ISSN 2181-8622

Manufacturing technology problems

Scientific and Technical Journal Namangan Institute of Engineering and Technology

Volume 9
Issue 3
2024

UDC: 667.287.5

SYNTHESIS OF METAL PHTHALOCYANINE PIGMENT BASED ON NPK AND CALCULATION OF PARTICLE SIZE USING THE DEBYE-SCHERRER EQUATION

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Abstract: This article presents a comprehensive investigation into the chemical composition, structural characteristics, and particle size of a newly synthesized metal phthalocyanine pigment, employing advanced physical and chemical analytical techniques. The research utilizes a novel experimental approach to elucidate the synthesis process. Specifically, the particle size of the metal phthalocyanine pigments was assessed using the Debye-Scherrer equation. The synthesis of high-intensity metal phthalocyanine pigment is thoroughly examined, and a diagrammatic representation of the components constituting the NPK-based metal phthalocyanine pigment is provided.

Keywords: Debye-Scherrer equation, diffractogram, metal phthalocyanine, particle size, nanoparticle.

Introduction. Currently, a fundamentally new method of cancer diagnostics and treatment is being successfully developed, based on the ability of photosensitizers to selectively accumulate in affected tissues and, under local irradiation of a certain power and wavelength, generate oxygen-containing free radicals that lead to the death of tumor cells [1].

Numerous studies confirm the possibility of practical application of water-soluble phthalocyanines as such photosensitizers, since these compounds have the necessary properties: they have an intense absorption maximum in the region of 650-800 nm, are low-toxic, and are capable of efficient generation of singlet oxygen [2].

It has long been known that unsubstituted phthalocyanine ligands and metal complexes are practically insoluble in organic solvents and absolutely insoluble in water. Numerous phthalocyanines with various peripheral substituents also have similar properties. Recently, there have been constant reports of successes in the synthesis of water-soluble phthalocyanine ligands and complexes, which are achieved by introducing peripheral cationic or anionic substituents into the molecule, containing structural fragments that provide hydrophilicity of the ligands and complexes [3-6]. An extremely desirable property of an ideal sensitizer is simultaneous water and fat solubility. A feature of the products obtained is the ability to easily convert hydrophilic compounds into hydrophobic ones and vice versa, in addition, thanks to the developed methods for modifying peripheral substituents, compounds soluble simultaneously in water and organic solvents have been obtained. These phthalocyanines can be potential photosensitizers, and also have potential for use as complexing agents.

Materials and Methods

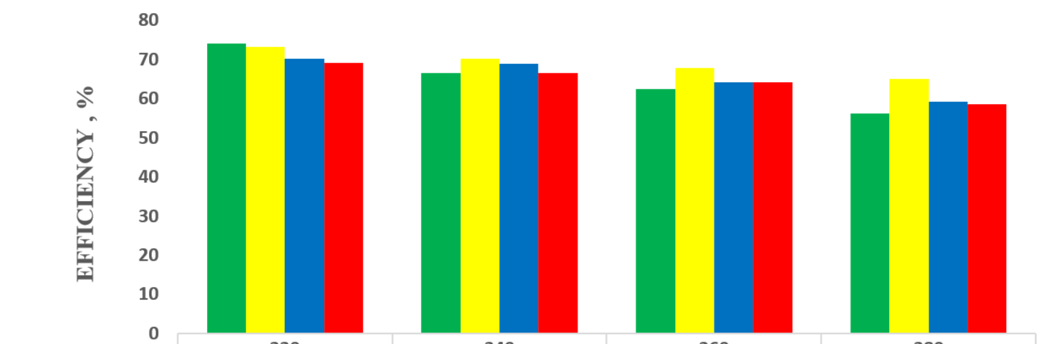
In the synthesized pigments, particular emphasis was placed on evaluating their intensity. Metal phthalocyanine pigments were produced using two distinct methodologies: the heating method and the solution method. The heating method was selected for this study, as it yielded the highest intensity of the pigments. Thus, the synthesis was conducted utilizing the heating approach. Seventeen grams (1 mol) of NPK and sixty grams (10 mol) of urea were sequentially introduced into a 250 ml high-temperature, acid-resistant metal container and mixed with a glass rod until complete dissolution at 130 °C. Subsequently, fifteen grams (1 mol) of phthalic anhydride, eight grams (0.5 mol) of copper(II) sulfate, and ammonium heptamolybdate, used as a catalyst at a concentration of 1% relative to the mass of phthalic anhydride, were incorporated into the mixture until a homogeneous dark blue state was achieved. The reaction mixture was heated in an oven at 260 °C for a duration of 3 hours. Following this, the resulting powdery mixture was allowed to cool to room temperature and subsequently heated to 50 °C for 20 minutes with the addition of 85% sulfuric acid. Boiling water was then introduced to the dissolved product and mixed thoroughly, facilitating the solubilization of unreacted starting materials and intermediate compounds. The NPKCuPc-37 pigment precipitated, settling at the bottom of the container. The resulting phthalocyanine pigment was filtered using a Buchner funnel and dried in an oven at 60 °C. The dry mass was then washed with ethyl alcohol to eliminate impurities[7]. The yield of the final product was determined to be 62.3%.

