



## Synthesis and characterization of copper phthalocyanine and tetracarboxamide copper phthalocyanine deposited mica-titania pigments

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### ABSTRACT

Combination pigments were synthesized by the deposition of copper phthalocyanine and tetracarboxamide copper phthalocyanine on a mica-titania pigment in dimethyl formamide solvent to improve color properties. The FT-IR and XRD analyses were performed to observe the crystal transformations of the pigments on the substrate. The stable beta form of copper phthalocyanine normally preferred in paint applications was obtained at 90 °C and 120 °C, while tetracarboxamide copper phthalocyanine remained amorphous at all temperatures experimented. Pigment surface morphologies were investigated by SEM analysis. Copper phthalocyanine crystalline rods were observed on the mica-titania substrate, however, the tetracarboxamide copper phthalocyanine pigment did not exhibit any such crystalline structure due to its amorphous structure, which was confirmed by XRD analysis. Furthermore, nitrogen elemental analysis was performed to determine the amount of copper phthalocyanines adsorbed to the mica-titania surfaces at different temperatures. The resulting combination pigments showed enhanced luster, good dispersion, hue, and high color intensity.

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### 1. Introduction

Phthalocyanine is a planar 18  $\pi$ -electron heterocyclic aromatic system with alternating nitrogen-carbon atom ring structure derived from porphyrin [1]. Phthalocyanines have been known for more than 70 years and have been extensively used as colorants [2–4]. Moreover, they have attracted interest for a variety of uses such as liquid crystals, photosensitizers, non-linear optics, solar cells, catalysis, and in various chemical sensing applications [5]. The peripheral and non-peripheral positions on the benzenoid ring of phthalocyanines can be substituted with many other molecules to impart new properties. In addition, over seventy different metal ions can be introduced into the central cavity to improve physical properties to suit a desired technological application [3,6]. Among them, copper phthalocyanine is one of the most important classes of colorants and has superior properties such as light fastness, tinting strength, covering power, and resistance to alkalis and acids [7].

Copper phthalocyanine exists in many polymorphic forms and the most commonly studied phases are alpha ( $\alpha$ ) and beta ( $\beta$ ).

It is reported that the metastable  $\alpha$ -polymorph undergoes a polymorphic transition to the stable  $\beta$ -polymorph when heated over 250 °C or treated with some aromatic hydrocarbons like xylene [8–10]. This transformation is not a simple process, but the metastable powder grows to a considerable extent without changing its crystal structure before the actual transformation takes place [11]. The resulting  $\beta$ -polymorph is in a relatively larger crystalline form [10,12]. The  $\alpha \rightarrow \beta$  transformation of the pigment can take place in paint formulations because many organic liquids used as thinners and diluents can induce this transformation. Large crystals change the shade and the tinctorial strength of the paint in a storage period between the preparation of the composition and its final use [13,14]. For these reasons, the  $\beta$ -form is preferred in industrial use.

The synthesis of metal phthalocyanines is usually achieved in high yields by cyclotetramerization of phthalonitrile, diiminoisoindoline, phthalic anhydride or phthalimide in the presence of a metal salt at high temperatures [15,16]. In order to synthesize peripherally or nonperipherally functionalized phthalocyanines, precursors with desired substituents can be used. Phthalocyanines can be produced in the medium of solvents or under microwave irradiation. In the last decade, an increased interest has been focused on the application of microwave irradiation in their

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synthesis. Numerous reactions can be performed under microwave assisted conditions in which significant rate enhancements, improved yield and selectivity, and a reduction in thermal by-products have been achieved [17,18]. In particular, the reaction time and energy input are supposed to be mostly reduced in the reactions which last for a long time at high temperatures under conventional conditions [17,19]. Copper phthalocyanine (CuPh) and tetracarboxamide copper phthalocyanine (TCuPh) were also synthesized in this research work under microwave irradiation conditions of reactants.

Phthalocyanines are absorption pigments which possess very high surface energy, and therefore, tend to self-agglomerate to form coarser particles in paint formulations or in other applications [20]. The agglomerated particles are generally mechanically crushed into smaller particles or under high shear mixing, and ultrasonic dispersion can also be performed to break the agglomerates [21,22]. The surface of the crushed pigment particles can also be chemically treated to enable the individual particles to stay in a stable dispersed state. However, when stored for an extended period of time the pigment particles can again agglomerate and adversely affect the color.

