ISSN 2181-8622

Manufacturing technology problems

Scientific and Technical Journal Namangan Institute of Engineering and Technology

INDEX COPERNICUS INTERNATIONAL

Google Scholar Crossref doi SLIB.UZ Scientific library of Uzbekistan

Volume 10
Issue 4
2025

NamMTI ILMIY-TEXNIKA JURNALI TAHRIR HAY'ATI A'ZOLARI

EDITORIAL BOARD OF SCIENTIFIC AND TECHNICAL JOURNAL OF NAMANGAN INSTITUTE OF ENGINEERING AND TECHNOLOGY

THERMAL ANALYSIS OF CARBOXYL-MODIFIED COBALT AND CALCIUM METAL PHTHALOCYANINE PIGMENTS

NURITDINOV ABDULLAZIZBEK
PhD student, Namangan State Technical University, Namangan, Uzbekistan
Phone.: (0899) 320-5325, E-mail.: nuriddinov9699@gmail.com

Abstract: In this study, the thermal behavior of the carboxyl-functionalized phthalocyanine pigment containing cobalt/calcium metal centers was investigated using TG/DTA techniques in the temperature range of 25–700 °C. The thermogravimetric (TG) curve revealed a two-stage decomposition pattern. The first mass-loss event, occurring between 18.47 and 326.94 °C, accounted for 1.828 mg (52.909%) and corresponds to the removal of physically adsorbed moisture, residual solvents, and the initial decarboxylation of the modified phthalocyanine framework. The second stage, observed within 326.94–701.09 °C, resulted in an additional mass loss of 0.929 mg (26.889%) and is attributed to the progressive breakdown of the macrocyclic aromatic structure.

The DTA thermogram exhibited a pronounced endothermic peak at 217.25 °C, associated with carboxyl group detachment and structural rearrangements, followed by a strong exothermic peak at 613.58 °C, indicating deep oxidative degradation of the phthalocyanine macrocycle. These results collectively confirm that the pigment undergoes primary decomposition related to its carboxyl functionalities, followed by extensive aromatic degradation at higher temperatures.

Overall, the obtained TG/DTA profiles demonstrate that the modified metal phthalocyanine pigment possesses high thermal stability, maintaining significant structural integrity even above 600 °C, which is a favorable characteristic for applications requiring enhanced heat resistance.

Keywords: phthalocyanine, cobalt phthalocyanine, calcium phthalocyanine, thermal analysis, TG/DTA, carboxyl modification.

Introduction. Metal phthalocyanines (MPcs) constitute a structurally robust class of macrocyclic compounds that have attracted significant scientific and industrial interest due to their exceptional physicochemical stability, rich π-conjugation, and intense chromophoric properties. Structurally, MPcs possess a tetrabenzoporphyrazine framework, forming an expanded 18-π aromatic macrocycle capable of strong coordination with various transition-metal cations[1-3]. These structural features impart remarkable chemical inertness, high photostability, resistance to UV-induced degradation, and thermal endurance, making MPcs indispensable in modern pigment technology, organic optoelectronics, and surface-coating industries[4].

From a practical standpoint, MPcs are widely utilized as blue-green pigments in polymeric coatings, alkyd and acrylic enamels, polyurethane-based composites, flexographic and offset printing inks, and in advanced materials including photovoltaic cells, chemosensors, field-effect transistors, and catalytic systems. Their commercial success stems from high color strength, low solubility in binders, superior fastness to light, heat and chemicals, and the ability to retain optical properties under harsh operating conditions[5].

Among the various metal-centered phthalocyanines, cobalt (CoPc) and calcium (CaPc) derivatives exhibit distinctive electronic and structural features. Co-centered phthalocyanines demonstrate unique redox activity, narrow bandgap energies, and thermally stable coordination shells, which are advantageous for high-temperature coatings, electrocatalytic systems, and gas-sensing devices. Calcium phthalocyanines, though less explored, possess a semi-ionic coordination environment, rendering them more polar and better dispersible in polymer matrices. The combination of transition-

metal coordination and macrocyclic aromaticity results in superior thermal resistance, often exceeding 500–600 °C before structural degradation initiates[6].

However, contemporary research emphasizes that the functional performance of MPc-based pigments is not governed solely by the central metal ion but is strongly influenced by peripheral substituents attached to the macrocycle. In recent years, the incorporation of carboxyl groups (–COOH), sulfonyl groups (–SO_3H), amine functionalities, and halogenated fragments has been an important modification strategy to tune solubility, dispersion stability, metal–ligand interactions, and compatibility with polymeric binders. Carboxyl-modified MPcs, in particular, exhibit enhanced adhesion to substrates, improved colloidal stability in aqueous and polymer systems, and increased interactions through hydrogen bonding or covalent linkage with alkyd and acrylic binders. These characteristics result in improved film uniformity, reduced pigment aggregation, and enhanced mechanical and weather-resistance properties of coatings[7].

