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Physical Chemical Properties of Nitrogen and Phosphore Protector Cobalt Phthalocyanine (DAFCoPc) Pigment

M.O. Yusupov[1], G.I. Ismailova[2]

[1] Namangan Institute of Engineering and Technology, Namangan, Uzbekistan

Abstract

In this article stressed about synthesis of cobalt, nitrogen, phosphorus, diamidophosphate cobalt phthalocyanine (DAFCoPc) pigment and the various properties of cobalt, nitrogen, phosphorus, diamidophosphate cobalt phthalocyanine pigment, elemental analysis, thermal analysis and rent made. It can beclear that the elemental composition of the newly synthesized cobalt phthalocyanine pigment contains 8.4 % cobalt metal, 4.9 % phosphorus element, as well as various chemical elements. The synthesized cobalt, nitrogen, phosphorus, the newly formed diamidophosphate cobalt exhibits thermal stability due to the presence of the phosphorus element in the pigment cobalt phthalocyanine (DAFCoPc). Thermal analysis of DAFCoPc pigment from 100 °C to 500 °C was performed to study the exothermic and endothermic properties. According to X-ray phase analysis of the synthesized pigment, proved that the pigment structure is symmetrical, and that the compounds in it have specific properties.

Keywords: phthalocyanine pigment, element analysis, thermal analysis, exothermic, endothermic, cobalt diamidophosphate, phthalic anhydride, intensity

Introduction

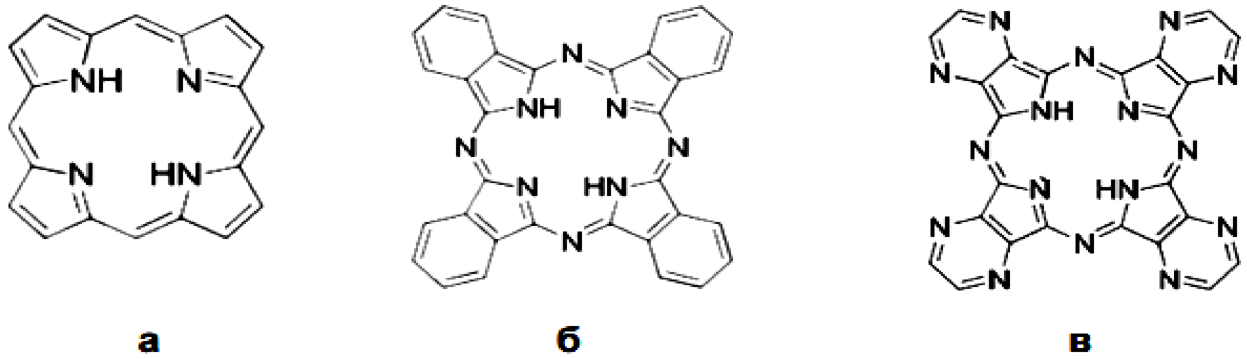
Paints have been widely used in various fields since ancient times. Currently, the volume of work in the construction industry in the world and in the country is growing rapidly, which, in turn, has led to a rapid increase in demand for paints and varnishes. In the paint industry, pigments play an important role.

Despite the fact that phthalocyanine pigments have been discovered over the past 100 years, the attractiveness and brightness of such pigments as objects of study has been the subject of different colors and people's interest. Today, world scientists pay great attention to the constant use of phthalocyanine pigments in various fields of science and technology [1]. Such pigments can be used as light stabilizers of polymeric materials [2].

Phthalocyanines (Pc) are a class of photoactive compounds whose unique physicochemical properties are studied in many areas of modern science. Pc metal complexes - phthalocyaninates (MPc) - are the products of large tonnage industrial synthesis (over 80 thousand tons per year), with most of them traditionally used as pigments in the composition of color printing inks, paints and varnishes, for coloring plastics and synthetic fibers [3].

However, the structure of the molecules and the features of the formation of phthalocyanine crystals are responsible for their extremely low solubility in most media and high hydrophobicity. This is manifested in the difficulty of dispersing MPc in polar systems (due to the lack of wetting) and flocculation of their particles in non-polar [3], significantly limiting the use of these pigments in traditional and new areas.