The use of phthalocyanines together with other pigments to make the so called 'combination pigment' can yield new pigments with enhanced properties. When phthalocyanine pigments are imparted on 'effect pigments' one can obtain new pigments with excellent spreading properties, brilliant colors, high color intensity, gloss, and stability. Most effect pigments are titania coated mica pigments, and they depict excellent brilliant colors.

Combination pigments can be produced by the deposition of absorption pigments (or dyes) on the surface of a flaky substrate coated with a metal oxide whereby pigment particles adhere quickly. The combination of two pigments can exhibit satisfactory spreading properties, high color effect, and good color saturation [21]. Additionally, the tendency of absorption pigment particles to flocculate is also eliminated or greatly reduced when the particles are bound onto the substrate surfaces. Furthermore, absorption pigments have high color intensity, light fastness, and bleed resistance properties which make the resulting combination pigments suitable for automobile finishes and other paint applications. As a flaky substrate, pearlescent pigments of titania coated on mica are of particular interest because the color is derived entirely from the interference effect. They make possible combination pigments with the widest range of colors [22].

There are very few patent studies related to the synthesis of combination pigments. These studies are quite complex since they involve several steps and components to synthesize the desired combination pigment. For example, milling was needed to disperse a phthalocyanine pigment in water, and/or additives were used to prevent the coagulation of the pigment and improve compatibility. All of these additional steps are time consuming, and detract from the economic feasibility of the pigment.

The main objective of this work is to synthesize combination pigments including mica-titania as a pearlescent pigment and CuPh and TCuPh as absorption pigments. In this method, because the phthalocyanines were soluble in DMF, no additional dispersing agents or processing steps were required; in addition, no compatibility binders were needed to adhere the phthalocyanines onto mica surfaces. Simple stirring of the dispersed phthalocyanines with mica-titania pigment gives the desired combination pigments with enhanced gloss, hue, and color properties. Furthermore, agglomeration of phthalocyanine molecules confronted in industrial applications was eliminated by the deposition of these particles onto the mica-titania substrate. CuPh and TCuPh were used to synthesize combination pigments at different temperatures, and crystalline forms of phthalocyanines on mica-titania surfaces were

investigated. The desired stable  $\beta$ -form of CuPh was successfully deposited onto the substrate.

## 2. Experimental

### 2.1. Materials

Mica-titania was synthesized according to the reported procedure [23]. Analytical grade phthalic anhydride, trimellitic anhydride, ammonium molybdate, urea, copper (II) chloride, sodium hydroxide (NaOH), hydrochloric acid (HCl), and dimethyl formamide were used in the experiments.

### 2.2. Preparation

#### 2.2.1. Synthesis of copper phthalocyanine pigments

**2.2.1.1. Synthesis of copper phthalocyanine (CuPh).** Urea (0.092 mol), phthalic anhydride (0.018 mol), copper (II) chloride (0.005 mol), and ammonium molybdate (0.0596 mol) were ground for 30 min in an agate mortar. The mixture was put into a flask and wetted with distilled water (5 mL). It was then heated in a microwave oven at 600 W for 5 min. The crude product was purified by washing in sequence with hot water (70 °C), 6 M HCl, 1 M NaOH, and with hot water again followed by filtration. After these steps, the pigment was washed with ethanol and filtered until the filtrate was colorless. The resulting pigment was dried in an oven at 100 °C.

**2.2.1.2. Synthesis of tetracarboxamide copper phthalocyanine (TCuPh).** Urea (0.092 mol), trimellitic anhydride (0.018 mol), copper (II) chloride (0.005 mol), and ammonium molybdate (0.0596 mol) were used and treated as above, excluding only the washing step with NaOH solution.

#### 2.2.2. Synthesis of combination pigments

**2.2.2.1. Synthesis of copper phthalocyanine deposited mica titania pigment (CuPhM).** The preparation of combination pigment was carried out by mixing CuPh with mica-titania pigment in DMF solvent. For this purpose, titania coated mica with the highest rutile content was used [23]. First, CuPh (40 mg,  $6.9 \times 10^{-5}$  mol) was dissolved in DMF (10 mL) while mixing the solution, mica-titania pigment (0.3 g) was added and stirred for an hour. The suspension was then filtered and washed with DMF. In order to remove any free CuPh, the wet cake was suspended in DMF and the CuPhM particles were allowed to settle and the supernatant DMF containing the CuPh was removed from the solution. In order to get rid of free CuPh particles, the wet cake was suspended in DMF and kept for a while to settle down CuPhM particles while the supernatant liquid containing free CuPh particles was removed from the solution. This process was repeated until the supernatant liquid was colorless. The wet cake was filtered and dried at 90 °C in an oven. CuPh deposited mica pigments were synthesized at different temperatures of 25 °C, 60 °C, 90 °C, and 120 °C.

