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**INORGANIC SYNTHESIS  
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# Synthesis and Properties of Modified Fillers Based on Calcium and Magnesium Carbonates

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**Abstract**—A possibility of modifying natural carbonate fillers for paint and varnish industry by solutions of salts of some nonferrous metals was studied. Reactions of carbonates with metal ions and physicochemical properties of the resulting materials were considered.

Paints and paint coatings to approximately 70% consist of fillers: natural or synthetic inorganic powders used in combination with chromatic or achromatic pigments to reduce the cost of paint-and-varnish compositions [1]. Colorless substances are used as fillers, but these components of paints and enamels are not inert. A proper choice of fillers makes it possible to improve physicochemical and physicomachanical properties of the painting systems. Fillers based on alkaline-earth metal carbonates gained the widest acceptance owing to their availability and relatively low price. In recent years, a cycle of studies on using natural carbonates as sorbents of such heavy and nonferrous ions as Cu(II), Fe(III), Cr(III), Pb(II), Ni(II), Co(II), etc., has been carried out and summarized in [2]. It was found that solid carbonates, when in contact with solutions of salts of the above metals, react with them to give difficultly soluble colored compounds with solubility products lower than those of the starting compounds [2–4]. These compounds are M(II) and M(III) carbonates, subcarbonates, or hydroxides.

The carbonates can be partially transformed by a two-stage treatment into other colored chemical compounds of M(II) and M(III), which are also high-quality pigments, for example, hexacyanoferrates(II) or phosphates [5, 7]. Moreover, the phosphates are thermostable up to 1000°C and higher.

According to the obtained data, 30–40% transformation of the starting carbonates into reaction products ensures an intense color of the materials.

The capability of alkaline-earth metal carbonates to selectively sorb ions of nonferrous metals from various solutions offers possibilities of utilizing various

metal-containing wastes, including wastes of electroplating productions and of metal working, to produce colored materials.

Here we report on the modification of natural chalk and dolomite<sup>1</sup> with solutions of M(II) and M(III) salts and of  $K_4[Fe(CN)_6]$ , including modification in the presence of phosphate anion, and on the physicochemical properties of the resulting compounds.

## EXPERIMENTAL

We used natural dolomite and chalk as the base of pigments and fillers. According to the differential thermal analysis (DTA) data, dolomite contains 84% calcium–magnesium carbonate, and chalk, 96% calcite  $CaCO_3$ . To prepare modifying solutions, we used the following salts:  $CuCl_2 \cdot 2H_2O$  (pure grade),  $CuSO_4 \cdot 5H_2O$  (pure grade),  $Cu(NO_3)_2 \cdot 3H_2O$  (chemically pure grade),  $Co(NO_3)_2 \cdot 6H_2O$  (pure grade),  $Cr(NO_3)_3 \cdot 9H_2O$  (pure grade),  $Fe(NO_3)_2 \cdot 9H_2O$  (analytically pure grade),  $FeSO_4 \cdot 7H_2O$  (analytically pure grade),  $K_4[Fe(CN)_6] \cdot 3H_2O$  (chemically pure grade), and also copper-containing wastes  $3Cu(OH)_2 \cdot CuCl_2 \cdot xH_2O$  ( $x = 1–3$ ) and copper shavings, which were dissolved in nitric acid.

We modified natural carbonates with solutions of M(II) and M(III) salts under static conditions at room temperature. A 100-g portion of natural chalk or dolomite was added to 350 ml of 0.9–1.8 N solution of an M salt [ $M = Cu(II), Fe(III), Cr(III), Co(II)$ ] and allowed to stand for a day at room temperature with intermittent stirring. Then the solid phase was separated, washed with distilled water, dried in air, and ground

<sup>1</sup> Both are industrially mined in the Vitebsk oblast, Belarus'.

in a mortar. To study physicochemical properties, we used the fraction of less than 0.05  $\mu\text{m}$ .