Phthalocyanines (Pc) - tetraazobenzoporphyrins, higher heterocyclic compounds, consist of isoindole (benz [c] pyrrole) rings, interconnected via sp^2-hybridized nitrogen atoms, structurally related to natural porphyrins (Pic. 1a, b). However, unlike porphyrins, phthalocyanines are not found in nature, they are completely synthetic compounds. The main difference between the phthalocyanine macrocycle and the porphyrin system is the presence of four phenylene rings and nitrogen atoms in the meso positions instead of carbon.



Picture 1. Molecular structure of (a) porphyrin, (b) phthalocyanine, and (c) tetrapyrazinoporphyrazine macrocycles

Porphyrazines are phthalocyanine analogs in which phenylene groups are substituted by various alkyl, aryl substituents and macrocycles. When replacing the phenylene fragment with pyrazine, tetrapyrazinoporphyrazines can be obtained (Pic. 1c), which already contains sixteen nitrogen atoms. The vast majority of phthalocyanines produced (~ 90%) are used as pigments and dyes [4].

Since the discovery and identification in the early 1900s [5] phthalocyanines have been widely used as dyes and pigments in the paint, varnish, printing, textile and paper industries because of their rich and bright blue-green color, photo stability, insolubility in most solvents and chemical inertness.

Despite the very large number of Pc derivatives obtained in recent decades, several representatives of this class of compounds that were discovered back in the 30s of the last century continue to have the highest industrial value: metal-free H_2Pc, copper complex CuPc, and chlorinated derivatives CuPc-Cln (n = 1- 15) [3]. The approaches to their preparation are well studied and debugged in industry, which ensures their low cost (7-15 € for CuPc) [3].

In general, the synthesis of the basic structure of Pc requires the presence of phthalogen for the construction of isoindole fragments and a nitrogen source for the formation of azomethine bridges between them. Cyclic tetramerization of phthalogens is accelerated in the presence of metal ions that perform a coordinating function [6].

Most global manufacturers obtain CuPc by heating to 200 °C a mixture of phthalic anhydride, urea, copper chloride and a catalyst (usually ammonium molybdate or molybdenum oxide) in a high boiling point (> 180 °C) solvent (most often in kerosene, trichlorobenzene or nitrobenzene). The highly exothermic reaction of the formation of an aromatic macrocycle proceeds from 2 to 8 hours with a yield of up to 90%. This process can also be carried out without the use of a solvent: —dry sintering‖ of the same components at an elevated temperature of 200-300 °C. In this case, the reaction proceeds faster, more environmentally friendly and technologically simpler, as the resulting product requires additional purification. To obtain higher purity phthalocyanines, phthalonitrile is used as phthalogen, which also contains a sufficient number of nitrogen atoms for the formation of a macrocycle. As with phthalic anhydride, the process can be carried out in a solvent medium or by fusion using the same catalysts. A distinctive feature of this method is the formation, along with the main product, of partially chlorinated CuPc (when using copper chlorides as a source of metal ions), which, nevertheless, can be useful for obtaining a pigment resistant α phase form. Chlorination is suppressed in the presence of ammonium or urea salts. Industrial production of phthalocyanine pigments from phthalonitrile is greatly limited by its inaccessibility [3].

Green polyhalogenated pigments can be obtained in a similar way to CuPc synthesis — based on halogenated phthalic anhydride or phthalonitrile [7], but, due to the high cost of substituted phthalogens, the main industrial route for their synthesis is gas phase chlorination (bromination) of CuPc in a eutectic mixture of NaCl / $AlCl_3$ at 200 °C in the presence of a catalyst (e.g., $FeCl_3$). The hue of such pigments depends on the ratio of Cl and Br atoms in the molecule, as well as the total number of halogen atoms (it is not economically feasible to introduce more than 14-15 substituents, as well as to obtain exclusively brominated or fluorinated derivatives) [3].

