

## ADVANCED MATERIALS WITH STABLE CRYSTALLINE STRUCTURE

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**Abstract.** In recent years, metallic phthalocyanines have received a special attention mainly because they are the starting point in obtaining functionalized materials that are important for many scientific areas such as gas detection sensors, solar cells with dyes, devices for nonlinear optics, pigments with excellent tinctorial properties or fotosensitizers for photodynamic therapy. Some of the metallic phthalocyanines are characterized by the polymorphism phenomena, their crystalline forms presenting different applied characteristics that are sometimes not suited for the desired applications. Copper phthalocyanine is included among these phthalocyanines, characterized by 5 crystalline forms ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ ) with  $\alpha$  and  $\beta$  forms showing interest in paint and varnish industry. This paper presents results obtained from the experimental studies of the synthesis and physical-chemical characterization of  $\alpha$ -stable crystalline form for copper phthalocyanine, a pigmentary material obtained by means of embedding chloromethylated copper phthalocyanine in raw phthalocyanine,  $\alpha$ -unstable form. The resulted materials were characterized by IR and UV-VIS spectrometry, X-ray diffraction, thermogravimetry and solvents resistance.

**Keywords:** copper phthalocyanine, pigments, stable crystalline forms

### 1. INTRODUCTION

Phthalocyanine pigments are a well known class of colouring materials with marked commercial utility because of their excellent thermal stability, excellent fastness to light and chemical degradation properties, bright hues and high tinctorial strength. Since their discovery in 1907 by Braun and Tscherniac during the synthesis of o-cyanobenzamide from phthalimide and phthalic acid numerous information concerning their synthesis, photochemical and photophysical properties have emerged. They are now prepared and used industrially as dyes and colouring agents.

Phthalocyanines are prepared and used as dyes and pigments with excellent tinctorial properties, catalysts in photodegradation reactions of pollutants or in organic synthesis, chemical and gas detection sensors, optical storage devices, conducting polymers and photosensitizers in photodynamic therapy [1, 2].

Copper phthalocyanine is the most common of the phthalocyanine pigments and it's especially used in the blue colour range. Some of the striking features which make it a very useful for a variety of applications are the following: tinting strength, covering power, light fastness, good stability and resistance to the effects of alkalis and acids [3-5].

Copper phthalocyanine pigments are known to exist in a number of crystalline forms ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ ,  $\pi$ ,  $\chi$ ,  $\rho$ ) which differ greatly from each other in both physical

and tinctorial properties. Of these forms, the so-called  $\alpha$ - and  $\beta$ -modifications have been most widely used as pigments [6 - 10].

In relation to tinctorial properties,  $\alpha$ -copper phthalocyanine exhibits red shade blue pigmentations in surface coating binders whereas the  $\beta$ -modification exhibits green-shade blue pigmentations in such substrates. However, the  $\alpha$ -form is also characterized by the tendency to revert to the more stable  $\beta$ -form with an accompanying change of shade, especially when are in contact with the aromatic solvents used in many surface coating media (paints, inks, varnishes) [11-13].

In trying to overcome this undesirable property of forming large crystals by storage in liquid vehicle in paints and varnishes a number of methods were used, such as: acid pasting of the crude pigment in a strong acid, grinding of crude copper phthalocyanine with inorganic salts, incorporation of a small amount of chlorine into the molecule, or the use of copper phthalocyanine derivatives as additives on performed copper phthalocyanine [14-16].

The present work is a study on copper phthalocyanine in  $\alpha$ -stable crystalline form, obtained by mixing copper phthalocyanine as crude paste or dry powder with chloromethylated copper phthalocyanine also as crude paste or dry powder, followed by drying and grinding (as appropriate). The pigmentary material was physical-chemical characterized by means of IR and UV-VIS spectrometry, X-ray diffraction,

thermogravimetry and solvents resistance. The results will be presented in the next sections of the paper.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials and methods

All chemicals have been used as commercial sources with no purification prior to use: copper phthalocyanine 98% (Sigma-Aldrich), paraformaldehyde 98% (Sigma-Aldrich), chlorosulfonic acid 97% (Acros Organics), and sulphuric acid 98% (Scharlau).

**IR spectra** were registered in the region 400-4000  $\text{cm}^{-1}$  with a SPECORD spectrometer using KBr pellets.

**UV-VIS spectra** have been recorded with a SPECORD spectrophotometer in the range of 250-800 nm. Solutions  $10^{-5}$  M in  $\text{H}_2\text{SO}_4$  were used.

