

Investigation of phthalocyanine diamidophosphate-nickel by thermal analysis

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Abstract. The article presents the results of a study of the synthesis of a new type of pigment - nickel phthalocyanine diphosphate (DAPNiPc), which contains macroheterocyclic compounds. The influence of the method of obtaining a pigment in the liquid and solid phases on its physicochemical properties and intensity has been studied. The gross formula of the pigment is given and the areas of its practical application are shown. Thermal analysis on a Setaram LabSys Evo instrument (France) was used to study the thermal stability of a highly intense pigment of the organic nickel phthalocyanine pigment, which was compared with the closest analog, the copper phthalocyanine pigment. Thermal studies of exothermic and endothermic processes were carried out in the temperature range of 100-500 °C. The results of the mass loss of the pigment upon heating are presented. It is shown that, due to the content of phosphorus-containing compounds, the synthesized pigment has high heat resistance and intensity.

1 Introduction

At present, advanced technologies are being developed in the world, such as the production of electrical and optical materials based on phthalocyanine pigments, solar cells, and chemical sensors. An important advantage of phthalocyanine pigments is their very low toxicity; they are used in the production of packaging materials for food products, children's toys, and medicines. Also, phthalocyanines and their derivatives play an important role in obtaining light and heat resistant dyes, which are characterized by high chemical resistance and color stability [1].

Today, there is a scientific basis in the world for solving a number of problems to improve the properties of phthalocyanine-based pigments and their effective use, including: simplification and safety of methods for the synthesis of phthalocyanine pigments; creation of new types of phthalocyanine pigments soluble in water and solvents; increased production of phthalocyanine pigments. It is necessary to find and expand the scope of new compositions that can purposefully change the anticorrosion, static and dynamic strength properties of phthalocyanine pigments [2].

Phthalocyanine is a planar 18 π -electron heterocyclic aromatic system with an alternating nitrogen and carbon ring structure derived from porphyrin. Phthalocyanines have been known for over 70 years and are widely used as dyes. Moreover, they have generated interest

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for various applications such as liquid crystals, photosensitizers, non-linear optics, solar cells, catalysis, and various chemical sensor applications. The peripheral and non-peripheral positions of the benzene ring of phthalocyanines can be replaced by many other molecules to impart new properties. In addition, more than seventy different metal ions can be introduced into the central cavity to improve the physical properties according to the desired process application. Among them, copper phthalocyanine is one of the most important classes of dyes and has excellent properties such as light fastness, coloring power, hiding power, and alkali and acid resistance [3].

About 25% of the volume of organic pigments produced are phthalocyanine pigments. In this regard, phthalocyanines containing nitrogen and phosphorus-containing groups are of particular scientific and practical interest. In this case, it is possible to obtain varnish coatings in the presence of phthalocyanine pigments [4].

More than 90% of the amount of phthalocyanines produced in the world (over 80 thousand tons / year) is used as colorants - pigments and dyes, while about 40% - in the composition of color printing inks, 30% - in paints and varnishes, 20% - for coloring of plastics, 10% - in other formulations. Pcs derivatives account for approximately 25% of all commercially available synthetic organic pigments [5].

Such a demand for phthalocyanines were provided by a set of properties that are critical for pigments: color brightness, high resistance to fading and weather conditions (light and weather resistance), the action of solvents, acids and alkalis, thermal stability, economy of use (due to the high extinction coefficient). Moreover, the availability of the starting compounds and the simple technology for the synthesis of phthalocyanines provide them with a good price-quality ratio [6].

According to the Color Index, unsubstituted and partially chlorinated blue copper phthalocyaninates are named Pigment Blue (abbr. P.B.) 15 (15:X, X=1-6) and number 74160; perhalogenated green pigments - Pigment Green (P.G.) 7 C.I. 74260 (CuPc-Cl₁₄₋₁₅) and P.G.36 C.I. 74265 (CuPc-Cl₄₋₈-Br₄₋₁₂); metal-free γ -H₂Pc - P.B.16 C.I. 74100.

The exact color of the Pc pigment (Figure 1) depends on its crystalline form (ϵ - and α -modifications are reddish, β - and γ -modifications are greenish) and on the number and type of halogen atoms (P.G. 7 has a blue-green color, P.G. 36 - yellowish green) [7].



Fig. 1. Shades of the main phthalocyanine pigments based on commercially available pigments from Heliogen (trademark of BASF) [8].