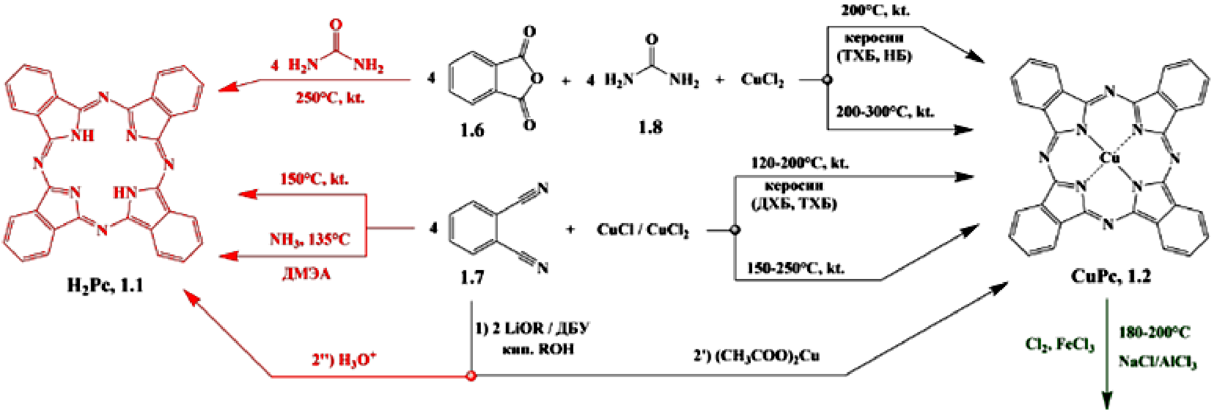
In the world today, research is focused on improving the quality and efficiency of phthalocyanine-based pigments. About 25% of the volume of organic pigments produced is phthalocyanine pigments [8].

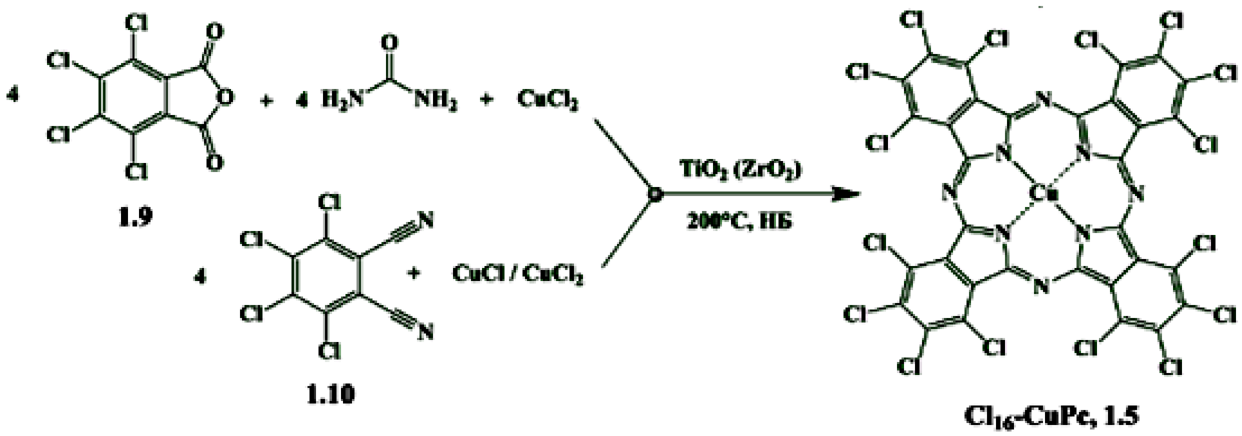
In this regard, phthalocyanins, which contain nitrogen and phosphorus storage groups, are of particular scientific and practical interest. In this case, it is possible to obtain varnish-paint coatings obtained in the presence of phthalocyanine pigments. It is necessary to study the process of synthesis of phthalocyanins containing these nitrogen and phosphorus, to develop their physicochemical properties, as well as the capabilities and technology of the field of application [1].

