

Original Article

Study of Synthesis and Pigment Characteristics of the Composition of Copper Phthalocyanine with Terephthalic Acid

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Abstract - Dyes are currently one of the most valuable synthetic chemical compounds. Such compounds must have a stable colour and resist external influences. Among them, phthalocyanines are stored in different groups and metals and have a special place. The paper presents the synthesis of a direct compound of copper phthalocyanine with terephthalic acid added during industrial extraction. The optimal time of the compound synthesis process has been determined to be 2 hours and the temperature to be 185 °C. The composition of the compound has been confirmed by element analysis and IR-spectroscopy methods. Based on SEM images, the compound was found to be homogeneous. The obtained compound has been tested for compliance with standard pigment requirements. Enamel containing 11% of the appropriate pigment corresponds to blue industrial enamel, and its properties such as gloss, viscosity, drying time, elasticity, adhesion, resistance to water and temperature have been studied. Thermal analysis of the pigment shows that the main decomposition process is between 300 °C and 339 °C, and the maximum decomposition reaches up to 70%. Thermal analysis of the prepared enamel revealed that the basic decomposition exceeds 300 °C and the loss at 400 °C is around 44%. The resulting pigment can be used as an effective dye for painting various surfaces and colouring plastics.

Keywords - Pigment, Dye, Terephthalic acid, Copper, IR spectroscopy, Thermal analysis.

1. Introduction

A phthalocyanine is an aromatic group containing 18 delocalized electrons, characterized by the formation of intensely coloured compounds. In particular, its metal complexes are widely used as pigments. The thermal stability of these compounds is also high [1]. Phthalocyanine groups have also been shown to be colourless compounds in the monomolecular state, absorbing light in the blue range because they are present in the form of complexes, dimers, and supramolecular compounds [2]

Among these compounds, copper phthalocyanine has a special place, and its properties are widely studied. Widely used in industry. It can even be used as a dye for inert polymers such as polyethylene and polypropylene. Its colour intensity has also been studied optically and spectroscopically [3].

Compounds stored in the phthalocyanine group of copper are synthesized in several ways. Phthalocyanines are poorly soluble in water, but water-soluble phthalocyanine can be synthesized by adding different groups. For example, using 3-diethyloaminophenol during synthesis has improved

the solubility of cationic phthalocyanine complexes retained in the amino group in water [4]. Different derivatives of phthalanitriles synthesize phthalocyanine pigments with different compositions. 4 - [(4'-carboxy) phenylamino] phthalonitrile [5], 4- (2-naphthoxy) -5- (morpholine-4-year) phthalonitrile, 4-tert-butyl-phthalonitrile [6], 4-nitrophthalonitril [7], the properties of various copper phthalocyanines obtained using 4-hydroxyphthalodinitrile [8], 4- (2-carboxyphenyltiol) phthalanitrile [9] were also studied.

Scientists have found that combining copper phthalocyanine with NN'-dimethylperylene-3,4,9,10-dicarboximide can effectively cover the surface of silver electrodes and reduce the level of corrosion [10]. In addition, the X-ray photoelectron method has studied the resistance to relatively high temperatures, electrical conductivity and the ability to effectively use the coating of various electronic devices [11,12]. Modern technology includes electronics, sensors, and phthalocyanines, which replace various valuable compounds used in solar cells [13]. Copper (II), cobalt (II), nickel (II) and zinc 3,3', 3'', 3''' - tetraaminophthalocyanins are used as antibacterial agents [14].



Copper phthalocyanine is also synthesized in the xerohelial matrix of silicic acid by the sol-gel method; one of the main properties of this composite is the dimerization properties of copper phthalocyanine are lost, and the colour intensity increases with concentration [15].

It is possible to change the properties of pigments by adding various additional compounds. For example, a green G-grade pigment based on copper phthalocyanine is resistant to water and abrasion when covering fabric surfaces [16]. It is also recommended to use polymerized emulsions with the addition of up to 40% styrene compounds to increase the hydrophobic properties of pigments [17]. Red films were obtained from a nanostructured compound in the presence of trifluoric acid to copper phthalocyanine [18]. A composite compound obtained by electropolymerization of a mixture of copper tetrasulfofthalocyanine with aniline can also be used as a catalyst [19].

