

Synthesizing Copper and Cobalt Phthalocyanines on the Basis of Coke-Plant Wastes

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Abstract—The synthesis of copper and cobalt phthalocyanines from coke-plant waste—specifically, the primary distillation fraction from phthalic anhydride—has been developed. The introduction of this process in the phthalic-anhydride shop at coke plants provides the opportunity for resource and energy conservation.

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The conservation of energy and materials is especially important for coke production. In coking, unique aromatic hydrocarbons accumulate, but they are not extracted or utilized. The construction of coke batteries without equipment for trapping and processing the coking byproducts cannot be regarded as an environmentally acceptable approach.

In the past, pyridines, phenols, indene, coumarone, anthracene, carbazole, and other materials were extracted from the coking byproducts, and highly effective technologies were used for the production of high-purity mesitylene, pseudocumene, naphthalene, and benzene. That is no longer the case. The only Russian phthalic-anhydride shop, at OAO ZSMK, has been closed.

It would be expedient to create systems capable of utilizing coke-plant wastes and byproducts in the production of specific materials that are in high demand: powder paints for coating the inner surface of gas pipelines; glass plastics; electrical and thermal insulators; and metal-phthalocyanine catalysts and pigments [1–3]. By siting such facilities at coke plants, we may reduce transport costs and also energy costs in the preparation of the raw materials. In addition, existing coke-plant equipment may be used for the purification of exhaust gases and wastewater, with considerable reduction in capital costs.

In the present work, we address practical matters relating to the synthesis of cobalt phthalocyanine and copper phthalocyanine: the technological conditions, the recipe, the catalyst, the cobalt or copper salt, and the plasticizer.

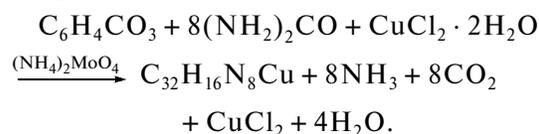
Transition-metal phthalocyanines are active catalysts of the redox removal of NO_x from gases [4, 5], as well as the oxidation of mercaptans, hydrogen sulfide, and sulfohydryl compounds. Such phthalocyanines are stable in the presence of sulfur compounds and are

highly selective. Accordingly, they are widely used for the removal of sulfur compounds from gas emissions [6] and the removal of mercaptans from petroleum fractions [7]. In addition, metal phthalocyanine pigments are important disperse organic dyes. They are stable with respect to light and the atmosphere, with pure and bright coloration, universal in application, and resistant to chemical reagents [8].

Metal phthalocyanines are of particular interest for use in microelectronic, electrochemical, and optoelectronic systems [9]. Films of phthalocyanine and copper phthalocyanine are used in gas sensors [10]; and cobalt phthalocyanine is used as a cathode catalyst in the manufacture of galvanic elements [11, 12]. The semiconductor characteristics of these materials may be enhanced and modified by molecular modification [9]. They have also been used in carbon fibers and nanomaterials [13].

There is no industrial production of phthalocyanine pigments in Russia. In our view, the development of production facilities for phthalocyanine catalysts and pigments should be a high priority.

In laboratory and industrial conditions, copper phthalocyanine and cobalt phthalocyanine may be produced by dry sintering and also in the presence of plasticizing agents. The synthesis of copper phthalocyanine is investigated on the basis of the reaction of urea, phthalic anhydride, and metal salts—copper(II) sulfate, copper(I) chloride, copper(II) chloride, copper(II) acetate, and copper(II) carbonate—in the presence of ammonium-molybdate catalyst, by the following reaction