In our country, certain scientific and practical results are being achieved in the creation of varnish materials with the participation of phthalocyanine pigments, as well as multi-component and functional varnish coatings. Based on the normative measures taken in this direction, certain results have been achieved; in particular, large-scale measures are being taken to develop a scientific basis for obtaining multi-component coatings and to supply the domestic market with import-substituting products [9].

Many types of phthalocyanine Pc compounds have been studied in recent years, and these types of pigments were discovered in the 1930 s [4]. Several representatives of phthalocyanine compounds are of high industrial importance, including: metal-free H_2Pc, copper complex CuPc, and chlorine-derived CuPc-Cln (n = 1-15) compounds [3].

The extraction methods are well-studied and are manufactured on an industrial scale (€ 7-15 per H_2Pc) in order to reduce costs. [10] The main methods of synthesis of phthalocyanine pigments are shown in Picture 2.





Picture 2. Basic methods of synthesis of phthalocyanine pigments.

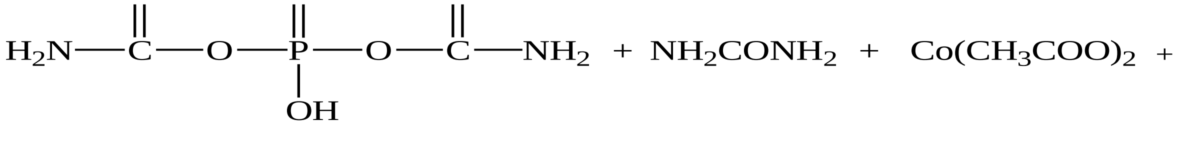
In general, the synthesis of the basic structure of phthalocyanin requires a source of nitrogen to form an isoindol fragment of phthalogen and to form azomethin bonds between them [11]. Cyclic tetramerization of phthalogenes is accelerated in the presence of metal ions performing a coordination function [12].

In many paint plants, phthalic anhydride (1.6), urea (1.8), copper chloride, and catalyst (usually ammonium molybdate or molybdenum oxide) are heated to a high boiling point (> 180 °C) by heating CuPc (1.2) to 200 °C. in a solvent (usually paraffin, trichlorobenzene, or nitrobenzene). The high exothermic reaction of aromatic macrocycle formation lasts from 2 to 8 hours with a yield of up to 90 %.

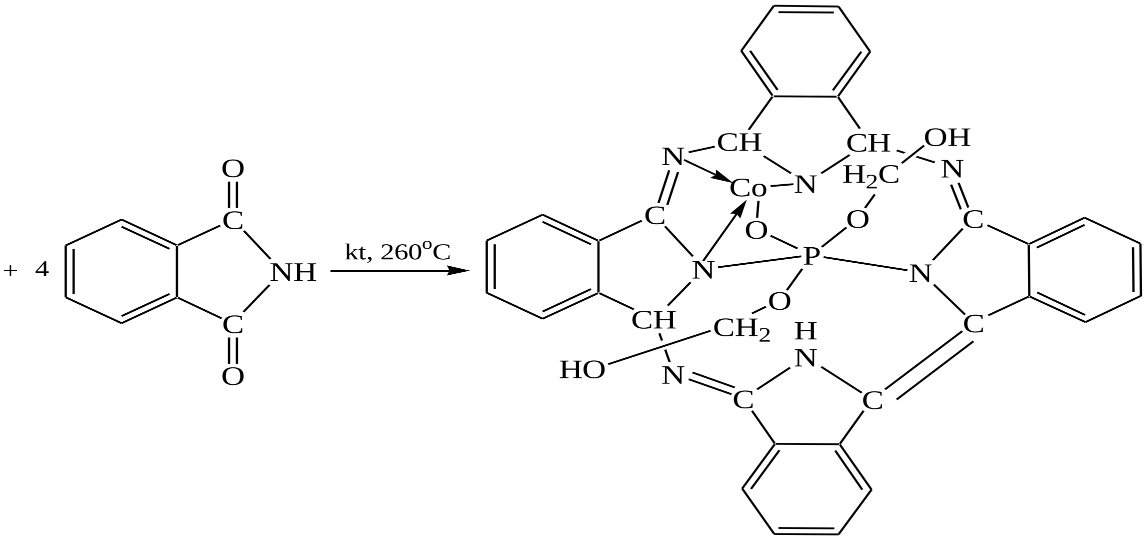
This process can also be done without a solvent: “dry breaking” of the same components at a temperature of 200–300 °C is a faster, more environmentally friendly, and technologically easier method of production because the resulting pigment requires additional cleaning [13].