The effect of initial reactant ratio and temperature on pigment yield for high intensity pigment NPKCuPc-37 is presented in Table 1.

Table 1. Impact of initial reactant ratios and temperature on the yield of metal phthalocyanine pigment derived from inorganic mineral components.

№	FA: $(NH_2)_2CO$: $CuSO_4$:NPK	T, ⁰C	ω,%	№	FA: $(NH_2)_2CO$: $CuSO_4$:NPK	T, ⁰C	ω,%
1		220	74,1	9		220	70,1
2	1:10:0,5:1	240	66,4	10	1:10:0,5:0,5	240	68,8
3	37-sample	260	62,3	11	35- sample	260	64,2
4		280	56,2	12		280	59,1
5		220	73,1	13		220	69,1
6	1:10:0,5:2	240	70,2	14	1:10: 0,5:4	240	66,5
7	34- sample	260	67,8	15	36- sample	260	64,2
8		280	64,9	16		280	58,5

Based on the obtained results, the optimal ratio of starting materials for the synthesis of metal phthalocyanine pigment derived from inorganic substances was determined to be N:P:K at 20:20:20, corresponding to a ratio of 1:1:0.05. It was observed that at a temperature of 260 °C, the yield reached 62.3%. These conditions were identified as optimal for the synthesis of metal phthalocyanine pigments based on inorganic components [8].



	220	240	260	280
1:10:0,5:1:0,5	74,1	66,4	62,3	56,2
1:10:0,5:1:0,5	73,1	70,2	67,8	64,9
1:10:0,5:0,5:1	70,1	68,8	64,2	59,1
1:10: 0,5:4:1	69,1	66,5	64,2	58,5

Figure 1. Effect of temperature and ratio of starting products on the yield of pigments for obtaining metallic phthalocyanine pigment obtained on the basis of inorganic substances.