To obtain hexacyanoferrate modifications, we first treated natural carbonates with 0.9 N solutions of  $\text{CuCl}_2$  and  $\text{FeSO}_4$  [the solid-to-liquid ratio (g : ml) was  $M_s : V_1 = 100 : 350$ ] and then, after washing with distilled water, with a 0.1 N solution of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  ( $M_s : V_1 = 100 : 750$ ). The resulting intermediate compounds were treated with potassium dichromate to oxidize Fe(II) by the procedure given in [1].

When obtaining the phosphate modification, we used the product of treating dolomite with a solution of phosphoric acid, which consisted of a mixture of calcium and magnesium hydrophosphates [5]. We colored this mixture with solutions of M(II) and M(III) salts.

We treated carbonates with metal salt solutions for 1 day, though kinetic studies showed that the chemical processes are 80% complete within several hours [3–7].

The concentrations of the modifying salt solutions (0.9–1.8 N) and the ratio between the solid and liquid phases were chosen on the basis of the data on the adsorption of M(II) and M(III) ions by carbonates and phosphates [3–7] in such a way as to ensure partial transformation of the starting phases into the reaction products. The amount of metal ions absorbed from the solution was determined by photometry or by complexometric titration [3, 4, 6, 7] as the difference between their concentrations in the starting solution and in the solution after a contact with a carbonate.

The samples of modified carbonates were heat-treated at 200–800°C.

We determined the specific surface area of the samples  $S_{\text{sp}}$  ( $\text{m}^2 \text{g}^{-1}$ ) by the air adsorption at the liquid nitrogen temperature [8].

The differential thermal analysis (DTA) was carried out with an MOM (Hungary) derivatograph by heating in air at a rate of 10  $\text{deg min}^{-1}$  in an open conical crucible. The sample weight was 600 mg.

We determined the phase compositions of the starting carbonates and products of their chemical treatment by the X-ray phase analysis on a DRON-2 diffractometer with the  $\text{CuK}\alpha$  radiation.

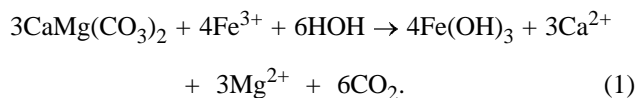
We determined pH of the aqueous extract, the bulk density, and the oil absorption of modified colored carbonates by the procedures designed for inorganic pigments [9, 10]. The covering power was determined by the visual procedure designed for pigmented paint and varnish materials (relative error  $\pm 5\%$ ) [9].

The color properties of the materials obtained by the chemical and thermal treatment of natural carbonates are given in Table 1. The combination of chemical and thermal methods for modifying carbonates allowed a wide variety of colored materials to be obtained on their basis. The color intensity of the obtained materials is a function of the modifying solution concentration and is determined by the nature of the modifying agent. A copper chloride solution gave a brighter color than copper nitrate and sulfate solutions.

With the aim to study in detail the physicochemical properties of the colored materials obtained on the basis of chalk  $\text{CaCO}_3$ , dolomite  $\text{CaMg}(\text{CO}_3)_2$ , and phosphated dolomite  $\text{CaMg}(\text{CO}_3)_2 \cdot \text{H}_3\text{PO}_4$ , we selected several samples modified in the systems  $\text{CaCO}_3\text{--CuCl}_2$ ,  $\text{CaCO}_3\text{--CuCl}_2\text{--K}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{CaCO}_3\text{--FeSO}_4\text{--K}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{CaMg}(\text{CO}_3)_2\text{--Fe}(\text{NO}_3)_3$ ,  $\text{CaMg}(\text{CO}_3)_2\text{--H}_3\text{PO}_4\text{--Co}(\text{NO}_3)_2$ ,  $\text{CaMg}(\text{CO}_3)_2\text{--H}_3\text{PO}_4\text{--CuCl}_2$ , and  $\text{CaMg}(\text{CO}_3)_2\text{--H}_3\text{PO}_4\text{--Cu}(\text{NO}_3)_2$ . In the latter case we prepared a solution of copper nitrate from both the reagent-grade salt,  $3\text{Cu}(\text{OH})_2 \cdot \text{CuCl}_2 \cdot x\text{H}_2\text{O}$  wastes, and copper shavings.