Material and Methods

DAFCoPc for the synthesis of phthalocyanine pigment in a special container made of high-temperature, acid-resistant nerjavika with a capacity of 500 ml 9.8 g (0.1 mol) orthophosphate acid 18 g (0.3 mol) urea 130 °C full 7 g (0.04 mol) of cobalt (II) acetate, 6 g (0.10 mol) of urea, 24 g (0.17 mol) of phthalimide, ammonium heptamolybdate as a catalyst in the amount of 1 % by weight of phthalimide, stirring with a glass rod until dissolved. Add and mix until homogeneous (reddish color). The reaction is heated in an oven to 260 °C for 3 h. The resulting powdery reaction mixture is then cooled to 50 °C and heated to 40 °C for 20 min with the addition of 85 % sulfuric acid. Add boiling water to the melted product and mix. A 1M $NaHCO_3$ solution is added to neutralize the soluble primary and intermediate products. The DAFCoPc pigment precipitates. The precipitated phthalocyanine pigment is filtered and removed in a Buchner funnel and the product is dried in an oven at 50 °C. The dry mass is cleaned of impurities in ethyl alcohol and re-purified in distilled water in a Büchner funnel. The yield of the resulting product is 80 %. The synthesis of diamidophosphate cobalt phthalocyanine pigment is as follows:



$$H_2N-\overset{\overset{\displaystyle O}{||}}{C}-O-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{||}}{P}}-O-\overset{\overset{\displaystyle O}{||}}{C}-NH_2 + NH_2CONH_2 + Co(CH_3COO)_2 +$$



Results and Discussion

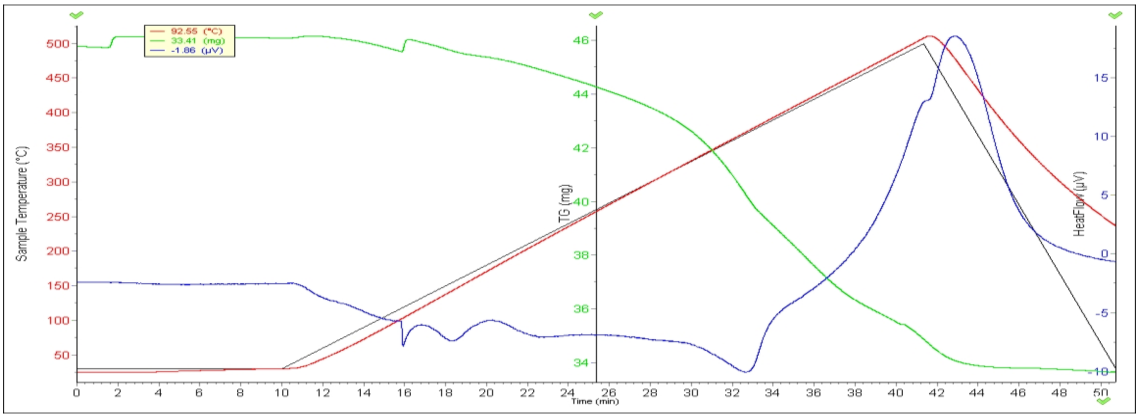
A pigment containing a phthalocyanine group containing a cobalt metal was synthesized, and in order to determine the amount of metal in them, the synthesized DAFCoPc pigments were studied using the element analysis method EDS - Oxford Instrument. Table 1 below shows the elemental analysis of the DAFCoPc pigment.