Scientists have proven that by extracting nanoparticles of copper phthalocyanine, it is possible to maintain the ability to dye even in very small amounts [20]. Supramolecular compounds of perylene (N, N' -bis (2-(trimethylammonium iodide) ethylene) perylene-3, 4, 9, 10-tetracarboxydimide) with zinc phthalocyanine were synthesized and used as a pigment [21]. The possibility of using phthalocyanines as catalysts in the catalytic oxidation processes of organic compounds was studied, and it was found that the catalytic activity of the copper phthalocyanine dimer is optimal in an environment with pH 11 [22].

The relative stability of phthalocyanine dyes results in the long-term storage of dyes that store various heavy metals in the natural environment. The degree of decomposition of these dyes by various representatives of the fungi has been studied now, and high efficiency has been achieved [23]. In a new direction, various catalysts are used for photocatalytic decomposition of organic matter in waste. The principle of operation of such catalysts is also based on their ability to absorb strong light and its good transmission, and the possibility of using various compounds of phthalocyanins for this purpose has been studied [24].

The process of synthesizing expensive dyes is very complex and does not fully meet environmental requirements. Therefore, methods have been developed to synthesize these compounds from various wastes stored by the phthal group [25]. During the production of pigments, heavy metals are released into the wastewater. The sorption

of metals from these effluents is of great ecological importance [26].

2. Materials and Methods

2.1. Chemicals

Terephthalic acid, copper salt, phthalic anhydride, urea, and 93% sulfuric acid.

2.2. Methods

The IR spectrum of the synthesized pigments was analyzed in a 400 and 4000 cm^{-1} field manufactured in Japan by SHIMADZU IR-Fure spectrophotometer and MIRA 2 LMU scanning electron microscope (SEM).

The thermal stability of the organic pigment formed by the interaction of copper-containing phthalocyanine with terephthalic acid was analyzed by differential-thermal and thermogravimetric methods.

3. Experimental part

3.1 Synthesis of metallic phthalocyanine pigment (TaCuPc) retained by terephthalic acid.

An additional terephthalic acid was added to the starting material for synthesizing copper phthalocyanine based on the method described in the literature [1]. Terephthalic acid, phthalic anhydride, urea, copper salt, and a catalyst were mixed in a special 500 ml high-temperature, acid-resistant container. The synthesis process was carried out by heating at high temperatures. The resulting mixture of substances is slowly heated in an oven SNOL-8,2 / 1100 to 130-135 $^{\circ}\text{C}$ until a liquid is formed. Phthalic anhydride and urea are liquefied at this temperature, while terephthalic acid is soluble in this liquefaction. Once fully liquefied, the mixture is heated in an oven at 185 $^{\circ}\text{C}$ for 1 h.

A porous substance is formed in the vessel when the reaction is complete. The obtained substance was cooled to room temperature and mixed by pouring 10 ml of 92% concentrated sulfuric acid, resulting in a dark green solution. The solution is washed several times with boiling distilled water until a neutral medium is formed. In this case, the primary products and intermediates that do not react are dissolved. The resulting TaCuPc organic pigment precipitates and is filtered in a Buchner funnel using a vacuum pump. The final product is dried in a drying oven at 60 $^{\circ}\text{C}$ until it reaches a permanent mass. The dried organic pigment is crushed in a mortar, passed through a sieve, and the finished organic pigment is weighed on a scale (Figure 1).



Fig. 1 Synthesized new organic pigment - TaCuPc samples

3.2. Preparation of alkyd enamel using organic pigment TaCuPc.

According to the composition of raw materials in Table 1, industrial alkyd enamel was prepared.

After the addition of lacquer, titanium dioxide, TaCuPc and bentogel, it was dispersed in a bead mill at room temperature for 2 hours ($d = 3-3.5 \text{ mm}$, $1500-2000 \text{ min}^{-1}$) until homogeneous, and a pigment paste was prepared, then enamel with the addition of desiccant and methyl ethyl oxide taken.

