Synthesis and analysis of a new high intensity phthalocyanine pigment containing nitrogen, sulfur and copper

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Abstract. The article presents the results of research on obtaining highly intensive pigments based on organic and inorganic substances. The process of synthesis of copper chloride (CuCl) raw material with phthalic anhydride, inorganic and organic substances was studied. As a result of the study, copper chloride (CuCl) and a sample of the pigment obtained as a result of neutralization with sulfuric acid were analyzed using an X-ray spectrum. According to the results of the analysis, a new type of pigment based on copper phthalocyanine (CuPc) was selected as the most optimal option, and physico-chemical analysis of the sample (elemental analysis (SEM_EDX)) was studied. It has been determined that the highly intensive pigment obtained as a result can be used as an import substitute product in the construction and textile industry.

1 Introduction

The creation of solar cells, chemical sensors, and electrical and optical materials based on phthalocyanine pigments are only a few examples of the cutting-edge technologies that are now being developed worldwide. The extremely low toxicity of phthalocyanine pigments, which are used to make packaging for food goods, toys for kids, and pharmaceuticals, is a significant benefit. Additionally, the production of light- and heat-resistant dyes, which exhibit great chemical resistance and color stability, depends heavily on phthalocyanines and their derivatives [1].

Organic pigments refer to a class of pigments made from organic compounds with color properties and a number of other pigments. Pigment characteristics include light resistance, water immersion resistance, acid resistance, alkali resistance, organic solvent resistance, heat resistance, crystal shape stability, dispersion, and concealment strength. The intermediate products, production equipment and synthesis process required to produce it are similar to paint production, so organic pigments are often organized in the paint industry. Compared to common inorganic pigments, organic pigments usually have a greater coloring capacity [2]. Organic pigments are commonly used to color ink, coating, rubber products, plastic products, cultural and educational materials, and building materials. Organic pigments are classified

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by structure as follows: Azo pigments make up 59%, phthalocyanine pigment 24%, triarylmethane pigment 8%, special pigments 6%, polycyclic pigments 3% [3].

Porphyrins and phthalocyanines are of great interest, both from the point of view of fundamental research and in applied fields. The distribution of roles between these two fundamental types of tetrapyrrole pigments differs significantly. Phthalocyanines are technologically much more accessible - their global industrial production is measured in thousands of tons, and their applications are numerous and familiar to every person - light-resistant green and blue dyes and pigments, optical materials for laser discs, etc. At the same time, porphyrins predominate in fundamental research, since the possibilities for targeted modification and selective synthesis of porphyrins far exceed those for phthalocyanines. Thus, each of these systems has its own characteristics, advantages and disadvantages, depending on the specific application task. Phthalocyanines, for example, have strong adsorption in the long-wavelength range, which is critical when used as photosensitizers for photodynamic therapy [4], in the creation of organic solar cells, etc. However, at the same time, the solubility of phthalocyanines is extremely low and their metal complexes in conventional organic solvents makes working with these compounds much more difficult. Porphyrin systems, on the contrary, do not have the latter drawback, but unlike phthalocyanines, classical porphyrins absorb electromagnetic radiation in the long-wave region extremely weakly [5].

Phthalocyanines, or tetrabenzotetraazaporphyrins (Figure 1) are synthetic analogues of porphyrins 2, widespread in nature, included, in particular, in chlorophyll, hemoglobin, cytochromes, the role of which in biological processes can hardly be overestimated.

Phthalocyanines themselves do not occur in nature. Phthalocyanine was first obtained by accident in 1907 by heating an alcohol solution of o-cyanobenzamide in the form of an insoluble blue substance. Twenty years later, copper phthalocyanine was obtained from o-dibromobenzene and CuCN. The structure of phthalocyanine was established by Linstead in the 30s. X-ray diffraction method. He also owns a series of classic works on synthesis methods, structure and properties of a number of phthalocyanines with various metals and substituents - the first systematic study of this class of compounds [6]. In subsequent years, phthalocyanines were studied quite intensively [7] and found a large number of practical applications. Despite their “age,” the interest of researchers in phthalocyanines and their analogues continues to grow, both from a theoretical point of view due to their unique electronic structure (see Section 1.2), and from the standpoint of potential applications as new materials, modeling photosynthesis, etc. (see below). This is confirmed by the Society of Porphyrins and Phthalocyanines, which publishes the Journal of Porphyrins and Phthalocyanines, and the recently published reference book The Porphyrin Handbook in 20 volumes, 6 of which are devoted to phthalocyanines [8].