Recent literature reports indicate a rising interest in the synthesis of new carboxyl-substituted phthalocyanine complexes involving Cu^{2+}, Co^{2+}, Ca^{2+}, Zn^{2+}, and mixed-metal systems. These newly developed pigments have been evaluated for photoactive dye applications, catalytic oxidation reactions, anticorrosion protective films, and as reinforcing fillers in polymer nanocomposites. Despite the growing research in Cu- and Zn-based carboxylated MPcs, studies focusing on cobalt–calcium systems remain scarce. Very limited information is available regarding their combined electronic structure, coordination stability, or thermochemical behavior under elevated temperatures[8].

Understanding the thermal behavior of MPc pigments is scientifically and technologically crucial. Organic coatings, printing inks, polymer composites, and protective films often undergo high-temperature exposure during curing, processing, or long-term operation. Parameters such as decomposition onset temperature, mass-loss stages, endothermic–exothermic transitions, and thermal stability thresholds directly influence the service life, optical stability, and chemical resistance of these coating systems[9]. Thermogravimetric analysis (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) are therefore widely applied to characterize decomposition pathways and evaluate the suitability of MPc pigments for high-temperature industrial applications.

Research Object and Subject.

The object of the present study is a phthalocyanine pigment modified with carboxyl groups and containing cobalt and calcium metal ions in its central cavity. The pigment was synthesized from carboxyl-substituted phthalonitrile derivatives using Co^{2+} and Ca^{2+} salts, urea, and several auxiliary components involved in the cyclotetramerization process. Upon completion of synthesis, the pigment was subjected to multistage purification steps, including repeated washing, neutralization, filtration, and controlled drying. The final product was ground and classified to obtain a particle fraction in the range of 40–60 μm.

Structurally, the pigment represents a cobalt/calcium phthalocyanine macrocycle functionalized with carboxyl groups along its periphery. This targeted modification plays a decisive role in influencing its thermal behavior and stability characteristics.

Thermal Analysis Instrumentation and Measurement Conditions.

Thermal analysis was performed using a synchronous thermoanalytical system operating in combined TG + DTA mode. The experimental parameters were selected as follows: temperature range of 25–700 °C, heating rate of 10 °C/min, and an inert nitrogen (N_2) atmosphere with a flow rate of 50 mL/min. The sample mass was approximately 3.45 mg, determined from the initial mass recorded on the TG curve. An alumina (Al_2O_3) crucible, chosen for its thermal inertness, was used throughout the measurements.

The resulting thermograms (TG and DTA curves) were recorded and processed using dedicated instrument software. The software enabled the determination of the onset (Start) and end (End) temperatures for each decomposition stage, the corresponding mass-loss values (mg and %), as well as DTA peak temperatures and the associated heat effects (mJ, J/g).