The α -form of copper phthalocyaninate (P.B.15:1), which is stable due to partial chlorination, is more often than other blue Pcs used for coloring plastics and in paints and varnishes, including for obtaining solid and metallic shades of automotive coatings. This form of CuPc has excellent resistance to organic solvents, light and weather resistance, high thermal stability and migration resistance in all media, has a high coloring power in polyolefins, and most binders containing P.B.15:1 meet all the necessary requirements at temperatures up to 300 °C. The unstable α -form of CuPc (P.B.15) due to its high coloring ability is limitedly used in water-borne paints and up to 200 °C, at higher temperatures and in the presence of aromatic solvents it recrystallizes into the β -form.

The stable β -form of copper phthalocyaninate (P.B.15:3) is widely used in multicolor printing inks, for dyeing plastics and rubbers, and for printing on textiles. The pure turquoise color of this form of CuPc is used as the cyan standard in offset and letterpress printing systems. Due to the difficulty of dispersion, P.B.15:3 is of limited use in polyolefins, but is highly stable in plasticized PVC.

Flocculation-resistant pigments P.B.15:2 and P.B.15:4 are obtained by surface treatment of α -CuPc-Cl_{0.5-1} or β -CuPc with their water-soluble derivatives [9].

The ϵ -form of CuPc (P.B.15:6) has the most pronounced reddish blue hue of all phthalocyanine pigments and a very high tinting power. However, due to significant instability, this crystalline modification is of limited use in color filters for LCD and TFT displays. Also limited (when creating metallized paints) is the unstable γ -form of metal-free phthalocyanine (P.B.16), which has a greener tint and increased coloring power compared to β -CuPc.

All blue phthalocyanine pigments can cause warping of partially crystalline thermoplastics (polyethylene, polypropylene), to prevent which CuPc with an increased degree of chlorination (CuPc-Cl₃) is used.

Green P.G.7 and P.G.36 have light, weather and solvent resistance even greater than blue Pcs, but at the same time reduced (due to high molecular weight) coloring power. The main area of their use are paints and varnishes, especially used outdoors. The glazing form P.G.36, like P.B.15:6, is used as part of color filters for LCD displays [10].

Water-soluble derivatives of MPC are used as dyes. Copper phthalocyaninates with 2-4 sulfo groups in the molecule are important dyes for cotton (Acid Blue 249, Direct Blue 86, 87), less sulfonated MPC are vat dyes (Vat Blue 29). Salts of sulfonic acids Pcs with oleophilic ammonium cations are used as fat-soluble dyes for fuels [18]. Based on sulfamido- and aminomethyl-substituted phthalocyanines, direct dyes (Direct Blue 100 and 199) were obtained for paper, leather, and textiles, as well as a number of active dyes for cotton [11–15]. Carboxyl-containing phthalocyanines have been studied as dyes for synthetic polymer fibers [15].

An important advantage of phthalocyanine pigments is their very low toxicity (LD₅₀ > 10 g/kg, which is 70 times higher than that of CuCl₂), the absence of mutagenicity and carcinogenicity [16], which allows them to be used in food packaging materials, in the manufacture of children's goods, medicine, and in formulations that come into contact with human skin [17].

Complexes of phthalocyanines with transition metals have found application as catalysts for the purification of hydrocarbons from sulfur compounds and in the neutralization of toxic effluents. Heterogeneous catalysts obtained by fusing a mixture of CoPc with salts of metals of variable valence onto a polymer matrix are highly efficient [18].

Phthalocyanine derivatives with mesomorphism can serve as "structural action" additives in the composition of tribologically efficient and environmentally friendly lubricants. Promising is the use of Pcs in the composition of solid layered lubricants (TLS) and plastic lubricants (PS), which have a long service life at temperatures above 180°C, high moisture resistance, and good colloidal stability. On the basis of Pcs, it is planned to create permanent triboactive lubricating compositions for friction units [19].

Thus, due to the unique combination of valuable properties, Pcs derivatives are widely used in many branches of modern materials technology (Figure 2).

