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THERMAL ANALYSIS STUDY OF PHTHALOCYANINE PIGMENT CONTAINING NICKEL, NITROGEN, POTASSIUM, AND PHOSPHORUS

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Abstract. In this study, the thermal properties of the Ni.N.P.K.Pc pigment, which contains nickel (Ni), nitrogen (N), phosphorus (P), and potassium (K), were investigated. The pigment sample was analyzed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA results revealed that the thermal decomposition of the pigment occurs step by step, with a total weight loss of 33.087 %, while the remaining 66.913% represents a stable inorganic residue. The decomposition stages indicate the thermal stability of the organic and inorganic components present in the pigment. These findings confirm the high thermal stability of the pigment and its potential applicability in both environmental and industrial contexts.

Keywords: phthalocyanine, o-cyanobenzamide, photo cells, silicon, npk fertilizer, nickel(ii) chloride, phthalic anhydride.

Annotatsiya. Ushbu tadqiqotda nikel (Ni), azot (N), fosfor (P) va kaliy (K) elementlarini o‘z ichiga olgan Ni.N.P.K.Pc pigmentining termik xossalari o‘rganildi. Pigment namunasi termogravimetrik tahlil (TGA) va differensial skanerlovchi kalorimetriya (DSC) usullari yordamida tahlil qilindi. TGA natijalari pigmentning bosqichma-bosqich termik parchalanishini ko‘rsatdi, umumiy massa yo‘qotilishi 33,087 % ni tashkil etdi, qolgan 66,913 % esa barqaror noorganik qoldiq sifatida qayd etildi. Parchalanish bosqichlari pigment tarkibidagi organik va noorganik komponentlarning termik barqarorligini ifodalaydi. Olingan natijalar pigmentning yuqori termik barqarorligini va uni ekologik hamda sanoat sohalarida qo‘llash imkoniyatlarini tasdiqlaydi.

Kalit so‘zlar: ftalosiyanin, o-siyanobenzamid, fotoelementlar, kremniy, NPK o‘g‘it, nikel(II) xlorid, ftal angidrid.

Аннотация. В данном исследовании изучены термические свойства пигмента Ni.N.P.K.Pc, содержащего никель (Ni), азот (N), фосфор (P) и калий (K). Образец пигмента был проанализирован с использованием термогравиметрического анализа (TGA) и дифференциальной сканирующей

калориметрии (DSC). Результаты TGA показали, что термическое разложение пигмента происходит поэтапно, при этом общая потеря массы составляет 33,087 %, а оставшиеся 66,913 % представляют собой стабильный неорганический остаток. Этапы разложения отражают термическую стабильность органических и неорганических компонентов, входящих в состав пигмента. Полученные результаты подтверждают высокую термическую стабильность пигмента и его потенциальное применение в экологических и промышленных областях.

Ключевые слова: фталоцианин, о-цианобензамид, фотоэлементы, кремний, удобрение NPK, хлорид никеля(II), фталевый ангидрид.

Introduction

The discovery of a family of compounds known as phthalocyanines dates back over 110 years. The first member, metal-free phthalocyanine (H2Pc), was discovered in 1907 by Braun and Tcherniac while they were working at the South Metropolitan Gas Company in London. They identified it as an insoluble, dark-colored impurity during the synthesis of o-cyanobenzamide from phthalimide and acetic acid[1]. Although they were the first to recognize a phthalocyanine, detailed research on these compounds did not begin until about 20 years later.In 1928, a phthalocyanine was observed for the third time by Dandridge, Dunsworth, and their colleagues while working for Scottish Dyes Ltd in Cronshaw, Scotland. They noticed a green-blue impurity during the synthesis of phthalimide from phthalic anhydride and ammonia in a glass-lined steel vessel that had a crack in its lining. Further investigation revealed that this impurity contained iron and waslater identified as FePc.Following the discovery of copper phthalocyanine (CuPc), it quickly became a popular commercial pigment. Since then, H2Pc and its various derivatives have been utilized as dyes, pigments, and inks.[2] In 2012, between 70,000 and 80,000 tons of phthalocyanines were produced globally. Of this amount, 40% was used for printing, 30% for coloring paints, 20% for coloring plastics, and the remaining 10% for other applications. The manufacture of phthalocyanines represented a billion-dollar industry worldwide in 2012.Recently, phthalocyanines have also been used as absorbers in photo cells.