**X-ray diffractions (XRD)** were obtained with a DRON UM1 diffractometer, operating at 32 kV and 25mA, using Cu  $K\alpha$  radiation (1.5418 Å), with iron filter. The working conditions were: step size by 0.03° (2 theta), scanning rate = 8s/step and diffraction range 2–15° (2 theta).

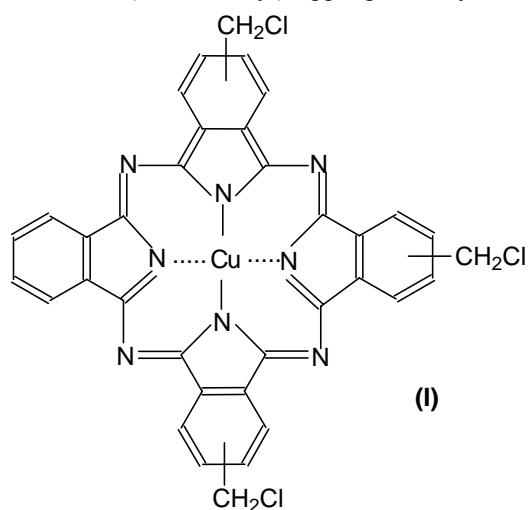
**Thermal analysis** of the materials were carried out on a Du Pont TG-DTA analyzer in oxygen gas atmosphere with open sample holder and small platinum boat in static air at a heating rate of 5 °  $\text{min}^{-1}$

### 2.2. Synthesis

Tris(chloromethyl)copper phthalocyanine was synthesised according to the literature [11]. A mixture of 5 g sulphuric acid and 30g chlorosulfonic acid is cooled to below 30 °C and then 3 g of copper phthalocyanine are added. The mixture is stirred for about 30 minutes and while maintaining the temperature between 30-40 °C, 10 g paraformaldehyde are added. The mixture is agitated 30 minutes at 30-40 °C and than is heated slowly, over 2 hours, to 90-95 °C.

After 6 hours the reaction mass is cooled to room temperature and poured, under vigorous stirring, into 200 g water-ice. The resultant slurry is filtered and the filter cake is washed with cold water until pH=6-6.5. After drying and grinding is obtained a blue-green powder with a chlorine content of 16. 4% (Schöniger combustion) which corresponds to tris(chloromethyl)copper phthalocyanine (formula I).

**Formula I:** tris(chloromethyl)copper phthalocyanine



The pigmentary material was obtained by grinding in a mortar of a mixture from 2.5 g copper phthalocyanine and 0.25 g tris(chloromethyl)copper phthalocyanine for 30 minutes. The resulted powder was characterized by IR and UV-VIS spectrometry, X-ray diffraction and thermogravimetry.

## 3. RESULTS AND DISCUSSIONS

### 3.1. IR and UV-Vis spectral analysis

IR spectrum was registered and it is shown in Fig. 1.



**Fig. 1.** FTIR spectrum of tris(chloromethyl)copper phthalocyanine

In Table 1 the experimental data are summarized. Based on registered IR spectrum for copper phthalocyanine, some assignments can be made: C=C macrocycle ring deformation ( $1668\text{ cm}^{-1}$ ,  $1612\text{ cm}^{-1}$ ), C=N stretching ( $1528\text{ cm}^{-1}$ ,  $1508\text{ cm}^{-1}$ ), C-H in plane bending ( $1466\text{ cm}^{-1}$ ), C-C stretching in isoindole ( $1436\text{ cm}^{-1}$ ,  $1422\text{ cm}^{-1}$ ,  $1356\text{ cm}^{-1}$ ,  $1334\text{ cm}^{-1}$ ), C-N stretching in isoindole ( $1302\text{ cm}^{-1}$ ,  $1288\text{ cm}^{-1}$ ), C-N in plane bending ( $1182\text{ cm}^{-1}$ ,  $1166\text{ cm}^{-1}$ ), C-H in plane bending ( $1144\text{ cm}^{-1}$ ,  $1120\text{ cm}^{-1}$ ), C-H in plane deformation ( $1104\text{ cm}^{-1}$ ,  $1092\text{ cm}^{-1}$ ,  $1078\text{ cm}^{-1}$ ,  $1068\text{ cm}^{-1}$ ), metal-ligand vibration ( $1000\text{ cm}^{-1}$ ,  $972\text{ cm}^{-1}$ ,  $950\text{ cm}^{-1}$ ,  $912\text{ cm}^{-1}$ ,  $900\text{ cm}^{-1}$ ), in plane vibration ( $884\text{ cm}^{-1}$ ,  $864\text{ cm}^{-1}$ ,  $816\text{ cm}^{-1}$ ,  $800\text{ cm}^{-1}$ ), C-H out of plane deformation ( $790\text{ cm}^{-1}$ ,  $768\text{ cm}^{-1}$ ,  $762\text{ cm}^{-1}$ ,  $738\text{ cm}^{-1}$ ), C-C out of plane ring deformation ( $636\text{ cm}^{-1}$ ). The presence of bands at  $864\text{ cm}^{-1}$ ,  $738\text{ cm}^{-1}$ ,  $722\text{ cm}^{-1}$  and  $660\text{ cm}^{-1}$  may suggest the presence of  $\alpha$ -crystalline form of copper phthalocyanine.