Table 1: Elemental analysis of cobalt-containing DAFCoPc pigment

Element	C	N	O	Co	P	Mo
Share, %	59,4	13,2	13,9	8,4	4,9	0,2

As can be seen from Table 1, the DAFCoPc pigment composition we synthesized had a cobalt metal content of 8.4 % and a phosphorus content of 4.9 %. This proves that the consumption of reagents in the synthesis process was selected correctly. Thermal Analysis - The thermal stability of synthesized nitrogen and phosphorus-retaining phthalocyanine pigments was analyzed by differential-thermal and thermogravimetric methods in the French LABSYS EVO STA device.

LABSYS evo STA (Simultaneous Thermal Analysis) TGA and also TGA-DTA, TGA-DSC analysis methods analysis is an easy-to-use, reliable and highly efficient thermal analysis platform. The derivatograph was studied at a speed of 10 degrees / min, T-900, TG-200, DTA - 1/10, DTG - 1/10 galvanometer sensitivity, by automatically recording the derivatogram on photographic paper. A sample of the studied pigments in a mass of 35–46 mg was placed in a crucible made of aluminum oxide and platinum resistant to a temperature of 1650 °C without a cap with a diameter of 10 mm. The dynamic mode of heating was carried out in atmospheric conditions. The pigments synthesized during the analysis were thermally analyzed at a temperature of 20 - 500 °C. In addition, the endothermic and exothermic points of pigments have been proven.



Picture 3. Derivatogram of DAFCoPc pigment.

In Picture 3, a temperature of 500 °C was selected for the nitrogen and phosphorus-retaining DAFCoPc pigment and the results of the pigment analysis were studied according to the derivatogram image.

Five endothermic effects were observed at 30, 55, 65, 75, 420 °C and four exothermic effects at 95, 98, 160, 500 °C. DAFCoPc pigment was obtained from an open-crucible crucible made of aluminum oxide and platinum resistant to a temperature of 1650 °C. The percentage lost was C % = 2.7 / 46 • 100 = 5.8 %, and the amount of energy expended at this temperature was 5.31 µV • s / mg. At this temperature, the decrease in the mass of the pigment DAFCoPc and the loss of adsorbed water absorbed in the internal system of the complex and the reduction of interconnected volatile nitrogen atoms. Subsequent observations were made at 300 °C and the initial mass was 46 mg. = 12.8 % and the amount of energy consumed at this temperature was 4.89 µV • s / mg.

In this case, the decrease in mass is due to the decomposition of nitrogen derivatives in the DAFCoPc pigment and the carbon-bonded compounds in the ring. Thermal analyzes were also performed at 100, 400, and 500 °C, and total losses were calculated for each temperature.

At the last temperature of 500 °C, the mass of 46 mg of pigment was 34.1 mg ha, the mass in% was 25.8 % and the amount of energy consumed was 5.13 µV • s / mg. The DAFCoPc pigment retains a residual mass of 34.1 mg due to the molecules that form a bond with phosphorus, and the mass of the pigment is reduced by 11.9 mg from the total mass obtained when kept at such a high temperature for 43 minutes. Based on the results of the above analysis, the appearance of the new DAFCoPc pigment synthesized is in the form of randomly arranged particles, ie amorphous.

Table 2: Thermal analysis of DAFCoPc pigments exposed to high temperatures

№	**Temperature °C**	**Residual mass, mg**	**Lost mass, mg**	**Lost mass, %**	Amount of energy consumed **(µV*s/mg)**
46 mg of DAFCoPc pigment was obtained in total mass					
1	100	45,3	0,7	1,5	1,6
2	200	43,3	2,7	5,8	5,31
3	300	40,1	5,9	12,8	4,89
4	400	36,2	9,8	21,3	3,02
5	500	34,1	11,9	25,8	5,13

Conclusion

In conclusion, it can be said that a complex dye pigment containing nitrogen, phosphorus, cobalt and phthalate was synthesized. The metal content of the pigment was analyzed by elemental analysis and found to contain 8.4 % cobalt. The temperature rise of the pigment was studied and analyzed by thermal analysis. The complex arrangement of organic groups in the pigment plays an important role in increasing the intensity of the pigment. The new pigment is synthesized in a unique way, which allows to achieve high economic efficiency and reduce foreign exchange costs.

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