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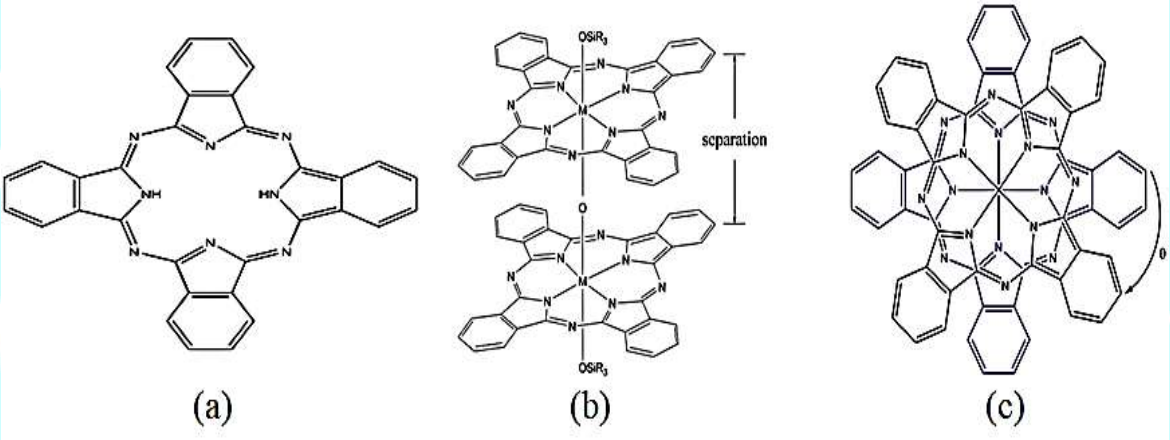


Figure 1. (a) Phthalocyanine macrocycle, H2Pc. Phthalocyanine dimer (b) ring-ring separation and (c) torsion angle.

Another notable development is the use of a specific phthalocyanine compound, $HO[SiPcO]SiMe_2(CH_2)_3NMe_2$ (Pc_4), as a sensitizer in photodynamic therapy. Silicon phthalocyanines [3] possess several properties that make them suitable for research. Like H2Pc, they are generally stable against oxidation, hydrolysis, photolysis, and thermolysis. Additionally, as group IV metal phthalocyanines, silicon phthalocyanines can accommodate two trans axial [4] ligands. These axial ligands can be utilized to modify the solubility of silicon phthalocyanines. The phthalocyanine macrocycle is notable for its ease of modification and its remarkable stability in the face of oxidation, hydrolysis, photolysis, and thermolysis. It has the capacity to chelate approximately two-thirds of the elements in the periodic table, which highlights its versatility. While copper phthalocyanine (CuPc) has received the most extensive research attention, it is worth acknowledging that other metal phthalocyanines [5] are also gaining significant interest in the scientific community.

Materials and Methods

In our quest to create the organic metal phthalocyanine pigment, we precisely mixed 27 g of nickel(II) chloride, 69 g of NPK fertilizer, 30 g of phthalic anhydride, 180 g of urea, and an appropriate catalyst in a 550 ml beaker designed to withstand high temperatures. The mixture was gently stirred at a lower temperature until it completely dissolved. We then initiated the reaction at temperatures between 180 and 190 °C to achieve a consistent and uniform blend. This careful procedure resulted in a heavy blue pigment. After the reaction, the mixture was allowed to cool to room temperature before being placed in a vacuum oven [6], where it was heated for 130 minutes to ensure optimal results. Once removed from the oven, the pigment was further cooled and treated with sulfuric acid to remove any unreacted substances. Concentrated sulfuric acid was slowly added along the beaker's walls, and once a uniform substance was formed, boiling water was introduced. This method successfully made the pigment medium acidic, which we then neutralized

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by washing with distilled water. After filtration, the pigment was dried in an oven at a controlled temperature of 50-60 °C. The newly synthesized pigment is notable for its excellent heat resistance, outstanding durability against sunlight, and vibrant coloring capabilities, significantly enhancing its potential applications. Additionally, we are pleased to report that the pigment yield after the reaction was an impressive 85%.