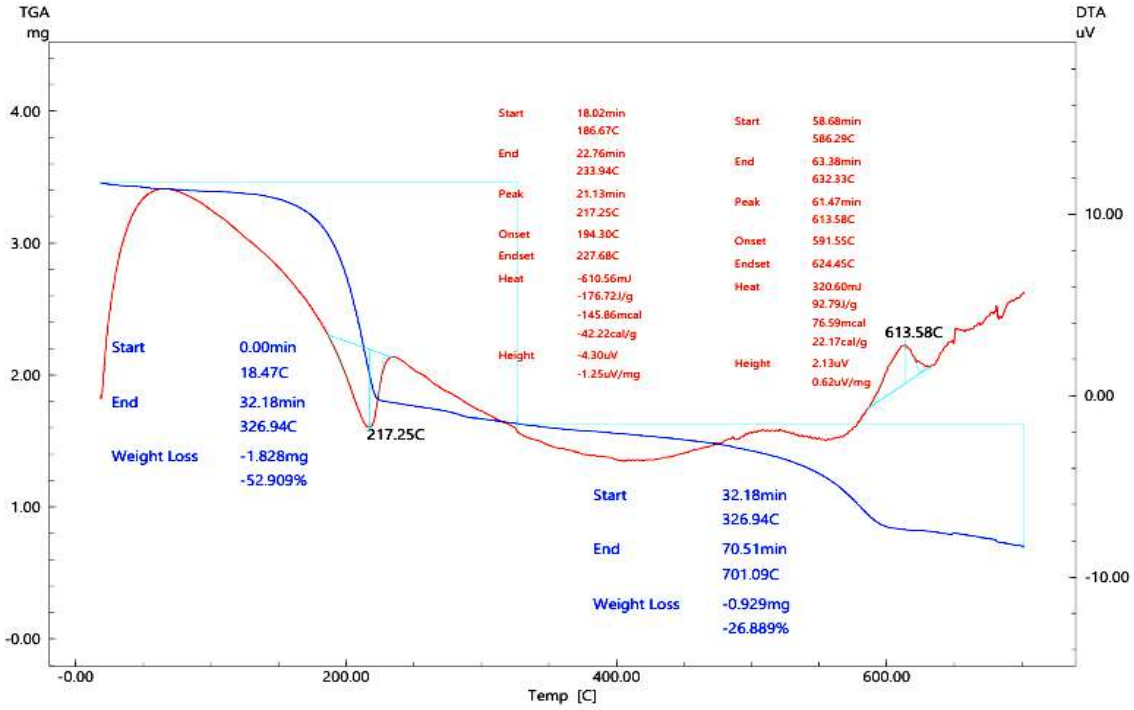

Figure 1. Thermogravimetric analysis of the metal phthalocyanine pigment modified with carboxyl groups

Thermogravimetric Analysis Results

The TG curve of the pigment demonstrates that its thermal degradation proceeds in two major stages (Figure 1). The mass-loss parameters obtained from the thermogram are summarized in Table 1.

Stage I – Mass loss within 18.47–326.94 °C

The first significant mass-loss event begins at 18.47 °C and continues up to 326.94 °C. In this stage:

Mass loss: 1.828 mg

Relative mass loss: 52.909%

During the initial heating period (30–120 °C), a gradual decrease in mass is observed. This behavior corresponds to the release of physically adsorbed moisture, residual solvents, and low-molecular-weight volatile organic components. Such processes are typically endothermic and appear as a smooth, shallow endothermic signal on the DTA curve.

As the temperature increases, the rate of mass loss rises significantly within 180–260 °C. In this region, a pronounced endothermic peak is recorded on the DTA curve with the following characteristics:

Peak temperature: 217.25 °C

Onset: 194.30 °C

Endset: 227.68 °C

This endothermic effect is associated with the decarboxylation of –COOH groups, i.e., the release of CO_2, as well as the cleavage of peripheral substituent chains. The endothermic nature indicates the energy-absorbing rupture of chemical bonds.

Between 220 and 320 °C, the mass loss continues, though the TG curve becomes relatively flatter. During this period, along with the carboxyl groups, remaining light substituents bound to the phthalocyanine ring decompose progressively. When the temperature reaches 326.94 °C, the first stage ends, and nearly half of the total sample mass has been lost.

Thus, the first decomposition stage primarily corresponds to the degradation of peripheral fragments, indicating that the phthalocyanine macrocycle itself remains largely intact up to this point. Therefore, the 18.47–326.94 °C interval can be considered a "pre-degradation zone."

Stage II – Mass loss within 326.94–701.09 °C

The second major mass-loss event starts at 326.94 °C and continues up to 701.09 °C. In this stage:

Mass loss: 0.929 mg

Relative mass loss: 26.889%

Mass loss in this interval occurs more slowly but steadily. After approximately 500 °C, the TG curve begins to decline more sharply, indicating the onset of deep degradation of the macrocycle.

This stage mainly corresponds to the decomposition of the aromatic phthalocyanine skeleton. It involves sequential cleavage of C–N and C–C bonds within the π-conjugated structure, fragmentation of the macrocyclic rings, and the formation of volatile organic products such as CO, CO_2, and NO_x.

At around 700 °C, the total mass loss reaches approximately 79.8%. The remaining fraction (~20.2%) is most likely composed of metal oxides (CoO/Co_3O_4, CaO) and carbonaceous residue. In an inert nitrogen atmosphere, the carbon residue is typically

larger, while in an oxidizing atmosphere the proportion of metal oxides is expected to be higher.

Summary of Thermogravimetric Data

Table 1. Mass-loss stages of the carboxyl-modified Co/Ca phthalocyanine pigment according to TG analysis

Stage	Temperature range (°C)	Δm (mg)	Mass loss (%)	Probable process description
I	18.47–326.94	1.828	52.909	Release of water and volatiles, decarboxylation of –COOH groups, degradation of peripheral fragments
II	326.94–701.09	0.929	26.889	Aromatic degradation of the phthalocyanine macrocycle, breakdown of carbon skeleton and organic residues
Total	18.47–701.09	2.757	79.798	Overall decomposition of the pigment, formation of metal oxides and carbonaceous residue

The table shows that the majority of mass loss (approximately 53%) occurs during the first stage. This indicates that peripheral organic fragments introduced through carboxyl modification represent a significant portion of the pigment structure. However, the core phthalocyanine macrocycle remains largely stable up to temperatures above 350 °C.