The phase composition, covering power, pH of aqueous extract, density, specific surface area, and oil absorption of the compounds obtained in the listed systems are given in Table 2. Similar properties of the starting nonmodified carbonates are also given there for comparison.

The X-ray phase analysis showed that the products of the reaction of  $\text{CaCO}_3$  with  $\text{Cu}^{2+}$  ions and of  $\text{CaMg}(\text{CO}_3)_2$  with  $\text{Fe}^{3+}$  ions are amorphous: the X-ray patterns contain no reflections of new phases, but involve only the diffraction peaks of the starting  $\text{CaCO}_3$  or  $\text{CaMg}(\text{CO}_3)_2$  phases. The examination of published data points to the fact that the product of the reaction of the carbonates with iron ions is  $\text{Fe}(\text{OH})_3$ , as Fe(III) does not give carbonates [11]. The reaction is described by the equation



Reactions of chalk with solutions of copper salts can yield various compounds: carbonate, basic carbonates and chlorides, or copper hydroxide. The published information on this problem is rather ambiguous. We used for modification a 1.8 N solution of copper chloride with pH 2.7. After the reaction with calcium carbonate pH of the mother liquor increased to 5.7. It is most probable that under the conditions in

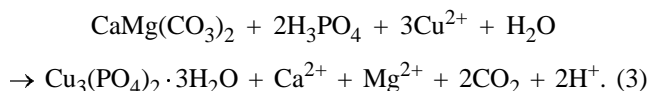
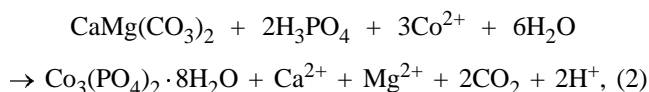
**Table 1.** Color properties of modified natural carbonates depending on the conditions of the material preparation

Solution, g-equiv l <sup>-1</sup>	pH	Color before and after heat treatment at indicated temperature, °C				
		starting	200	400	600	800
Chalk						
CuSO <sub>4</sub> , 1.8	3.35	Light green	Green	Dark grey	Dark grey	Black
CuCl <sub>2</sub> , 1.8	2.70	"	"	Dark brown	"	Dark grey
Fe(NO <sub>3</sub> ) <sub>3</sub> , 1.8	0.90	Light brown	Light brown	Light brown	Light brown	Brown
Cr(NO <sub>3</sub> ) <sub>3</sub> , 1.8	1.00	Blue	"	"	Green (khaki)	Green
CuCl <sub>2</sub> , 0.9	3.65	Light brown	–	–	–	–
K <sub>4</sub> [Fe(CN) <sub>6</sub> ], 0.1	6.25	"	–	–	–	–
FeSO <sub>4</sub> , 0.9	0.97	Dark blue	–	–	–	–
K <sub>4</sub> [Fe(CN) <sub>6</sub> ], 0.1	6.25	"	–	–	–	–
Dolomite						
CuSO <sub>4</sub> , 1.8	3.35	Light green	Green	Gray	Dark gray	Black
CuCl <sub>2</sub> , 1.8	2.70	"	"	Brown	"	Dark gray
Fe(NO <sub>3</sub> ) <sub>3</sub> , 1.8	0.90	Golden brown	Golden brown	Reddish brown	Reddish brown	Brown
Cr(NO <sub>3</sub> ) <sub>3</sub> , 1.8	1.00	Gray	Brown	Brown	Green (khaki)	Green
FeSO <sub>4</sub> , 0.9	0.97	Dark blue	–	–	–	–
K <sub>4</sub> [Fe(CN) <sub>6</sub> ], 0.1	6.25	"	–	–	–	–
Phosphated dolomite						
CuSO <sub>4</sub> , 1.8	3.35	Turquoise	Turquoise	Turquoise	Turquoise	Turquoise
Fe(NO <sub>3</sub> ) <sub>3</sub> , 1.8	0.90	Light yellow	Light yellow	Light yellow	Light yellow	Light yellow
Cr(NO <sub>3</sub> ) <sub>3</sub> , 1.8	1.00	Gray	Brown	Brown	Brown	Gray
Co(NO <sub>3</sub> ) <sub>2</sub> , 1.8	4.05	Pink	Violet	Violet	Violet	Violet
CuCl <sub>2</sub> , 0.9	3.65	Plum violet	–	–	–	–
K <sub>4</sub> [Fe(CN) <sub>6</sub> ], 0.1	6.25	"	–	–	–	–