Results and Discussion

The Ni.N.P.K.Pc pigment experiences a systematic thermal decomposition process. At lower temperatures (30–250°C), the pigment releases moisture and volatile compounds. Upon reaching moderate temperatures (250–500°C), organic molecules undergo decomposition. At elevated temperatures (above 500°C), significant thermal degradation of the primary phthalocyanine structure is observed. The substantial residual mass remaining after this process indicates a notable richness in inorganic components within the pigment. A graphical representation of the thermal stability and decomposition stages of the Ni.N.P.K.Pc pigment is provided in Figure 2.

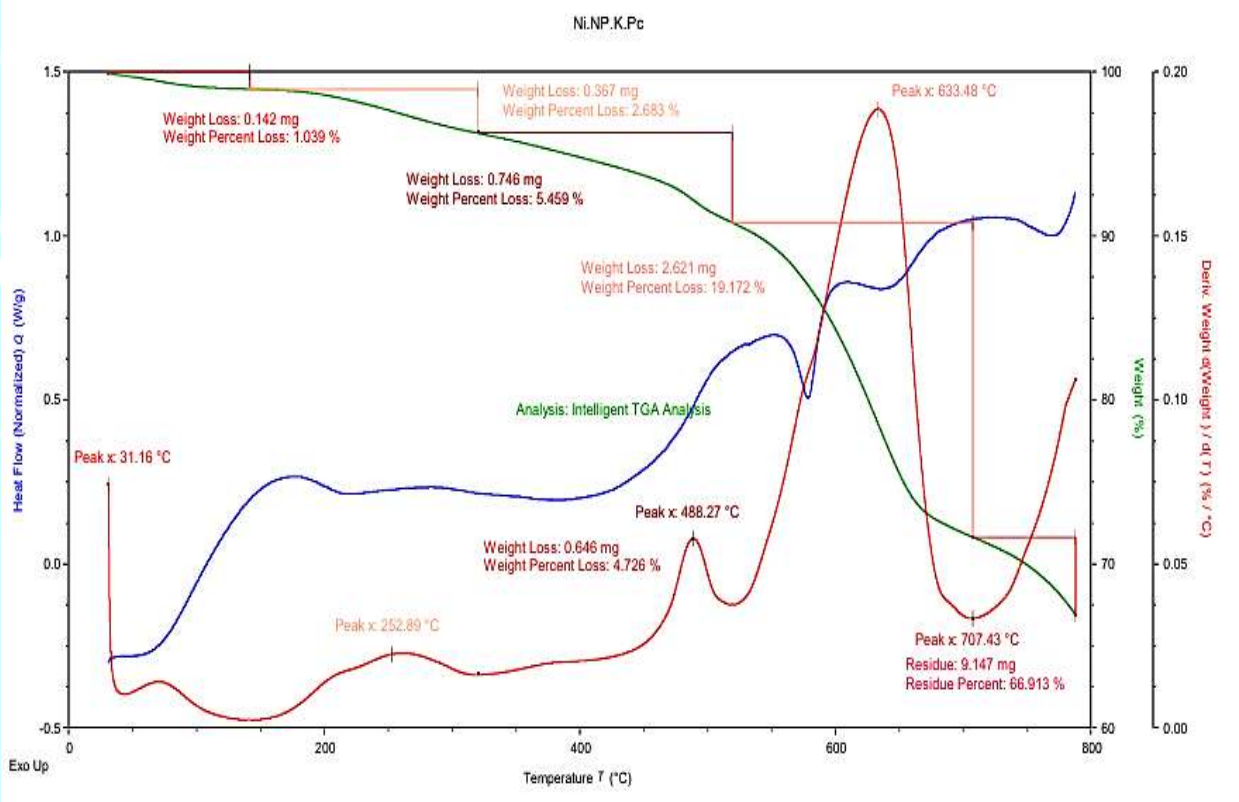


Figure 2. Derivatogram of the Nickel Phthalocyanine pigment

The thermal properties of the Ni.N.P.K.Pc pigment were evaluated using Thermogravimetric Analysis (TGA). Based on the obtained data, the pigment's stability with increasing temperature and its decomposition stages were determined, and each stage was correlated with specific physicochemical processes (see Table 1). According to the analysis results, the pigment lost 1.039% of its weight at 31.16 °C, which is associated with the release of adsorbed water or other

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low-temperature volatile components in the sample.In the next stage, at 252.89 °C, a weight loss of 2.683% was observed, corresponding to the evaporation of low-molecular-weight organic compounds or partial decomposition products. When the temperature reached 488.27 °C, a weight loss of 5.459% was recorded, indicating the thermal degradation of the main organic skeleton of the pigment (i.e., the phthalocyanine ring).The largest weight loss occurred at 633.48 °C, amounting to 19.172%, which corresponds to the structural breakdown of the pigment and large-scale thermal decomposition. In the final stage, at 707.43 °C, a weight loss of 4.726% was observed, attributed to the decomposition of more stable remaining organic residues.