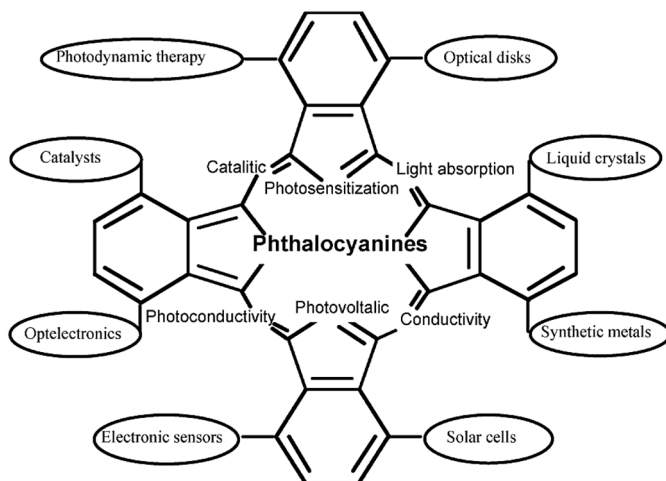


Fig. 2. Modern applications of phthalocyanines [20]. Further, aspects of the use of phthalocyanines that are directly related to this work are considered in more detail.

2 Experimental Methodology

Synthesis of nickel phthalocyanine (DAPNiPc) based on diamidophosphate. The synthesis was carried out in two ways: in a solvent medium and by heating at high temperatures [3].

1-way. For this, 73.6 g (0.4 mol) of diamidophosphate, 24 g (0.4 mol) of urea, 235.6 g (1.6 mol) of phthalimide, 70.8 g (0.4 mol) of nickel(II) chloride (II). To the mass of nickel acetate and phthalimide add 1% ammonium heptamolybdate and 550 ml of dimethyl sulfoxide (DMSO) as a solvent. The reaction is carried out at a temperature of 150-180 °C for 3-4 hours with stirring. Upon completion of the reaction, the reaction mass is cooled and filtered on a Buchner funnel, and the dark turquoise pigment remaining in the funnel is again washed with distilled water. The washed product is dried in an oven at 50 °C. Product yield 93%.

2-way. Synthesis was carried out at high temperature by heating. 9.8 g (0.1 mol) of phosphoric acid and 18 g (0.3 mol) of urea were loaded into a beaker, stirred with a glass rod until urea was completely dissolved in phosphoric acid at 130 °C, then a mixture of the remaining ingredients was added, which consist from: 7 g (0.04 mol) nickel(II) chloride, 6 g (0.1 mol) urea, 24 g (0.17 mol) phthalimide. After adding all the reagents, the reaction mass was stirred and the catalyst was added in an amount of 1 % by weight of phthalimide. The reaction mass is mixed until homogeneous (red). The reaction mixture is heated to 260 °C for 3 hours. The resulting powder reaction mixture is cooled to 50 °C and 85 % sulfuric acid is added in the amount necessary to completely dissolve the resulting powder. Further, hot water is added to this mixture, while the pigment is deposited on the bottom of the vessel, the liquid is decanted, the pigment is washed with hot water and filtered. The resulting pigment is dried in a drying cabinet at 50-60 °C until completely dry. Product yield 80%.

3 Results and its discussion

The new pigment diamidophosphate-nickel-phthalocyanine (DAP-NiPc) was obtained in two different ways. Based on the results obtained, the second method was chosen. The proposed reaction mechanisms and the formula of the resulting substance are based on elemental analysis and IR spectral analysis:

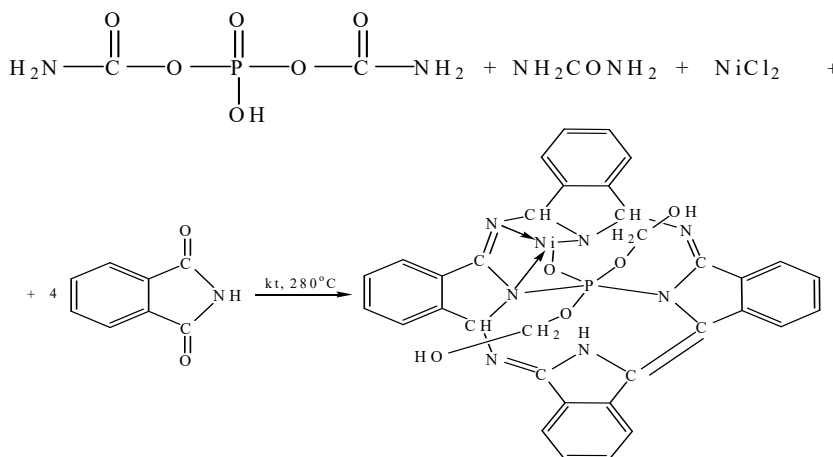


Fig. 3. New pigment, diamidophosphate-nickelphthalocyanine (DAPNiPc).