Table 1. The new organic pigment is a new alkyd enamel composition based on TaCuPc, which belongs to the blue PF-115 class

№	Name of raw materials	Composition, mas. %
1	PF-060 brand varnish (52%)	69,8
2	R-706 brand pigment - titanium dioxide	0,5
3	BG-4 brand bentogel	0,4
4	Mel (micro calcite)	21,5
5	MIX brand descriptive	0,2
6	TaCuPc brand new organic pigment	5,2
7	Methyl ethyl ketoxime	0,3
8	C-4 135/220 brand nephras	2,1

The new organic pigment TaCuPc was prepared using a small dye preparation device - a laboratory bead mill - to prepare all dyes. The requirement for paint products is that the colouring pigment mixes well and comes into a homogeneous system. As a result, the agglomerates of the pigment particles are sharply crushed to achieve the agglomerates' spread or obtain a fine suspension. In the dyeing process, the pigment and dye raw materials were mixed at high speed using a dispersed knife in a special steel container, and the solids were transferred to the same suspension medium. The organic pigment TaCuPc was completely mixed in this device for 2 hours and coated on a metal plate (Fig 3).

3.3. Comparison of PF-115 enamels with the addition of organic pigment TaCuPc following GOST 6465-76.

Table 2. Comparison of physical and mechanical properties of PF-115 enamel prepared with the addition of synthetic pigment TaCuPc according to the interstate standard GOST 6465-76

№	Name of indicators	standard of indicators	The result		
1	The colour of the enamel coating		Suitable		
	a)	Light blue 423		423	
	b)	Blue		427, 428	
2	The outside of the coating. Appearance		Suitable		
	a)	Light blue 423		Once the enamel dries, it forms a smooth, homogeneous coating without foreign particles	
	b)	Blue			
3	The gloss of the coating on the photoelectric light-emitting device is not less than%		The normal, according to GOST 896-69		
	a)	Light blue 423		50	51
	b)	Blue		50	50
4	Conditional viscosity at $20 \pm 0.5 \text{ }^\circ\text{C}$ (viscometer measured at VZ-246))		The normal, according to GOST 8420-74		
	a)	Light blue 423	80-120	105	
	b)	Blue	80-120	110	
5	Mass fraction of non-volatile substances, %		The normal, according to GOST 7537-72		
	a)	Light blue 423	60-66	61	

	b)	Blue	60-66	62
6		Dilution rate at 20 ± 0.5 °C for 28-30 s (measured on viscometer VZ-246), not more than%	The normal, according to GOST 17537-72	
	a)	Light blue 423	20	20
	b)	Blue	20	20
7		The degree of grinding, mkm, is not much	The normal, according to GOST 6589-74	
	a)	Light blue 423	25	25
	b)	Blue	25	25
8		The viscosity of the dried coating is not more than g / m ²	The normal, according to GOST 8784-75	
	a)	Light blue 423	60	60
	b)	Blue	40	40
9		Construction time at a temperature of 20 ± 2 °C, not more than an hour	The normal, according to GOST 19007-73	
	a)	Light blue 423	24	24
	b)	Blue	24	24
10		Bending elasticity of the coating, not more than mm	The normal, according to GOST 6806-73	
	a)	Light blue 423	1	1
	b)	Blue	1	1
11		The impact strength of the coating (measured on a U-1 instrument) is not less than cm	The normal, according to GOST 4765-73	
	a)	Light blue 423	40	40
	b)	Blue	40	40
12		The hardness of the coating (measured on the pendulum M-3) is not less than SB (symbol)	The normal, according to GOST 5233-89	
	a)	Light blue 423	0,25	0,25
	b)	Blue	0,25	0,25
13		Coating adhesion, not more than points	The normal, according to GOST 51140-98	
	a)	Light blue 423	1	1
	b)	Blue	1	1
14		The resistance of the coating to the static effects of water at a temperature of 20 ± 2 °C, not less than an hour	The normal, according to GOST 9,403-80	
	a)	Light blue 423	2	2
	b)	Blue	2	2
15		Resistance to static action of 0.5% solution of coating detergents, not less than min	The normal, according to GOST 9,403-80	
	a)	Light blue 423	15	15
	b)	Blue	15	15
16		The resistance of the coating to the static effects of transformer oil at a temperature of 20 ± 2 °C, not less than s	The normal, according to GOST 9,403-80	
	a)	Light blue 423	24	24
	b)	Blue	24	24

Synthesized TaCuPc brand PF-115 enamel samples prepared with the addition of new organic pigment were confirmed to meet the standard requirements of GOST 6465-76.