Tests results for reagents used in the synthesis of metal phthalocyanines*

Reagent	Composition, wt %			Time for synthesis, h	Results of synthesis		
	metal salt	phthalic anhydride	urea		color of metal phthalocyanine	yield, wt %	
						copper phthalocyanine	cobalt phthalocyanine
$\text{CuCl} \cdot 2\text{H}_2\text{O}$ (I)	9.6	55.0	35.0	4	Bright blue	69.3	—
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	9.8	55.5	34.3	4	Bright blue	37.5	—
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	12.2	53.1	34.3	4	Dark blue	43.4	—
$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	9.6	55.7	34.3	4	Black	18.0	—
$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	8.6	54.7	36.3	30	Blue	31.6	—
$(\text{CuOH})_2\text{CO}_3$	9.0	54.4	36.2	4	Black	18.6	—
$(\text{CuOH})_2\text{CO}_3$	9.0	54.4	36.2	30	Blue	37.2	—
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	13.2	53.4	33.0	4	Blue	—	30.0
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	13.2	53.4	33.0	4	Blue	—	35.0
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	13.9	53.3	32.8	4	Blue	—	29.0

* Mole ratio of phthalic anhydride and metal salt 4 : 1; mole ratio of phthalic anhydride and catalyst 1 : 0.1; temperature during synthesis 195°C.

In laboratory conditions, the copper phthalocyanine is produced by two methods. The first is based on dry sintering of the components at 180–225°C and heating for 3–30 h. Stoichiometric proportions of phthalic anhydride, urea, the copper salt, and ammonium molybdate are placed in heat-resistant crucibles, with careful preliminary crushing and mixing by means of a mortar and pestle, placed in a cold drying chamber, heated at 1.5 deg/min to the required temperature, and held for a specified time.

In the second method, the copper phthalocyanine is synthesized in the presence of plasticizing agents. Stoichiometric properties of phthalic anhydride, urea, the copper salt, ammonium molybdate, and the plasticizer are placed in a 0.5-dm³ three-neck flask, fitted with a thermometer, a mixer, and a tube; the proportion of the dry components and the plasticizer is 1 : 0.5–0.7. Experiments are conducted in the range 180–225°C. The plasticizer is placed in the flask and heated to 80–100°C. Then the dry components (after preliminary crushing and mixing) are introduced. The mixture is heated to the required temperature at 1.5 deg/min and held with constant mixing.

The copper phthalocyanine obtained is purified by solution in sulfuric acid (density 1.84 g/cm³), with subsequent neutralization, filtration, and washing in hot water. The paste of copper phthalocyanine settles in the plasticizer and is filtered out in vacuum. The residue is washed with hot water and also purified with sulfuric acid. After drying, we obtain a finely crystalline bluish violet powder.

Various copper and cobalt compounds are tested by sintering, so as to select the reagent that is cheapest and most available. The table summarizes the test results.

We find that, when using copper sulfate and chloride, the copper phthalocyanine is formed in 2 h; the process is slower when using copper carbonate or acetate. For CuCl, the color of the product is bright blue, as against dark violet for CuSO₄ and a dirty greenish blue for the other salts. The yield is 18–69.3% for copper phthalocyanine and 29–35% for cobalt phthalocyanine.

Comparison of the IR spectra of all the samples indicates little difference, except that the spectral structure for copper phthalocyanine produced from CuCl is characteristic of the α modification. Derivatographic analysis of copper phthalocyanine in comparison with the Dutch pigment adopted as the standard indicates that the relative mass loss of the synthesized samples is greater, on account of the inadequate purification and roasting of the copper phthalocyanine.

We now consider the suitability of petroleum products and coke-plant byproducts as plasticizers. Such materials are readily available, inexpensive, chemically inert, nontoxic, and technologically convenient. Their viscosity is minimal, and their boiling point is above the temperature used in synthesis of the copper phthalocyanine. The petroleum products considered are AMT-300 oil, transformer oil, compressor oil, turbine oil, axle oil, and kerosene. The coke-plant byproduct is a solvent.

Analysis of the results shows that transformer oil and kerosene are suitable plasticizers. In the other cases, the metal phthalocyanines obtained are not subjected to washing and drying in purification. The yield of copper phthalocyanine depends on the quantity of plasticizer (Fig. 1). Experiments show that the temperature is stable, there is no thickening of the reaction mass, and the kerosene separates well from the product.