Let's take a closer look at this unique molecule. Undoubtedly, the keen interest of researchers in phthalocyanines has largely an aesthetic origin. The molecules of most phthalocyanines have an almost flat structure. The symmetry of the molecules of the simplest PcM is close to D_4h, which is unusual for organic compounds. The symmetry of the phthalocyanine ligand PcH_2 is close to D_2h. This information is available from X-ray diffraction data [9], which originates from the early work of Linstead. There is also information about the molecular structure of phthalocyanine obtained by gas electron diffraction [10]. It is believed that in the gas phase and in solution, the molecules of the simplest phthalocyanine have ideal symmetry (D_4h for PcM, D_2h for PcH_2), which is broken in the crystal. This is evidenced by the data of electronic spectra and quantum chemical calculations [11].

Naturally, with the introduction of substituents, and also depending on the central metal atom, the symmetry may decrease. In this case, another feature of the structure of phthalocyanines appears - a wide possibility of structural modification due to the central

metal atom and substituents. Thus, phthalocyanine complexes are known for almost all metals of the periodic table D.I. Mendeleev [12]. The 16 positions on the periphery of the molecule can contain various substituents. In addition, it is possible to attach one, two or more axial ligands to the central metal atom. Depending on the ionic radius of the metal, as well as the presence of axial substituents, the metal can be either in the plane of the ring or out of it. The M–N distance in flat complexes is 1.8 – 2.0 E [13]. The formal charge of the phthalocyanine ligand is –2, which is due to aromatic stabilization (Hückel's rule 4n+2). Therefore, neutral complexes contain a divalent metal atom, two monovalent metal atoms, or two hydrogen atoms at the center.

Metal phthalocyanines of higher oxidation states require the presence of axial ligands. Thus, the diversity of phthalocyanine complexes is very large. It should be noted that for the vast majority of known complexes the substituents on different benzene rings are the same. Most often, tetrasubstituted phthalocyanines of this type are obtained only in the form of a mixture of 4 isomers, obtained by rearranging positions 8 and 11 (9 and 10), 15 and 18 (16 and 17), 22 and 25 (23 and 24) [14]. This, on the one hand, increases solubility, on the other, makes standard characterization methods less informative. Phthalocyanines with a different set of substituents on different benzene rings are much less studied (mainly due to the lack of suitable synthesis methods), but are relevant due to the wider possibilities for modifying the structure and properties [15]. Substituted phthalocyanines formally include their dimers and oligomers, the interaction (usually strong) of phthalocyanine fragments in which leads to new interesting properties. However, such systems are even less studied (for the same reason). A number of phthalocyanine analogues are known that contain polycyclic aromatic hydrocarbon rings instead of benzene rings (for example, 2,3-naphthalocyanines, Nc 3), as well as heterocyclic fragments [13–15]; tetraazaporphyrins 4 (porphyrazines, Pz) [16], the tetrabenzo derivatives of which are phthalocyanines themselves; subphthalocyanines (SubPc, 5) [17] and superphthalocyanines (SPc, 6).

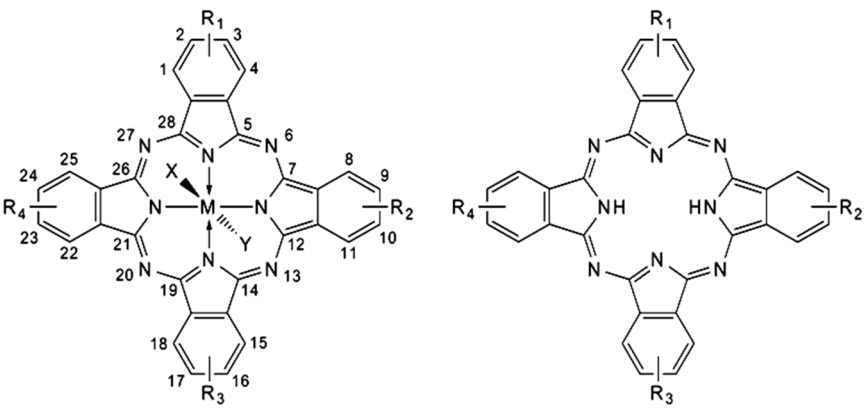

Fig. 1. Phthalocyanine structure.