To study the thermal properties of the resulting pigment, thermal analysis was carried out, the result of the derivatogram is shown in Figure 4

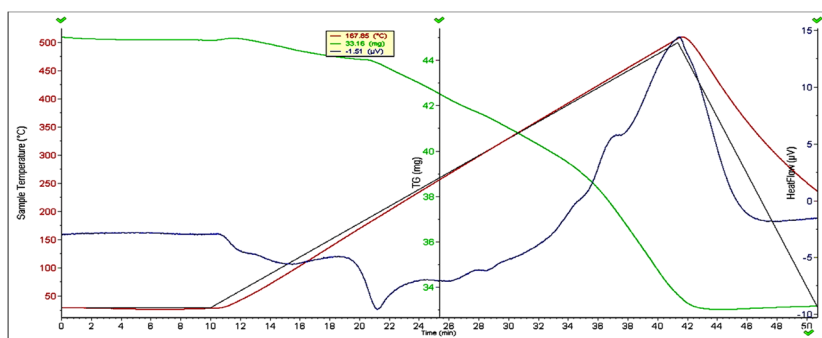


Fig. 4. Derivatogram of the DAP-NiPc pigment.

For the DAPNiPc pigment, a temperature above 500 °C was chosen, and as a result of pigment analysis, five endothermic effects were observed at temperatures of 30, 60, 80, 320 °C and four exothermic effects at 90, 120, 160, 325, 510 °C, the mass of the DAPNiPc pigment decreases due to residual moisture and adsorbed water of the internal structure of the complex. A subsequent mass loss was observed at 300 °C, the initial mass was 44 mg, and the amount of energy consumed at this temperature was 5.05 $\mu\text{V}\cdot\text{s}/\text{mg}$. The decrease in mass is associated with the decomposition of nitrogen derivatives in the DAPNiPc pigment and carbon-bound compounds in the ring. Thermal analysis was carried out up to 500 °C and the total mass loss was calculated for each temperature separately. The DAPNiPc pigment retains a residual weight of 34,1 mg due to molecules that form a bond with phosphorus, and the weight of the pigment is reduced by 9.9 mg from the total weight obtained by keeping it at this high temperature for 37 minutes. According to the results of the analysis, the newly synthesized DAPNiPc pigment has the form of randomly arranged particles; amorphous. Table 1 shows a comparison of the thermal analysis of the DAPNiPc pigment and the copper phthalocyanine pigment.

Table 1. Comparative thermal analysis of the DAPNiPc pigment and the copper phthalocyanine pigment obtained as a control.

№	Temperature °C	Residual mass, mg	Lost weight, mg	Lost weight, %	Power consumption ($\mu\text{V}^*\text{s}/\text{mg}$)
received 44 mg of pigment DAF-NiPc with a total mass					
1	100	43.5	0.5	1.13	2.6
2	200	42.1	1.9	4.31	4.98
3	300	40.2	3.8	8.63	5.05
4	400	38.4	5.6	17.7	4.58
5	500	34.1	9.9	22.5	5.19
received 24 mg of copper phthalocyanine pigment with a total mass					
1	100	23.8	0.2	0.83	2.45
2	200	20.6	3.4	14.2	1.91
3	300	15.4	8.4	35.0	3.09
4	400	9.8	14.2	59.2	4.08
5	500	5.1	18.9	78.8	5.93

The results of this derivatogram show that the main mass loss of the synthesized DAPNiPc pigment occurs in the range of 150-470 °C. And in the range of 50-150°C, the mass loss of the DAPNiPc pigment is negligible.

4 Conclusion

A new type of pigment, nickel diphosphate phthalocyanine (DAFNiPc), was synthesized in two ways: in the liquid phase in the presence of dimethyl sulfoxide and in the solid phase by heating the components at a high temperature. The pigment yield during synthesis in a liquid medium was 93%, but its intensity turned out to be low, and under the conditions of synthesis in the solid phase, a high pigment intensity was achieved at its 80% yield. The physicochemical properties of the new pigment synthesized in various aggregative states are compared with those of the closest analogue, copper phthalocyanine. The high thermal stability of the new pigment was discovered and possible areas of its practical application in the national economy were proposed.

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