The main UV-Vis transitions are included in Table 1.

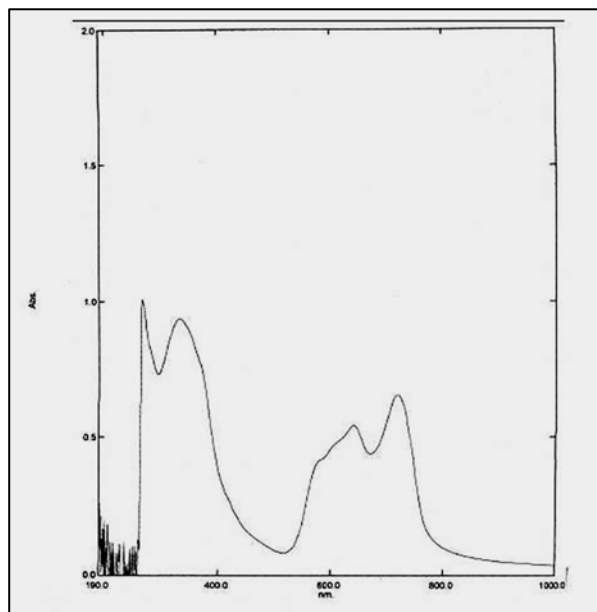
**Table 1:** UV-VIS and IR data

Crt. No.	UV-VIS abs	IR spectral data ( $\text{cm}^{-1}$ )
	$\lambda$ , nm	
1	253.4	3996(w), 2336(m), 2332(m),
2	299.5	1668(s), 1612(m), 1528(s),
3	307.2	1508(w), 1488(s), 1480(s),
4	333.5	1474(s), 1466(s), 1436(s), 1422
5	439.6	(w), 1356(s), 1334(w), 1302(s),
6	700.9	1288(w), 1230(s), 1192(s),
7	714.9	1182(s), 1166(w), 1144(s),
8	770.0	1120(w), 1104 (s), 1092(w),
		1078(s), 1068(m), 1012(s),
		1000(s), 972(s), 950(s), 912(s),
		900(m), 884(s), 864(s), 816(s),
		800(s), 790(s), 768 (m), 762(s),
		752(w), 738(s), 722 (w), 660(s),
		636(s), 596(s), 570(s), 524(s),
		504(s), 440(s), 432(s)

Note: w=weak; m=medium; s=strong.

It has been considered that the UV-VIS spectrum of phthalocyanines originate from the molecular orbitals within the aromatic 18  $\pi$ -electron system and from overlapping orbitals on the central metal. Extended conjugation of  $\pi$  electrons in copper phthalocyanine macrocycle shapes an intense and isolated band at 770 nm, the so called Q-band. The intense band in the UV spectral region at 333.5 nm is due to the electronic transition from  $\pi - \pi^*$  orbitals and is known as Soret band or B-band.

The additional spectrum bands can be attributed to the charge transfer metal-ligand or ligand-metal or even coupling excitation between  $\pi$  systems of dimer complexes.



**Fig. 2.** UV-VIS spectrum of tris(chloromethyl)copper phthalocyanine

### 3.2. X-ray diffraction

The data obtained after the X-ray diffraction analysis are summarized in Table 2.