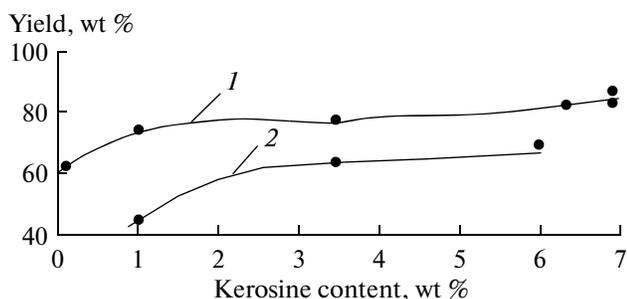


Fig. 1. Yield of copper phthalocyanine as a function of the plasticizer (kerosene) content: (1) CuCl (I); (2) CuSO₄.

To optimize the conditions, we consider the influence of the consumption of urea, the copper salt (cuprous chloride and cupric sulfate), and the catalyst (ammonium molybdate) on the yield of copper phthalocyanine. Kerosene is used as the plasticizer. With fixed phthalic-anhydride content, the content of urea, the copper salt (chloride and sulfate), and ammonium molybdate are varied. With increase in the consumption of urea, the copper salt, and ammonium molybdate, the yield of copper phthalocyanine increases, up to some limit. Thus, when the ratio of phthalic anhydride and urea is greater than 1 : 1, its influence on the yield of copper phthalocyanine is slight. Increasing the consumption of copper salt to more than 35 wt % also has little influence on the yield of copper phthalocyanine. Increase in the catalyst content has no significant influence on the yield.

Thus, with respect to phthalic anhydride, the consumption standards for urea, the copper salt, and ammonium molybdate are 100, 35, and 1.7 wt %, respectively.

Industrial trials are conducted in the phthalic-anhydride shop at OAO ZSMK (Fig. 2). The raw material employed is the waste from phthalic-anhydride production: the primary distillation fraction, which consists of yellow, pink, gray or brown flakes or dark brown melt with 98.0% phthalic anhydride; the crystallization temperature is 128°C. By contrast, for phthalic anhydride of superior and first grade, its content is 99.8% and the crystallization temperature is 130.8 and 130.6°C, respectively.

In the industrial trials, the copper phthalocyanine is produced in a periodic reactor at 210°C and very low pressure, in the presence of kerosene. The reactor is a heated vertical cylinder (volume 0.6 m³) equipped with a mixer. The materials employed are phthalic anhydride, urea, ammonium molybdate, and cuprous chloride.

In reactor 5 (Fig. 2), the required quantity of kerosene is introduced from tank 2, and the heater is switched on. The solid components are charged in the reactor at ≤100°C, when the mixer is working. At the end of charging, the temperature in the reactor is increased to 135°C. Then, molten phthalic anhydride is supplied from tank 1. The temperature in the reactor is raised to 190°C at 1.5 deg/min. The holding time at 190°C is 6 h. The temperature is maintained automatically by a valve in the line supplying steam to reactor 5.

During synthesis, the following gases and vapor are liberated: ammonia, carbon dioxide, water vapor, some