hand the amorphous product is copper hydroxocarbonate.

When phosphated dolomite was treated with salt solutions, the reflections of new phases resulting from the reaction with Cu<sup>2+</sup> and Co<sup>2+</sup> ions were identified in the X-ray pattern of the end products, whereas the peaks of the starting phases (calcium and magnesium hydrophosphates CaHPO<sub>4</sub>·2H<sub>2</sub>O and MgHPO<sub>4</sub>·3H<sub>2</sub>O) were, as a rule, absent from the patterns of the modified samples.

According to the X-ray data, the products of the reaction of phosphated dolomite with solutions of cobalt(II) and copper(II) salts are Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O and Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O. Their formation can be expressed by the equations



The products of chalk modification with potassium hexacyanoferrate(II) exhibit reflections of calcium carbonate and of copper and iron hexacyanoferrates(II).

The content of the starting phase, i.e., of an unreacted carbonate, in colored samples is 54–69%, as calculated from the amount of metal ions absorbed from solutions according to the equations of the corresponding chemical reactions (Table 2). Despite this fact, the synthesized materials are fairly uniformly colored without markedly contrasting disseminations of unchanged carbonates. This fact suggests that particles of unchanged phases are colored at the expense of surface processes: either owing to chemical reactions occurring on their surface or owing to the adsorbed metal ions.

Partial transformation of the carbonate phase into new chemical substances results in a characteristic change in the thermogravimetric parameters of the material. The data of differential thermal analysis of carbonates before and after their modification with M(II) and M(III) solutions are given in the Figs. 1a–1c, which show, in particular, that the starting car-

**Table 2.** Physicochemical properties of modified and nonmodified natural carbonates

Property	Chalk	Chalk + salt			Dolomite	Dolomite + Fe(NO <sub>3</sub> ) <sub>3</sub>
		CuCl <sub>2</sub>	CuCl <sub>2</sub> ·K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	FeSO <sub>4</sub> ·K <sub>4</sub> [Fe(CN) <sub>6</sub> ]		
Color	White	Light green	Light brown	Dark blue	Light yellow	Brown
Bulk volume after shaking up, cm <sup>3</sup> g <sup>-1</sup>	0.83	0.93	0.86	1.16	0.56	0.61
Covering power, g m <sup>-2</sup>	515	234	25	12	470	117
Phase composition	CaCO <sub>3</sub>	CaCO <sub>3</sub> + amorphous product	CaCO <sub>3</sub> + X***	CaCO <sub>3</sub> + Y****	CaMg(CO <sub>3</sub> ) <sub>2</sub>	CaMg(CO <sub>3</sub> ) <sub>2</sub> + amorphous product
Content of starting phase, %	100	69	60	57	100	54
pH of aqueous extract	8.0	7.1	8.2	7.1	8.9	6.7
Moisture content, %	0.32	2.43	0.89	3.70	0.17	6.05
Specific surface area S <sub>sp</sub> , m <sup>2</sup> g <sup>-1</sup>	1	2	2	–	0	53
Oil absorption, g/100 g	15	18	20	34	13	22