When preparing metal complexes of phthalocyanines from acids, anhydrides or imides, a source of nitrogen atoms is needed to form phthalocyanine, usually urea. The complexes are obtained by heating the starting compound with excess urea, a metal salt and a catalyst (ammonium molybdate) at a temperature of 180 to 300 °C. Severe reaction conditions limit the use of this method, however, in the case of unsubstituted complexes or substituents that are stable under the reaction conditions, product yields can be high [18].

Copper complexes of phthalocyanines can be prepared by heating substituted ortho-dibromobenzenes with copper cyanide in solvents such as dimethylformamide or quinoline.

The reaction is believed to proceed through the formation of phthalonitrile as an intermediate. Also described in the literature is an example of the low yield production of zinc complexes from substituted ortho-dichlorobenzenes by their reaction with zinc cyanide in the presence of a palladium catalyst [19].

The demand for pigments is growing rapidly. Its diversity and performance are advancing more and more demands, providing a good opportunity for the development of the organic pigment industry. The Organic Pigments Market is expected to reach US $ 6.7 billion by the end of 2026. Inorganic pigments are expected to be $ 2.8 billion by the end of 2024.

2 Materials and methods

Synthesis of phthalocyanine pigment containing copper, nitrogen and sulfur. Based on the conducted experiments, the amount and temperature of reactants obtained as initial products are of primary importance in obtaining highly productive copper-sulfur-retaining phthalocyanine pigments [16]. The ratio of initial reactants obtained and the effect of temperature on the yield of pigments for copper-sulfur phthalocyanine pigment are presented in Table 1.

Table 1. The effect of the mass ratio of copper chloride and ammonium sulfate as the main component of phthalocyanine pigment, which contains copper, nitrogen and sulfur, and the effect of temperature on the yield of pigments.

№	$CuCl:(NH_4)_2SO_4$	T, ^0C	ω,%	№	$CuCl:(NH_4)_2SO_4$	T, ^0C	ω,%
1	1.1:1	200	66.3	10	1:2.6	200	69.5
2		225	84.4	11		225	87.8
3		250	73.3	12		250	77.1
4	1:1.2	200	67.5	13	1:4.3	200	75.6
5		225	85.7	14		225	89.6
6		250	74.1	15		250	78.3
7	1:1.8	200	68.1	16	1:5	200	73.2
8		225	86.4	17		225	89.6
9		250	75.4	18		250	78.0

From the obtained results, it was found that when the ratio of initial reagents for the synthesis of CuPc pigment is 1:4.3 and the temperature is 225 °C, the yield is 89.6%. These results show that the optimal conditions for the synthesis of CuPc.

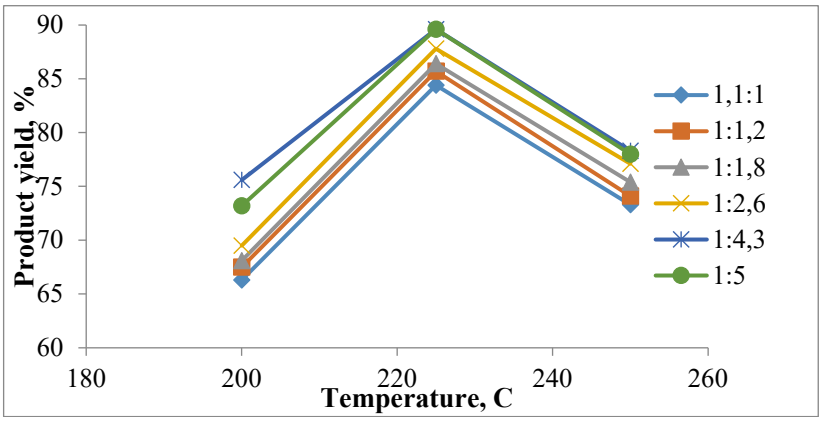

Fig. 2. Graphic representation of the mass ratio of the phthalocyanine pigment containing copper, nitrogen and sulfur and the effect of temperature on the yield of pigments.

The synthesis process is carried out through a SNOL heating furnace.