4. Results and Discussion

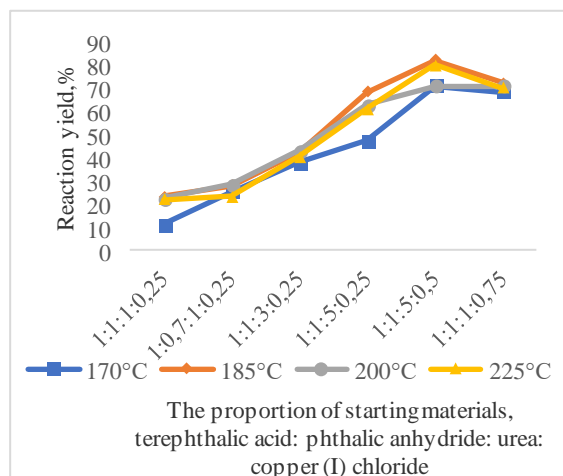
4.1. To study the dependence of temperature and starting materials ratio on product yield in the synthesis of new organic pigment TaCuPc.

Temperature plays an important role in the high-intensity, active properties of the pigment. At the same time, if the high temperature exceeds the norm, the yield of the resulting product decreases to a certain extent.

Table 3. Influence of temperature and ratio of starting materials on product yield in TaCuPc organic pigment synthesis

№	Ta:Pa: U:CuCl	T, °C	ω, %	№	Ta:Pa :U:Cu Cl	T, °C	ω, %
1	1:1:1: 0,25	170	11,5	13	1:1:5: 0,25	170	47,4
2		185	23,5	14		185	68,5
3		200	22,5	15		200	63,2
4		225	22,1	16		225	61,2
5	1:0,7:1: 0,25	170	25,4	17	1:1:5:0 ,5	170	71,2
6		185	28,3	18		185	82,5
7		200	28,4	19		200	81,3
8		225	23,6	20		225	80,2
9	1:1:3: 0,25	170	38,1	21	1:1:5: 0,75	170	68,5
10		185	42,4	22		185	72,4
11		200	43,1	23		200	71,1
12		225	40,5	24		225	70,3

The optimal conditions of the obtained TaCuPc organic pigment, the physicochemical properties of which have been studied, are mainly based on the data on the best optimal composition of the organic pigment obtained with the highest yield. Table 3 below examines the effect of temperature and starting material ratio on product yield in synthesising highly effective TaCuPc organic pigment.

**Fig. 2. Influence of starting material content and temperature on TaCuPc organic pigment reaction yield**

Many experiments have been carried out on synthesising TaCuPc organic pigment under different conditions and ratios. The resulting pigment yield was calculated as a temperature and component ratio. The optimum reaction temperature was 185–200 °C, and the organic pigment obtained in a 1:1:5:0,5 ratio was the highest yield. The graph representing the effect of temperature and mole ratios of the initially obtained substances is shown in Figure 2 below.

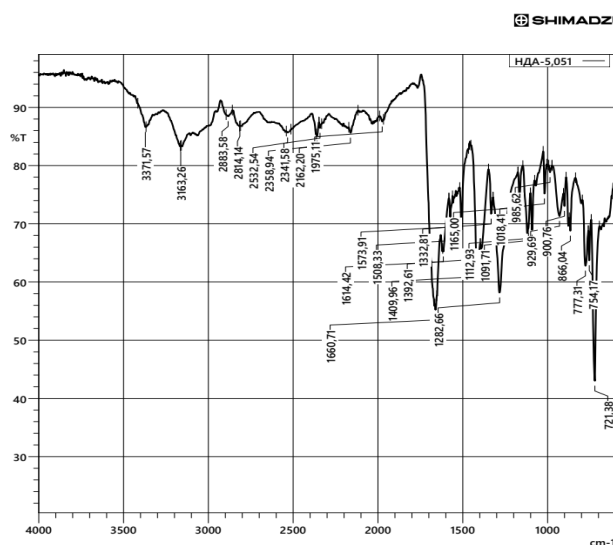
To determine the optimal conditions for the synthesis of organic pigment, the chemical process was carried out at

temperatures of 170 °C, 185 °C, 200 °C and 225 °C. As shown in Figure 2, a temperature of 185 °C was selected as the optimal temperature for active pigment synthesis, with a maximum yield of 82,5% at 1.5 hours and no significant increase after 2 hours. At 225 °C, the reaction yield is relatively low due to the partial decomposition of the products. Figure 3 shows a metal plate coated with a dye based on an organic pigment obtained at 185 °C.