**Table 2:** X-ray diffraction of  $\alpha$ -unstable CuPc vs.  $\alpha$ -stable CuPc

Crt. no.	CuPc $\alpha$ -unstable				CuPc $\alpha$ -stable			
	literature [4, 13]		laboratory		literature [12, 13]		laboratory	
	I. d. ( $\text{\AA}$ )	I. (%)	I. d. ( $\text{\AA}$ )	I. (%)	I. d. ( $\text{\AA}$ )	I. (%)	I. d. ( $\text{\AA}$ )	I. (%)
1	12.6	100	12.91	100	12.9	100	12.91	100
2	9.67	74	12.05	74	12.2	71	9.74	11
3	8.40	14	8.86	14	8.89	10	9.01	17
4	5.74	5	5.98	3	6.02	4	7.09	2
5	4.90	15	5.68	15	5.72	13	5.83	14
6	4.79	15	5.45	15	5.49	5	5.55	11
7	4.17	7	4.08	1	4.33	7	4.88	2
8	4.00	5	3.70	15	3.28	13	4.43	3
9	3.87	8	3.55	12	3.67	8	4.33	8
10	3.75	25	3.34	24	3.56	15	4.15	2
11	3.41	16	3.23	28	3.54	10	3.89	11
12	3.19	9			3.43	47	3.73	18
13	2.94	12			3.33	18	3.66	13
14	2.79	5			3.31	16	3.56	20
15	2.72	5			3.23	21	3.43	36
16					3.03	29	3.32	41
17					2.83	16	3.24	28
18					2.72	13	3.10	29
19							2.95	4
20							2.83	13
21							2.73	12

Note: I. d. = interplanar distance; I = intensity

By comparing experimental results with literature information it can be concluded that the applied laboratory method ensures obtaining of copper phthalocyanine in the  $\alpha$ -crystalline form, the pigmentary material being stable to boiling in solvents.

### 3.3. Thermal analysis

The results of the thermal analysis are summarized in Table 3.

**Table 3:** DSC/TGA of  $\alpha$ -unstable CuPc vs.  $\alpha$ -stable CuPc

Crt. No.	Compound	Temp (°C)	Content (%)	
			CuPc $\alpha$ -unstable	CuPc $\alpha$ -stable
1	Urea	170	0.4	0
2	Phthalimide	220	0.6	0
3	Phthalic anhydride	285	0.2	0.2
4	NH <sub>4</sub> Cl	305	0.2	0
5	Cyanuric acid	340	0.8	0
6	CuPc $\alpha$ -unstable	490	cca. 85	86
7	CuO (black residue)	>490	cca. 13	13.8

The performed thermal analysis revealed a weight loss of about 1.5 %, corresponding to free moisture and high stability to temperature. It was observed that the major loss in weight take place at 425-549°C, corresponding to the phthalocyanine residue degradation. It was established that the residual compound is copper oxide. All stages of thermal degradation are of exothermic nature.

### 3.4. Tinctorial characterization

The stability of crystalline form to boiling aromatic hydrocarbons is an essential and eliminatory test because it shows the behavior of the pigment during processing in order to obtain paints, varnishes or inks. It is known that changing pigment crystalline form during processing or during storage of the finished product has the effect of changing the shade, covering loss of strength and other specific properties.

Tinctorial characterization of the prepared pigmentary materials involved hue analysis (color shade), residue determination (on sieves with 15000 mesh/cm<sup>2</sup>), and fastness to solvent. All these characteristics were determined and evaluated comparatively with the pigment in the unstable crystalline form and in conformity with specific methods. The experimental data are included in Table 4.

**Table 4:** Results of tinctorial characterization

Crt. No.	Characteristics	CuPc $\alpha$ -unstable	CuPc $\alpha$ -stable
1	Hue (Shade of color)	red-blue	blue-green
2	Residue on sieve (15.000 mesh/cm <sup>2</sup> ), %	3.9	0.35
3	Solvents resistance: -toluene -butyl acetate -butanol -acetone	unstable unstable unstable unstable	stable stable stable stable
4	Particle size ( $\mu$ ) -primary -aggregates -agglomerates	5 25-30 150-200	3-5 10-15 50-60

After measurements of trichromatic coordinates on tapes of pigment paste in polymerized linseed oil deposited on paper it was found that the pigmentary material of copper phthalocyanine  $\alpha$ -stable crystalline form is characterized by a greener hue than the  $\alpha$ -unstable crystalline form.

It has also been found that the fineness of the stable product, as expression of residue on sieve with 15.000 mesh/cm<sup>2</sup>, is about ten times higher than the fineness for the product in the unstable crystalline form.

By boiling the two copper phthalocyanines in organic solvents followed by analyzing the particle size on a microscope it was observed a growth of pigment particle dimensions for the unstable crystalline form.

## 4. CONCLUSIONS

The experimental results show that embedding chloromethylated copper phthalocyanine in raw phthalocyanine (10-15% by total pigment weight) allows the obtaining of  $\alpha$ -stable crystalline form, an important material for paints and varnishes industry, the results of physical-chemical characterization being in good agreement with the literature information (where they exist).

The pigmentary material has good to very good resistance to aromatic solvents, one of the main component in coating formulas.

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