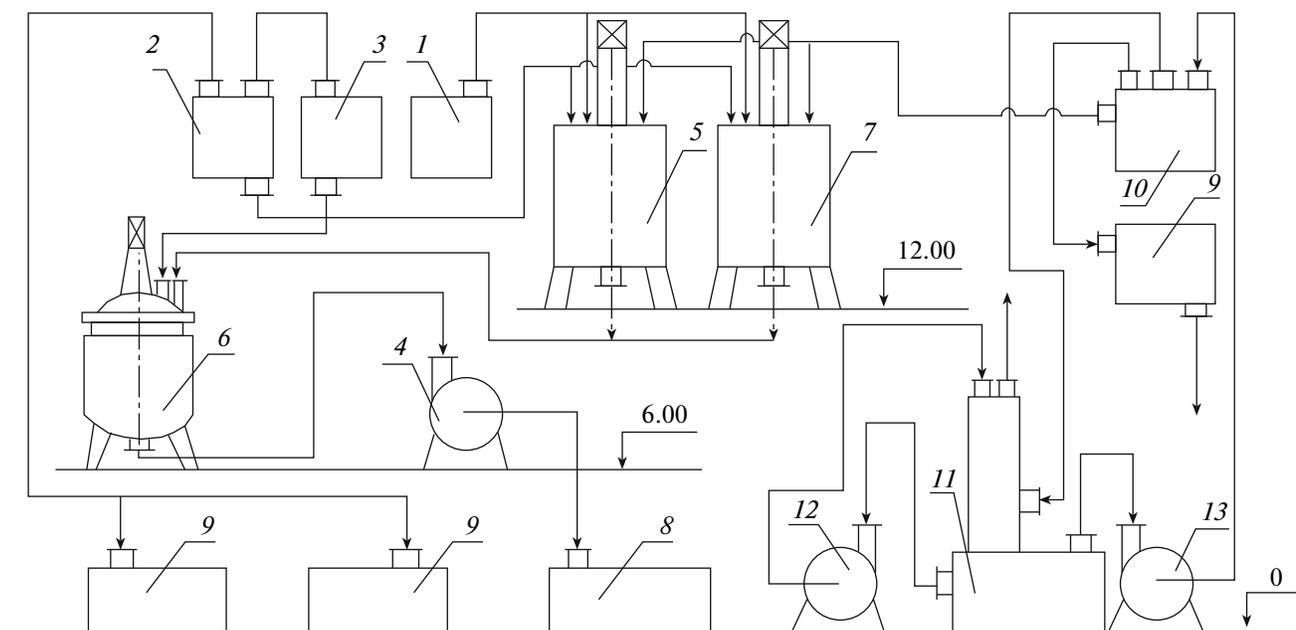


Fig. 2. Experimental industrial system for the synthesis of metal phthalocyanines: (1) phthalic-anhydride tank; (2) kerosene tank; (3) sulfuric-acid tank; (4) pump; (5–7) reactor; (8) centrifuge; (9) tank; (10) trap; (11) absorption column.

phthalic-anhydride vapor, and kerosene vapor. The resulting pressure excess is released through trap 10, which is intended for the extraction of phthalic-anhydride vapor by freezing on a cooled surface. At the end of freezing, the phthalic anhydride is melted by supplying steam to the coil instead of cold water. To reduce the frequency at which freezing is replaced by melting, the trap operates in freezing mode for several synthesis cycles before steam is supplied. Beyond trap 10, the waste gases are supplied to absorption column 11, irrigated by dilute sulfuric-acid solution for the absorption of ammonia. The resulting solution is sent to the plant's incinerator, and the waste gases are released to the atmosphere.

At the end of the process, the reaction mass is driven by nitrogen to reactor 6, to which we also supply sulfuric acid (density 1.84 g/cm³). The supply of 96% sulfuric acid is accompanied by constant mixing, at $\leq 80^{\circ}\text{C}$. With increase in temperature in the reactor, the supply of sulfuric acid is temporarily interrupted. The total treatment time is at least 2 h.

The impure copper phthalocyanine from reactor 6 is sent to reactor 7, which is filled with water at 80°C , while the mixer is operating. To prevent water loss as steam, the reactor is equipped with an inverse cooling unit. Then 42% sodium-hydroxide solution is added for neutralization. The suspension of copper phthalocyanine is held for 30 min at $95\text{--}100^{\circ}\text{C}$, with the mixer on, so as to dissolve the relatively insoluble impurities.