**Fig 3. Images of TaCuPc-based paint coating on a metal plate**

4.2. IR spectroscopic analysis of TaCuPc organic pigment

A new organic pigment TaCuPc was synthesized in the presence of terephthalic acid, phthalic anhydride, urea, metal salt and catalyst. Its IR spectrum (IR - Fure spectrometer SHIMADZU made in Japan) is shown in Figure 4.

**Fig. 4. IR spectrum of a new organic pigment of the synthesized TaCuPc brand**

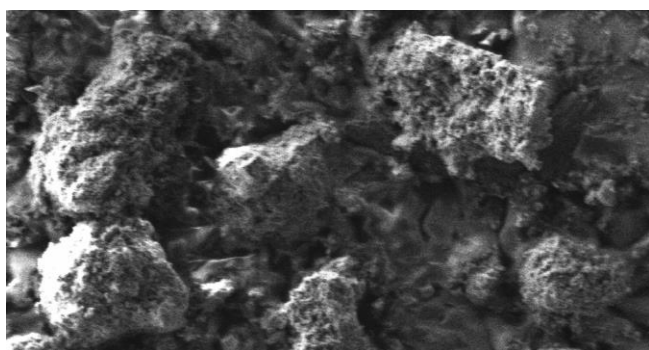
It is known from the literature that the salts of terephthalic acid contain crystalline hydrated water. Hydrogen bonds between water molecules are observed in the IR spectrum of copper terephthalate 3163.26 cm⁻¹. At 1392.61 cm⁻¹, there are absorption areas corresponding to carbon-hydrogen bonds. Formation of rings in copper terephthalate phthalocyanine is seen in the absorption region of 754 cm⁻¹, formation in the C-N + isoindole plane is seen in the absorption region of 1165 cm⁻¹, pyrrole rings are seen in

the absorption region of 1332 cm^{-1} , pyrrole nitrogen atoms are seen in the absorption region of 1409 cm^{-1} , $-N = 1508.33\text{ cm}^{-1}$ appears in the absorption region.

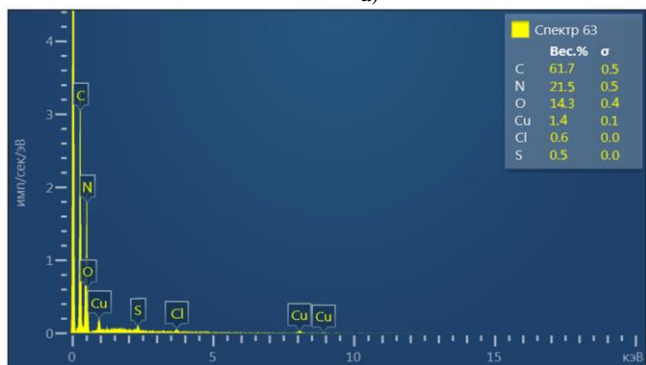
Due to the above nitrogen-retaining chromophore groups and the coordination of metal ions, the organic pigment acquires a stable and intense colour property.

4.3. Scanning electron microscopic analysis of organic pigment of TaCuPc brand

The synthesized new content (TaCuPc) organic pigment was studied by MIRA 2 LMU scanning electron microscope, equipped with INCA Energy 350 energy-dispersion microanalysis system. The analysis capacity of the microscope is 1 nm, and the sensitivity of the INCA Energy detector is 133 eV / 10mm², which allows the analysis of elements from beryllium to plutonium. Scanning electron microscope analyzes were performed under a high vacuum. Microanalysis of organic pigment chemical elements was carried out in the same device and studied in areas with an accelerating voltage of 20 keV and a current of 1 nA.



a)