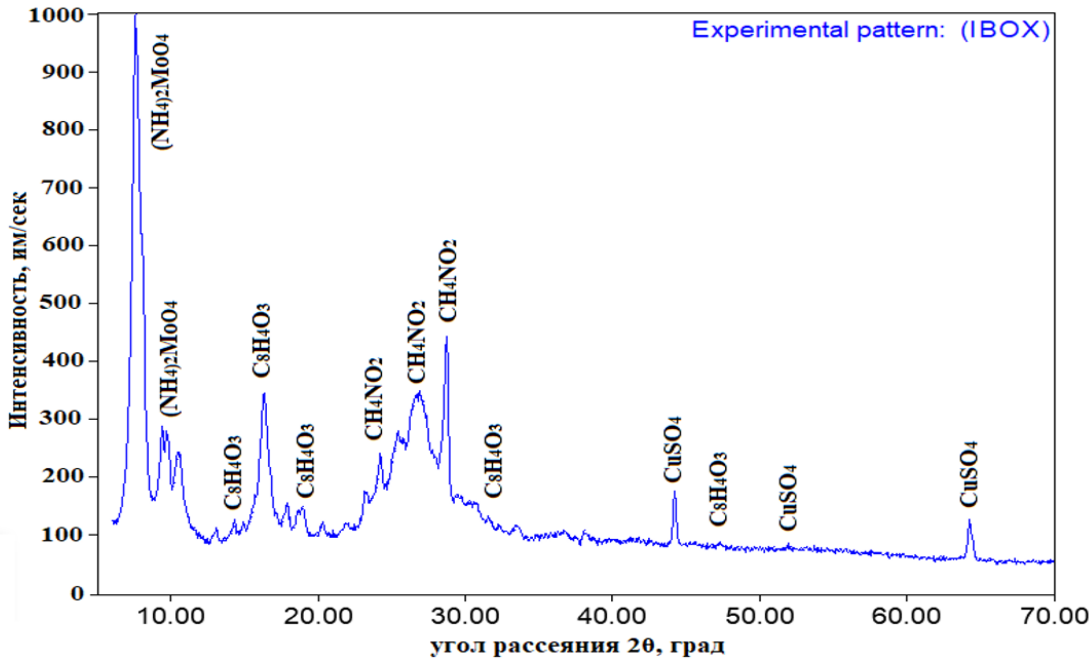


Figure 2. Diffractogram of NPKCuPc pigment.

Table 2. Diffractogram data of NPKCuPc pigment.

№	scanning angle [°2θ]	Peaks [cts]	FWHM integral width [°2θ]	d- interplanar distance [Å]	I-density of peaks
1	6,8487	6512	0,86550	12,89624	100
2	28,0069	2084	0,67330	3,18332	32
3	15,5583	1861	0,80910	5,69096	29
4	26,1989	1829	2,11760	3,39875	28
5	8,7610	1400	1,08380	10,08514	21
6	24,8513	1240	1,46260	3,57992	19
7	9,6524	1101	0,88980	9,15569	17
8	23,5539	820	0,97240	3,77409	13

To investigate the morphology and fractal dimensions of NPK CuSPc pigment particles synthesized from highly intensive inorganic materials, X-ray phase analysis was conducted. The coherent scattering field (CFT) dimensions, which represent the nanocrystal dimensions, were calculated using the Debye-Scherrer equation[9]. The particle size of the NPKCuPc pigment was determined based on the values obtained from this formula, emphasizing its dependence on the highly intensive inorganic components utilized in the synthesis. Example:

$$d = \frac{K\lambda}{\beta \cos\theta}$$ d=0,94•1.54178 / 0,86550 •0,2=8,372

Based on the above formula, the remaining values are also calculated.

Table 3. Particle size calculation of NPKCuSPc pigment according to the Debye-Scherrer equation.

№	scanning angle [°2θ]]	FWHM integral width [°2θ]	*d* (nm)- average size of crystals	*d* (nm) average
1	6,8487	0,86550	8,372	7,344
2	28,0069	0,67330	10,762	
3	15,5583	0,80910	8,956	
4	26,1989	2,11760	3,422	
5	8,7610	1,08380	6,686	
6	24,8513	1,46260	4,955	
7	9,6524	0,88980	8,143	
8	23,5539	0,97240	7,452	

The analysis demonstrated that the synthesized NPKCuPc pigments, characterized by high-intensity metal phthalocyanine containing nitrogen and inorganic substances, exhibited a nanoparticle size of 7.344 nm as determined by X-ray phase analysis [10].

Conclusions. This study investigated the synthesis of NPKCuPc high-intensity pigment through an extraction method in a heated environment. The mass ratio of the initial components influencing pigment yield was examined, revealing that the optimal ratio during the synthesis process was 1:10:0.5:1, resulting in a yield of 62.3%. The presence of both organic and inorganic compounds within the pigment was confirmed using modern physicochemical analysis techniques. This research contributes to a broader understanding of metal phthalocyanine pigments and their potential applications.

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