Property	Phosphated dolomite	Phosphated dolomite + chalk			
		CuCl <sub>2</sub>	Co(NO <sub>3</sub> ) <sub>2</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub> *	Cu(NO <sub>3</sub> ) <sub>2</sub> **
Color	Light yellow	Blue	Pink	Light green	Light green
Bulk volume after shaking up, cm <sup>3</sup> g <sup>-1</sup>	1.13	1.47	1.03	1.32	1.45
Covering power, g m <sup>-2</sup>	674	342	206	252	210
Phase composition	CaHPO <sub>4</sub> ·2H <sub>2</sub> O + MgHPO <sub>4</sub> ·3H <sub>2</sub> O	Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O	Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O + CaHPO <sub>4</sub> ·2H <sub>2</sub> O	Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O
Content of starting phase, %	100	64	64	64	64
pH of aqueous extract	7.3	6.0	6.0	5.8	5.0
Moisture content, %	13.48	5.29	16.40	6.68	17.05
Specific surface area S <sub>sp</sub> , m <sup>2</sup> g <sup>-1</sup>	1	24	12	20	83
Oil absorption, g/100 g	28	36	23	37	49

\* The solution was obtained by dissolving copper shavings in nitric acid.

\*\* The solution was obtained by dissolving 3Cu(OH)<sub>2</sub>·CuCl<sub>2</sub>·xH<sub>2</sub>O.

\*\*\* X = K<sub>2</sub>Cu<sup>II</sup>[Fe<sup>II</sup>(CN)<sub>6</sub>]<sub>2</sub> + K<sub>2</sub>Cu<sup>II</sup>[Fe<sup>II</sup>(CN)<sub>6</sub>]<sub>2</sub>.

\*\*\*\* Y = Fe<sup>III</sup><sub>4</sub>[Fe<sup>II</sup>(CN)<sub>6</sub>]<sub>2</sub>.

bonates do not undergo thermal decomposition up to 800–900°C. The materials prepared by modifying dolomite and chalk with Fe(NO<sub>3</sub>)<sub>3</sub> and CuCl<sub>2</sub> solutions, respectively, have quite different thermogravimetric characteristics. As seen from Fig. 1, two ranges of thermal transformations can be distinguished. The first range is 117–550 (Fig. 1a) and 106–567°C (Fig. 1b), and the second range covers higher temperatures. The major process in the second range is carbonate decomposition, whereas the first stage, with endothermic effects at 150–300°C, corresponds to the release of

water contained in the chemical compounds, in particular, in iron(III) hydroxide (Fig. 1a) and in unidentified amorphous copper(II) compound (Fig. 1b).

When phosphated dolomite is treated with solutions of copper and cobalt salts, hydrated phosphates of alkaline-earth metals partially transform into hydrated copper and cobalt phosphates, the weight loss substantially decreases, but the temperature range of the substance decomposition does not change appreciably (Fig. 1c).