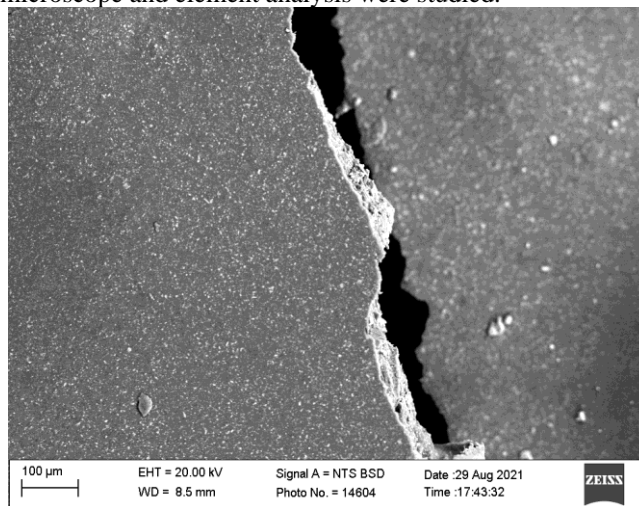


b)

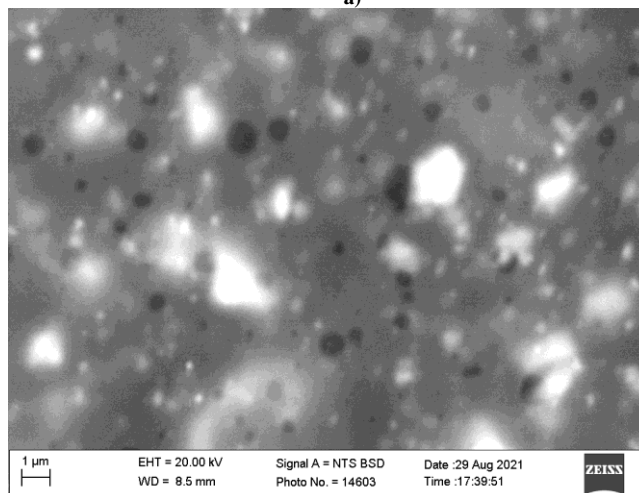
Fig. 5 Data from scanning electron microscopy (a) and element analysis (b) of organic pigment TaCuPc

When the 200-magnified images of a new-composition TaCuPc organic pigment sample were examined in SEM, no residues of the original substances that did not react were visible. This makes it possible to obtain information about the elemental composition of the substances formed in the reaction and the fact that the reaction took place by the end (Figure 5).

The synthesized TaCuPc organic pigment alkyd enamel coating was obtained, and the compound's scanned electron microscope and element analysis were studied.



a)



b)

Fig. 6. Imaging of alkyd enamel coating based on organic pigment TaCuPc on a scanning electron microscope (100 and 5000 times magnification)

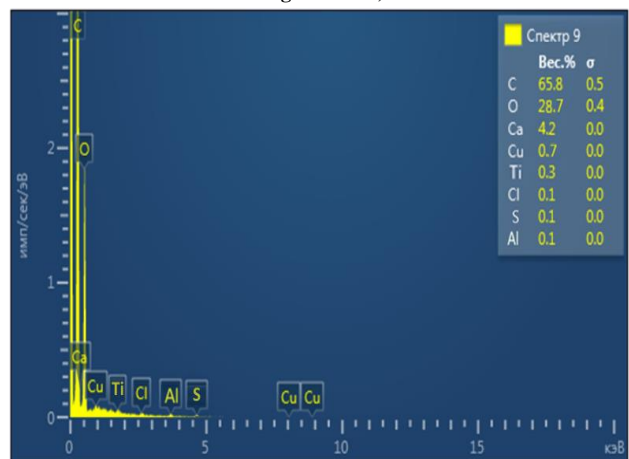


Fig. 7 Element analysis data of alkyd enamel coating based on organic pigment of TaCuPc brand

The obtained analyzes show that a sample of an alkyd enamel coating prepared based on an organic pigment synthesized in the presence of a new composition of terephthalic acid was evenly distributed in the dye composition of terephthalic acid particles in images 100 and 5000 times magnified in SEM. This ensures that the organic compound is homogeneous. It also provides information on the element composition of the paint (Figures 6-7).

4.4. Thermal analysis of TaCuPc organic pigment.

For the analysis, 4,373 mg of TaCuPc organic pigment was obtained, and the process was studied in the temperature

range of 30 - 600 °C. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of organic pigment are shown in Figure 8 below.