**2.2.2.2. Synthesis of tetracarboxamide copper phthalocyanine deposited mica titania pigment (TCuPhM).** The same procedure in Section 2.2.2.1 was applied except TCuPh (52 mg,  $6.9 \times 10^{-5}$  mol) was used instead of CuPh for the deposition. TCuPh deposited mica pigments were also synthesized at different temperatures which are 25 °C, 60 °C, 90 °C, and 120 °C.

### 2.3. Analysis

The chemical structure of the copper phthalocyanine pigments CuPh and TCuPh and the derived combination pigments were identified by FT-IR spectroscopy (IR Prestige-21 SHIMADZU). The

crystal structures of copper phthalocyanines and combination pigments were determined by XRD analysis (RIGAKU-D/Max-2200/PC). The XRD analysis was carried out by using  $\text{CuK}\alpha$  ( $\lambda = 0.154 \text{ nm}$ ) radiation operated at 40 kV and 20 mA for the crystal structure determination of CuPh and TCuPh on mica-titania surfaces. The XRD patterns were recorded in the  $2\theta$  range from  $5^\circ$  to  $40^\circ$  with a step size of  $0.02^\circ$ . Elemental (nitrogen) analysis (LECO, CHNS-932) was performed to determine the amounts of CuPh and TCuPh deposited on mica surfaces. The elemental analyzer offers simultaneous multi-elemental determination of carbon, hydrogen, nitrogen, and sulfur in homogenous microsamples (2 mg). SEM (Quanta 400F Field Emission) was used to examine the morphology of phthalocyanines on mica-titania surfaces. The measurements were undertaken in high vacuum mode of the instrument and the samples were coated with 10 nm Au/Pd.

#### 2.4. Determination of optical properties

The optical properties of pigments synthesized were determined by incorporating them in a paint formulation. For this purpose a long oil alkyd resin (60% resin + 40% white sprit) (Betek) was used. The paint was formulated as 89.52% by weight alkyd (resin), 7.96% white sprit (solvent), 0.31% cobalt naphthenate (drier), 0.24% lead naphthenate (drier), and 2% CuPhM or TCuPhM (pigment). The gloss values of paints having CuPhM or TCuPhM pigments were determined by using a gloss meter (Rhopoint, Novo-Gloss). The colors of the paints (i.e.  $L^*a^*b^*$  values) were determined by using a color measuring device (Datacolor 400).

### 3. Results and discussion

#### 3.1. FT-IR spectroscopy of copper phthalocyanines

The FT-IR spectrum of CuPh is given in Fig. 1. It has characteristic peaks at  $3041$  and  $2910 \text{ cm}^{-1}$  for aromatic C–H stretching,  $1610 \text{ cm}^{-1}$  for C=C macrocycle ring deformation,  $1506 \text{ cm}^{-1}$  for C=N stretching,  $1333 \text{ cm}^{-1}$  for C–C stretching in isoindole,  $1091 \text{ cm}^{-1}$  for C–H in plane deformation, and  $723 \text{ cm}^{-1}$  for C–H out of plane deformation of phenyl. The other peaks at  $1286 \text{ cm}^{-1}$ ,  $1165 \text{ cm}^{-1}$  and  $1119 \text{ cm}^{-1}$  correspond to C–N stretching in isoindole, C–N in plane bending, C–H in plane bending, respectively.

The FT-IR spectrum of TCuPh is given in Fig. 2. It has characteristic peaks at  $3037$  and  $2912 \text{ cm}^{-1}$  for aromatic C–H stretching,  $1614 \text{ cm}^{-1}$  for C=C macrocycle ring deformation,  $1504 \text{ cm}^{-1}$  for C=N stretching,  $1327 \text{ cm}^{-1}$  for C–C stretching in isoindole,  $1093 \text{ cm}^{-1}$  for C–H in plane deformation, and  $739 \text{ cm}^{-1}$  for C–H out of plane deformation of phenyl. The other peaks at  $1656 \text{ cm}^{-1}$ ,  $1583 \text{ cm}^{-1}$ ,  $1317 \text{ cm}^{-1}$ , and  $3163 \text{ cm}^{-1}$  correspond to C=O stretching of the amide, C–N stretching in isoindole, C–N in plane bending, C–H in plane bending, respectively.