From the reactor, the neutralized suspension of copper phthalocyanine is pumped to filtering centrifuge 8 and then washed with hot water (condensate). The required temperature is ensured by passing the condensate through a pipeline within a sleeve through which recycled water runs. The centrifugate is transferred to a tank for subsequent use. The wet copper phthalocyanine from the centrifuge is sent to a drying chamber on trays.

In laboratory conditions, cobalt phthalocyanine is synthesized from urea, phthalic anhydride, and a cobalt salt, analogously to the copper phthalocyanine. In industrial trials, cobalt phthalocyanine is produced from urea, phthalic anhydride, and hexahydrated cobalt chloride, in the presence of kerosene.

The specified proportions of phthalic anhydride, cobalt chloride, and urea, with 0.2 m³ kerosene, are loaded in a cold 0.6-m³ reactor 5 (Fig. 2). All the components are slowly heated to $160\text{--}170^{\circ}\text{C}$. Synthesis takes two days, with holding at the final temperature for at least 12 h.

After synthesis and temperature decline in the reactor, water is supplied and mixed for 6 h at 80°C . The resulting suspension is pumped to reactor 6. Water is supplied to reactor 5, with mixing. The suspension is then pumped again to reactor 6. This procedure is repeated until reactor 5 has been completely washed. After standing, the upper layer from reactor 6 is pumped by means of nitrogen to reactor 5, where it is

steamed to remove cobalt salts. Water at 80°C is supplied to reactor 6, with mixing and settling for two days. The upper layer of washing water is pumped to reactor 5. This operation is performed five times. The removal of free cobalt salts is monitored.

After complete separation of cobalt salts, the product is washed with an alkali solution to dissolve the other impurities. After mixing at 80°C for 2 h, the system stands for two days. The upper layer is removed, and washing with alkali is repeated three times. The quality of the product is monitored. The aqueous suspension of cobalt phthalocyanine in reactor 6 is steamed and dried at $\sim 120^{\circ}\text{C}$. After drying, the product is discharged through the reactor's lower outlet, ground, and packed in polythene bags.

The synthesis of cobalt phthalocyanine has been introduced industrially on a 6.0-m³ stainless-steel reactor with inductive heating. The inductor consists of three windings at the cylindrical walls and floor of the reactor. The temperature is monitored and maintained (to within $\pm 5^{\circ}\text{C}$) by means of a KSP-4 or USP-411 multiposition potentiometer with an automatic regulator. Inert gas is supplied to the reactor, which is equipped with a four-blade mixer (speed 40–50 rpm); an internal coil for water cooling or steam heating at the beginning of the process; a heat exchanger for trapping volatile products and returning them to the reactor; and an inclined condenser for distillation of the products. The filling of the reactor is 0.75. Prior to charging, the cleanness and adjustment of the reactor and all the lines and monitoring systems are verified.

Industrial tests on a 0.6-m³ reactor permit the production of batches of copper phthalocyanine with 76% yield; the content of copper phthalocyanine in the product is 90–92%. For cobalt phthalocyanine, the corresponding figures are 56% and 80–85%.

Analysis of the industrial samples shows that the cobalt phthalocyanine is of similar quality to the standard sample recommended as the active component in the catalyst for sulfur removal; and the copper phthalocyanine, in pigment form, is of similar quality to imported pigment.

CONCLUSIONS

(1) We have discussed practical matters relating to the synthesis of copper phthalocyanine and cobalt phthalocyanine on the basis of phthalic anhydride (from the primary distillation fraction), urea, and the corresponding metal salt. The best conditions for synthesis in the presence of plasticizing agents (kerosene or transformer oil) have been established when the catalyst is ammonium molybdate. The yield is 76 wt % for copper phthalocyanine and 56 wt % for cobalt phthalocyanine.

(2) The synthesis of copper phthalocyanine and cobalt phthalocyanine has been introduced in indus-

trial conditions. Trial batches of copper phthalocyanine (as pigment) and cobalt phthalocyanine (as a catalyst in sulfur removal) have been produced and tested by customers.

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