Analysis of the thermogravimetric curve of the organic pigment TaCuPc shows that the TGA curve occurs mainly in the temperature range where 3 intensive mass losses occur. The 1st mass loss interval corresponds to a temperature of 30,23 – 194,69 °C, the 2nd mass loss interval corresponds to a temperature of 194,69 – 339,96 °C, and the 3rd mass loss interval corresponds to a temperature of 339,96 - 600 °C.

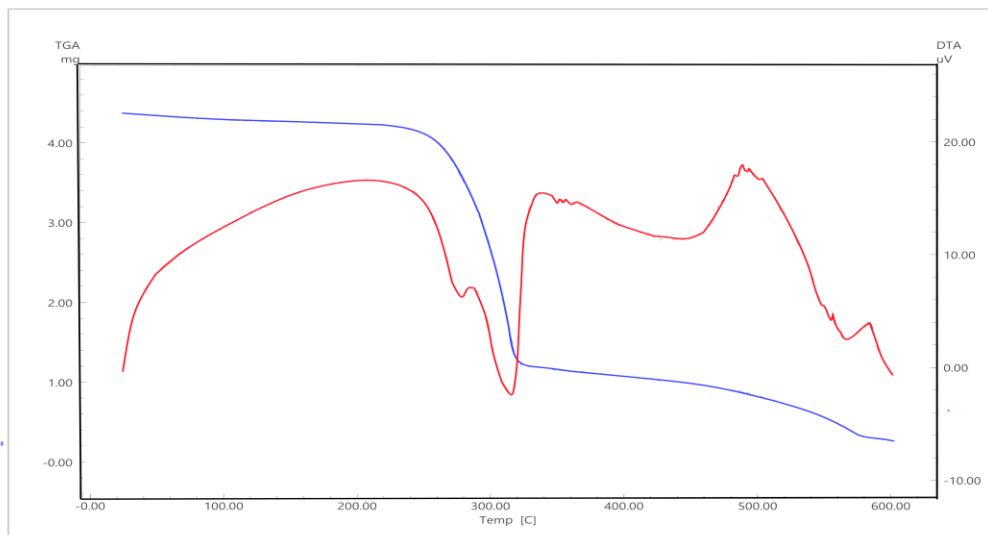


Fig. 8 Results of thermogravimetric (TGA) and differential thermal analysis (DTA) of TaCuPc organic pigment

Analyzes show that an intensive decomposition process occurs in the range where mass 2 is lost. The main amount of mass loss in this range is 3,061 mg or 69,9%. A detailed analysis of the thermogravimetric analysis curve and the differential thermal analysis curve is given in Table 4 below.

Table 4. Analysis of TGA and DTA curve results of TaCuPc organic pigment

N ₂	T, °C	Lost mass, mg (4,373 mg)	Amount of energy consumed (µV * s / mg)	Time spent (min)	dw (mg)	dw/dt (mg /min)
1	100	0.089	12.5	8.52	4.284	0,01
2	200	0.136	16.524	18.72	4.237	0,007
3	300	1.7	2.438	29	2.67	0,06
4	400	3.3	12.434	38.95	1.07	0,08
5	500	3.55	16.61	49.05	0.821	0,07
6	600	4.11	-0.604	59.37	0.26	0,07

As can be seen from the derivatogram of the organic pigment given above, the mass of the pigment gradually decreases with increasing temperature and is accompanied by endo-effects. The decrease in the mass of organic pigment with increasing temperature is caused by the loss of

adsorption water and the decomposition of the pigment-containing substances.

The differential thermal analysis of the organic pigment TaCuPc is shown in Figure 8. It is known from the differential thermal analysis of the organic pigment TaCuPc that energy absorption occurs in the range of 241,06 – 331,79 °C. The highest heat absorption occurs at 315,53 °C.

4.5. Thermogravimetric analysis of alkyd enamel based on organic pigment brand TaCuPc.

4,9 mg of this substance was taken for analysis, and the process was studied at a temperature of 30 - 600 °C. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of alkyd enamel are shown in Figure 9 below.

Analysis of the thermogravimetric curve of the obtained enamel shows that the TGA curve occurs mainly in the temperature range where 3 intensive mass losses are achieved. The 1st mass loss interval corresponds to a temperature of 26,83 – 229,69 °C, the 2nd mass loss interval corresponds to a temperature of 229,69 – 497,48 °C, and the 3rd mass loss interval corresponds to a temperature of 497,48 - 600 °C.