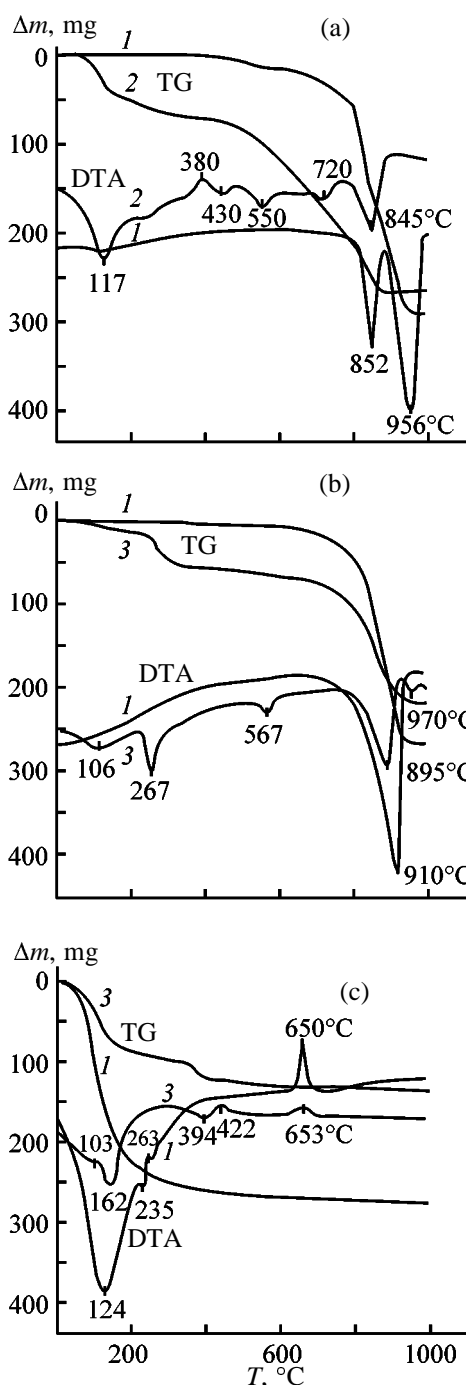
The modification of natural carbonates with acid solutions of metal salts changes not only their color, but also the other physicochemical characteristics (Table 2). The bulk volume of the materials obtained is  $0.61\text{--}1.47\text{ cm}^3\text{ g}^{-1}$ . For the initial chalk and dolomite these values are  $0.83$  and  $0.56\text{ cm}^3\text{ g}^{-1}$ , respectively. The modified fillers are characterized by pH of aqueous extract of  $5\text{--}8$ , whereas the initial carbonates have basic properties, pH of their aqueous extract is  $8.0\text{--}8.9$ .

The transformation of natural carbonates in solutions of salts with double- and triple-charged metal ions substantially increases the material surface area owing to two factors. First, compounds with a smaller particle size than in the initial carbonate are formed in the reaction with metal ions and, second, unchanged particles of natural carbonates decrease in size on treating with acid solutions of metal salts owing to their partial dissolution. Thus, the specific surface area of the initial materials, which does not exceed  $1\text{ m}^2\text{ g}^{-1}$ , increases after the modification by more than an order of magnitude: to  $12\text{--}83\text{ m}^2\text{ g}^{-1}$ .

The oil absorption of the colored fillers obtained is  $12\text{--}49\text{ g}/100\text{ g}$ , which allows them to be classed with readily dispersible substances. One of the most important characteristics of pigments is their covering power. It is seen from Table 2 that cyanoferrate modifications of carbonates have the best covering power:  $12$  and  $25\text{ g m}^{-2}$ . The material obtained from dolomite modified with  $\text{Fe}(\text{NO}_3)_3$  has the covering power of  $117\text{ g m}^{-2}$ , which is fairly close to the value given in [1] for natural iron oxide pigments. For blue, light green, and pink fillers obtained from phosphated dolomite and various copper and cobalt solutions, the covering power is  $206\text{--}342\text{ g m}^{-2}$ . Therefore, many of the obtained modified samples based on natural carbonates have a satisfactory covering power close to that of commercial pigments.

## CONCLUSION

(1) Chemical treatment of alkaline-earth metal carbonates in solutions of copper(II), iron(III), chromium(III), and cobalt(II) salts and of potassium hexacyanoferrate(II) results in their transformation into the corresponding transition metal carbonates, basic carbonates, and hexacyanoferrates(III), and in the presence of phosphate anions, into transition metal phosphates. The process is accompanied by substantial changes not only in color, but also in physicochemical characteristics of the materials.



**Fig. 1.** TG and DTA curves of starting and modified carbonates: ( $\Delta m$ ) weight loss and ( $T$ ) temperature. (a) Dolomite, (b) chalk, and (c) phosphated dolomite. Material: (1) initial, (2) modified with  $\text{Fe}(\text{NO}_3)_3$  solution, and (3) modified with  $\text{CuCl}_2$  solution.

(2) The synthesized materials are characterized by satisfactory covering power and oil absorption, allowing them to be considered not only as promising colored fillers of paint and varnish materials, but also as pigments proper.

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