Practical Significance of the Thermal Behavior

The practical implications of these results are summarized as follows:

Operating temperature for paints and enamels.

Since the pigment undergoes almost no degradation below 300 °C, it provides sufficient thermal stability for coating materials. Most industrial paints and enamels are not exposed to temperatures above 150–200 °C during production or service, confirming the pigment's suitability.

Effectiveness for PF-115 and similar alkyd enamels.

Carboxyl modification enhances pigment–binder interactions and improves pigment dispersion in alkyd matrices. Thermal analysis confirms that the pigment remains stable under drying-oven and operational temperatures.

Applicability in water-based and eco-friendly coatings.

–COOH groups significantly improve pigment dispersibility in aqueous media. High thermal stability ensures durable heat-resistant films, making the pigment promising for waterborne coatings.

Use in polymer composites and organic electronics.

Thermal stability up to 300–350 °C is compatible with processing temperatures of polypropylene, PET, epoxy resins, and other polymers. Therefore, the pigment can serve as a colorant in thermally loaded composite systems.

Fire performance and residual mass.

At 700 °C, around 20% residue remains, comprised of metal oxides and carbonaceous material. This residual layer may impart partial fire-resistance and ceramic-like properties to coating films.

Conclusion

The thermal behavior of the carboxyl-modified phthalocyanine pigment containing cobalt and calcium metals, studied using TG/DTA techniques, can be summarized as follows:

The pigment decomposes in two major stages: 18.47–326.94 °C (52.9% mass loss) and 326.94–701.09 °C (26.9% mass loss), with a total mass loss of approximately 79.8%.

The endothermic peak at 217.25 °C corresponds to decarboxylation of –COOH groups and degradation of peripheral organic fragments, representing a characteristic feature of carboxyl modification.

The strong exothermic peak at 613.58 °C indicates deep oxidative degradation of the aromatic phthalocyanine macrocycle.

The core structure of the pigment remains stable above 350 °C, making it a promising candidate for heat-resistant paints, enamels, polymer composites, and organic electronic materials.

The obtained thermal analysis data provide a fundamental basis for future studies involving aging resistance, migration testing, and photostability of coating systems containing this pigment.

References

1. Yusupov, M., Beknazarov, H., Abdulhafiz, T., & Elyor, S. (2019). Scientific and Technical Journal of Namangan Institute of Engineering and Technology, 1(7), pp. 55-62.

2. Robiddinova, M. S., Davronova M, Yusupov, M. O., & Sherkuziev, D. S. Scientific Bullettin of NamSU 2022 pp. 166-170

3. Yusupov M.O., Beknazarov Kh.S., Tillaev A., Dzhalilov A.T. International Journal of Advanced Science and Technology Vol. 29, No.03, (2020), pp.2244-2254

4. Cranston R.R., Robertson N., *Metal phthalocyanines: thin-film formation, microstructure, and applications.* **Beilstein J. Nanotechnol.** 2021;12:300–334.PMC

5. Achar B.N., Fohlen G.M. *Degradation study on the thermally stable nickel phthalocyanine pigments.* **Dyes Pigments.** 2003;56(1):1–10.ScienceDirect

6. Şahin S., et al. *Synthesis, spectroscopic properties and thermal properties of substituted phthalocyanines.* **J. Mol. Struct.** 2019;1186:96–105.ScienceDirect

7. Yusupov M.O., et al. *Physical Chemical Properties of Nitrogen and Phosphore Containing Phthalocyanine Pigments.* **NVEO Journal.** 2021; (4): 3011–3019.nveo.org

8. Odiljon K., et al. *Thermal analysis study of copper and calcium-containing phthalocyanine pigment.* **Organic Chemistry Journal.** 2025;8(134):1КиберЛенинка+1

9. Kulyk N.Yu., et al. *Thermal oxidative destruction of cobalt(II) phthalocyanines containing oxygen substituents.* **J. Therm. Anal. Calorim.** 2005;81(2):451–458.akjournals.com

CONTENTS

TECHNICAL SCIENCES: COTTON, TEXTILE AND LIGHT INDUSTRY

TECHNICAL SCIENCES: AGRICULTURE AND FOOD TECHNOLOGIES

CHEMICAL SCIENCES

TECHNICAL SCIENCES: MECHANICS AND MECHANICAL ENGINEERING