Table-1

Thermal Decomposition Stages of Ni.NP.K.Pc Pigment

Stage	Temperature (°C)	Weight Loss (mg)	Loss (%)	Probable Process
Stage 1	31.16	0.142	1.039	Release of moisture or adsorbed water
Stage 2	252.89	0.367	2.683	Release of low molecular weight volatile compounds
Stage 3	488.27	0.746	5.459	Initial decomposition of organic skeleton
0Stage 4	633.48	2.621	19.172	Decomposition of main phthalocyanine structure
Stage 5	707.43	0.646	4.726	Final decomposition of remaining organic residues
Total Loss	–	4.522	33.087	–
Residue	–	9.147	66.913	Presence of inorganic components (Ni, N,P, K)

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At the end of the analysis, the total weight loss was 33.087%. The residual mass accounted for 66.913%, indicating the presence of a high amount of inorganic components in the pigment (such as nickel (Ni), nitrogen-containing compounds (N), phosphorus (P), and potassium (K)). This confirms that the pigment exhibits high thermal stability and is suitable for reuse or application in high-temperature technological processes.

Conclusion

The thermal analysis of the newly synthesized organic Ni.N.P.K.Pc pigment was carried out. The results showed that the nickel-containing organic pigment possesses heat resistance and the ability to retain its physicochemical properties even at high temperatures. The analysis was conducted in the temperature range of 31.16 °C to 707.43 °C. It is noteworthy that at 633 °C, the highest weight loss of 19.172% was recorded, corresponding to the decomposition of the main phthalocyanine structure. The high residual mass indicates that the pigment is rich in inorganic components. It was also observed that the pigment retains its structural integrity well at ordinary room temperature.

REFERENCES

1. Barret, P. A.; Dent, C. E.; Linstead, R. P. Phthalocyanines. Part VII. Phthalocyanine as a Co-ordinating Group, A General Investigation of the Metallic Derivatives. J. Chem. Soc., 1936, 1719.
2. Chai, J.-D. Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. Phys. Chem. Chem. Phys. 2008, 10, 6615 6620.
3. Cheng, G.; Peng, X.; Hao, G.; Kennedy, V. O.; Ivanov, I. N.; Knappenberger, K.; Hill, T. J.; Rodgers, M. A. J.; Kenney, M. E. Synthesis, Photochemistry, and Electrochemistry of a Series of Phthalocyanines with Graded Steric Hindrance. J. Phys. Chem. A., 2003, 107, 3503-3514.
4. Chui, S-M.; Xue, L-Y.; Lam, M.; Rodrigues, M. E.; Zhang, P.; Kenney, M. E.; Nieminen, A-L; Oleinick, N. L. A Requirement for Bid for Induction of Apoptosis by Photodynamic Therapy with a Lysosome- but Not a Mitochondrion-Targeted Photosensitizer. J. Photochem. Photobiol., 2010, 86, 1161-1173.
5. Adamo, C.; Barone, V. Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The mPW and mPW1PW models. J. Chem. Phys. 1998, 108, 664-675.
6. Odiljon, K., Muzafar, Y., & Doniyor, Sh. (2024). synthesis and infrared spectroscopy (ir) studies of phthalocyanine pigment containing copper, calcium, nitrogen and npk. universum: технические науки, 10(12 (129)), 9-12.

ISSN 3030-3907

7. Kayumjanov, O., & Yusupov, M. (2025, July). Obtaining a pigment of metal phthalocyanine in a solvent environment and studying its properties. In American Institute of Physics Conference Series (Vol. 3304, No. 1, p. 040026).
8. Odiljon, K., & Muzafar, Y. (2025). THERMAL ANALYSIS STUDY OF COPPER AND CALCIUM-CONTAINING PHTHALOCYANINE PIGMENT. Universum: химия и биология, 3(8 (134)), 16-19.

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