Subformation to the catalyst AKM separately for 10% zinc oxide and calcium oxide (sample C3) no significant changes in the intensity of coloring the pigment does not cause, but reduces the digestion of the pigment, which is formed in the powdered state. The introduction of 10% magnesium oxide (sample C2) into the pigment charge leads to an increase in the intensity of its color and some shift in the short-wave region corresponding to the formation of the cobalt magnesium-aluminum spinel $xCoO\cdot(1-x)MgO\cdot Al_2O_3$.

The presence in the pigments of 10% molybdenum (VI) oxide, as part of the AKM catalyst, does not significantly affect the coloring properties of cobalt-magnesium-aluminum pigment. An increase in the concentration of cobalt (III) oxide in a pigment to 12% naturally increases the intensity of coloration to produce blue-blue and blue pigment shades. Increasing the concentration of magnesium oxide up to 10% and aluminum oxide (with increasing mass fraction of waste) in the charge up to 50% (sample C6) gradually reduces the intensity of pigment coloration, changing the color tone by diluting the chromophore compound with achromatic (white) aluminum (III) oxide , which allows to regulate the technological properties of pigments made using an activated AKM catalyst.

As a result of the regeneration of silicon carbide by the acidic method [11], washing rinses with a rather high concentration of ions of transition and heavy metals are formed, from which ferrous SiC-sludges were obtained for cleaning of high-precision cutting solutions of silicon wafers. Chromium (III) and zinc oxides were used as modifiers and mineralizers to obtain pigments of the void chrome, which allows to synthesize the product of a given color scale. The color of the décor varies from brown to void. The optimal ratio of the used sludge and chromium (III) oxide is achieved in samples B7 and B8, in batches which achieve significant savings both Cr_2O_3 and Al_2O_3. In this case, the color is close to the reference [6], and a further increase in the concentration of Cr_2O_3 in the charge composition of the pigment is inappropriate (sample B6). An increase in the concentration of ZnO in the sample B5, B6, shifts the color of the decor in the brown area.

Accordingly, in the case of SiC-slime cleaning, high-precision cutting of silicon wafers for complete replacement of Fe_2O_3 and partial replacement of Cr_2O_3, anhydrous pigments are synthesized. The void color is due to the formation of mixed spinels of the composition: $Zn_{(1-x-y)}Fe_xCr_y[Zn_{(x+y)}Fe_{(2-2n-x)}Cr_{(2n-y)}]O_4$ та $Zn_{1-x-y}Al_xCr_y[Zn_{x+y}Al_{2-2n-x}Cr_{2n-y}]O_4$.

Alumina production residues – Red-slime (RS) containing iron (III) and aluminum (III) compounds at concentrations in excess of their content in high quality natural ores can be recommended for the synthesis of brown pigment pigments. In the charge of Pigments Ч1-Ч7, a complete replacement of chemically pure Fe_2O_3 and Al_2O_3 oxides was provided for the RS. To form a stable brown color of the chromophore compounds, the spinel structures of the pigment model were loaded with chromium (III) with oxide, zinc oxide, and to create a gradient of color titanium (IV) with oxide. The presence of SiO_2 in the sludge structure and Na_2O in very high concentrations increases the speed of the spinel synthesis, and at a lower temperature, which reduces energy consumption in the production of pigments.

For pigments of brown color, made with the use of RS, the main crystalline phase is the zinc-iron-chromium spinel $Zn_{(1-x-y)}Fe_xCr_y[Zn_{(x+y)}Fe_{(2-2n-x)}Cr_{(2n-y)}]O_4$ which paints pigment in chocolate brown shades (pigment of optimal composition Ch1). In addition, the coffee-beige color of brown pigments (Ч2) is explained by the formation of spinel-like $Fe(Ti)_2O_4$[12].

Conclusions.

1. The possibility of utilization of industrial waste of high-zeolite – Red-slime, SiC-slime, medium-temperature catalyst STK-1, high-alumina - spent catalysts AKM, and high-zinc-containing - is a spent absorber of hydrogen sulfide NIAP-02-05 in the synthesis of inorganic pigments of different colors.

2. The method of solid phase syntheses has established the region of optimal composition of pigments of blue-green and choristy-brown colors.

3. It is shown that the use of industrial waste leads to significant savings in pure oxides of chromium (III), cobalt (III), ferrum (III), zinc, aluminum, while simultaneously solving the problems of the ecology of industrial regions of Ukraine.

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