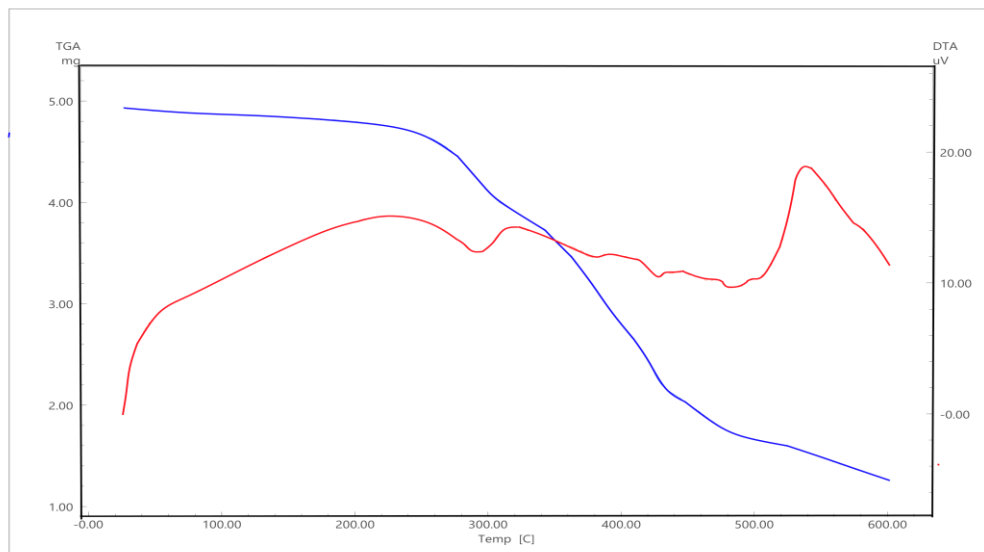


Fig. 9 Thermogravimetric (TGA) and Differential Thermal Analysis (DTA) of alkyd enamel based on organic pigment brand TaCuPc

Analyzes show that an intensive decomposition process occurs in the range where mass 2 is lost. The main amount of mass loss in this range is 3,076 mg or 62,343%. A detailed analysis of the thermogravimetric analysis curve and the differential thermal analysis curve is given in Table 5 below.

The analysis results show that while the mass loss in the 1st mass loss interval was 3,79%, 62,343% of the 2nd mass loss occurred. 3 - Mass loss in the mass loss range is 8,269%.

Table 5. Analysis of TGA and DTA curve results of lacquer paint based on TaCuPc organic pigment and alkyd varnish

No	T, °C	Lost mass, mg (4,934 mg)	The amount of energy consumed ($\mu V \cdot s/mg$)	Time spent (min)	dw (mg)	dw/dt (mg/min)
1	100	0.068	10.251	8.23	4.87	0.0083
2	200	0.138	14.648	18.47	4.8	0.0075
3	300	0.83	12.648	28.63	4.1	0.029
4	400	2.14	12.058	38.73	2.79	0.055
5	500	3.27	10.321	48.85	1.66	0.067
6	600	3.67	11.619	59	1.26	0.0622

It can be seen that the loss of excess moisture and crystal hydrate water occurs at the first mass loss. In the second main decomposition stage, in the case of low molecular

weight compounds such as carbon monoxide, and ammonia, after the decomposition of the organic part, a mixture of metal carbonates, oxides and partially coal remains. In the third decomposition stage, the carbonates decompose, and metal oxides and coal residues remain.

Differential thermal analysis of alkyd enamel shows that energy absorption occurs in the range of 236,3 – 319,05 °C, 370,62 – 388,09 °C and 416,39 – 434,34 °C. The highest heat absorption occurs at 290,25 and 427,48 °C. However, energy dissipation occurs in the range of 503,41 – 580,2 °C. The highest heat dissipation occurs at a temperature of 538,01 °C.

5. Conclusion

The properties of the compound of copper phthalocyanine synthesized in the presence of terephthalic acid were studied using scanning electron microscopy (SEM), thermal analysis and IR-spectroscopic analysis methods.

The new compound's pigment properties were studied per the requirements of GOST. Properties of enamel prepared by the standard method, such as water resistance, and thermal stability, were studied. The results show that pigment can be used effectively.

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