To carry out the reaction process in the SNOL heating furnace, we need 500 ml heat-resistant beaker and reactors

Substances:

1. Phthalic anhydride 1 mol
2. Urea 5 mol
3. Copper chloride 0.5 mol
4. Ammonium sulfate 4 mol
5. Ammonium molybdate 0.03 mol
6. Concentrated sulfuric acid (85%) 20 ml

A mixture of phthalic anhydride 1 mol, urea 5 mol, copper chloride 0.5 mol, ammonium sulfate 4 mol, and ammonium molybdate 0.03 mol is placed in a reaction glass in a high-temperature, acid-resistant stainless steel container with a capacity of 250 ml. The mixture is mixed in a HP-550-S heating oven at a maximum temperature of 249 ºC for 40-50 minutes until the mixture becomes homogeneous (light air color). The homogeneous mixture is heated to 243 ºC in a heating oven (SNOL) for 3 hours. The reaction lasted for 3 hours. Then the formed powdery reaction mixture is cooled to 50 ºC and dissolved in 85% sulfuric acid. Boiled water is added to the melted product and mixed. Primary products and intermediate products that have not reacted are dissolved. The formed CuPc pigment is deposited. Precipitated phthalocyanine pigment is filtered in a Buechner funnel and washed several times with distilled water. The washed product is dried in the ShS-8001 ShSU oven at a temperature of 50 ºC. Product yield is 80 %.

3 Results and discussion

The result of the X-ray analysis confirmed the presence of the above organic compounds in the above analysis.

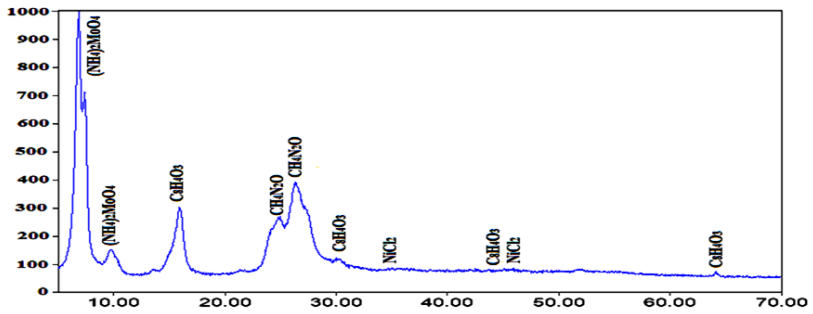

Fig. 3. X-ray analysis phthalocyanine pigment containing copper, nitrogen and sulfur.

The obtained pigment with a new composition was studied using elemental analysis methods and the results are as follows.

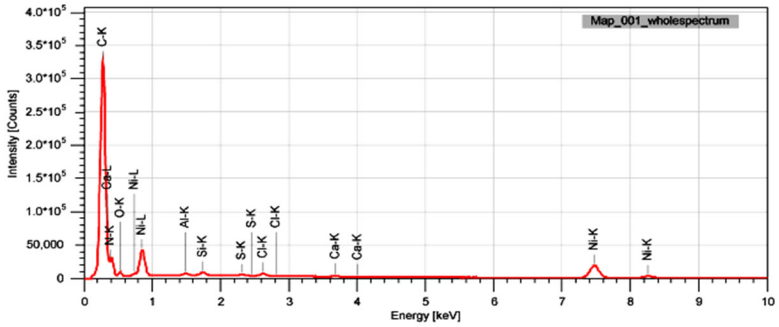

Fig. 4. Elemental analysis phthalocyanine pigment containing copper, nitrogen and sulfur.

The research carried out in this scientific work was carried out by the method of burning in a dry state.

4 Conclusion

Synthesis of organic high-intensity phthalocyanine pigment with a new composition, which preserves nitrogen, sulfur and copper, is studied by the heating method. The mass ratios of the initial components and the pigment yield in different masses were studied during the synthesis by heating at high temperature. It was proved that the optimal initial samples obtained during the synthesis were in the ratio of 1:4.3, and the output yield of the pigment was 89.6%. The organic and inorganic compounds in the pigment were proven using modern physical and chemical analysis methods.

Simple and convenient methods have been developed for the preparation of reduced metal phthalocyanines using various reducing agents (organic and inorganic). The developed methods for the reduction of phthalocyanines made it possible for the first time to obtain a large number of new anionic, anion-radical salts and coordination compounds of metal phthalocyanines, including phthalocyanine derivatives with acceptor substituents or an extended π-system. It is especially important that reduced forms of phthalocyanines are highly soluble in organic solvents. This makes it possible to obtain single crystals of compounds, which is necessary for the correct study of their crystal structure and various properties.

The results obtained will be used in the future to create more complex phthalocyanine systems, in particular, systems with partial charge transfer to the macrocycle. Further development of this area of research can lead to the production of compounds and materials that will have promising conductive, magnetic and optical properties, including the synergism of these properties.

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