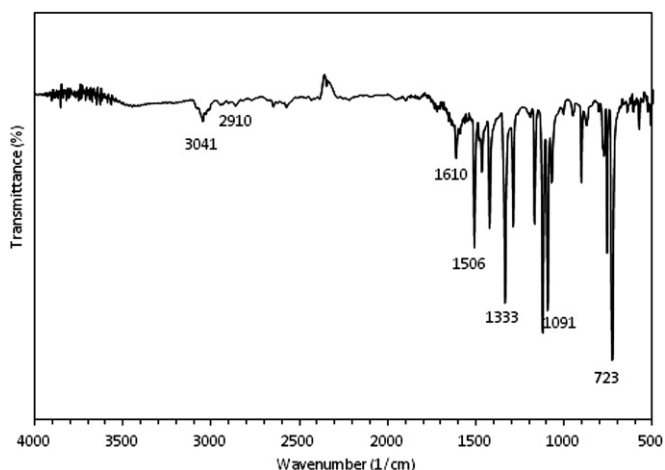


Fig. 1. FT-IR spectrum of copper phthalocyanine (CuPh).

N stretching,  $1328 \text{ cm}^{-1}$  for C–C stretching in isoindole,  $1093 \text{ cm}^{-1}$  for C–H in plane deformation and at  $738 \text{ cm}^{-1}$  for C–H out of plane deformation of phenyl ring which differed from CuPh to some extent due to substitution. TCuPh also shows additional bands that do not exist in the CuPh spectrum due to its four amide groups bonded to peripheral benzenoid rings of the macrocycle. These peaks include N–H stretching bands at  $3317 \text{ cm}^{-1}$  and  $3167 \text{ cm}^{-1}$ , C=O stretching of the amide at  $1656 \text{ cm}^{-1}$ , and N–H bending combined with C–N stretching at  $1583 \text{ cm}^{-1}$ .

#### 3.2. SEM micrographs of combination pigments

The SEM micrographs of the copper phthalocyanines coated mica-titania (CuPhM) pigments at different temperatures are shown in Fig. 3. On the surface of the mica-titania pigments rod-like crystallites with variable sizes can be observed in different samples. A discussion on structural analysis of these rods will be given in Section 3.5. In order to determine quantitatively the increase in the lengths of the rods, the average lengths of the crystallites were calculated and the results are presented in Table 1. It is worth mentioning here that there is a growth trend in the sizes of the rods with an increase in reaction temperature.

In Fig. 4, the SEM micrographs of TCuPhM synthesized at different temperatures are shown. In the SEM micrographs evidence of formation of TCuPhM pigment crystallites could not be found since there was no obvious morphological difference between the pigment coated surfaces and the pristine mica-titania surfaces. The crystallite growth may have been prevented by the amide branches of TCuPh.

#### 3.3. Elemental analysis of combination pigments

Nitrogen elemental analyses were performed for the combination pigments in order to determine the effect of temperature on the deposition of copper phthalocyanines onto the mica-titania substrates. Table 2 shows mass percentages of CuPh and TCuPh pigments on the substrate at different temperatures. A significant increase in the amount of CuPh on the substrate occurred with the increase of temperature. However, the amount of CuPh was found to decrease slightly at  $120^\circ\text{C}$  compared to that at  $90^\circ\text{C}$ ; probably some desorption occurs at  $120^\circ\text{C}$ . Although equal moles of TCuPh and CuPh were used in the combination pigment synthesis, lower amounts of TCuPh deposited on the substrate. Furthermore, the

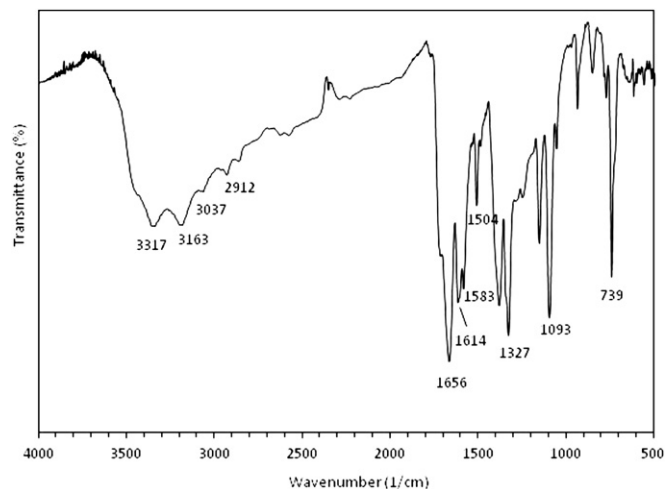


Fig. 2. FT-IR spectrum of tetracarboxamide copper phthalocyanine (TCuPh).

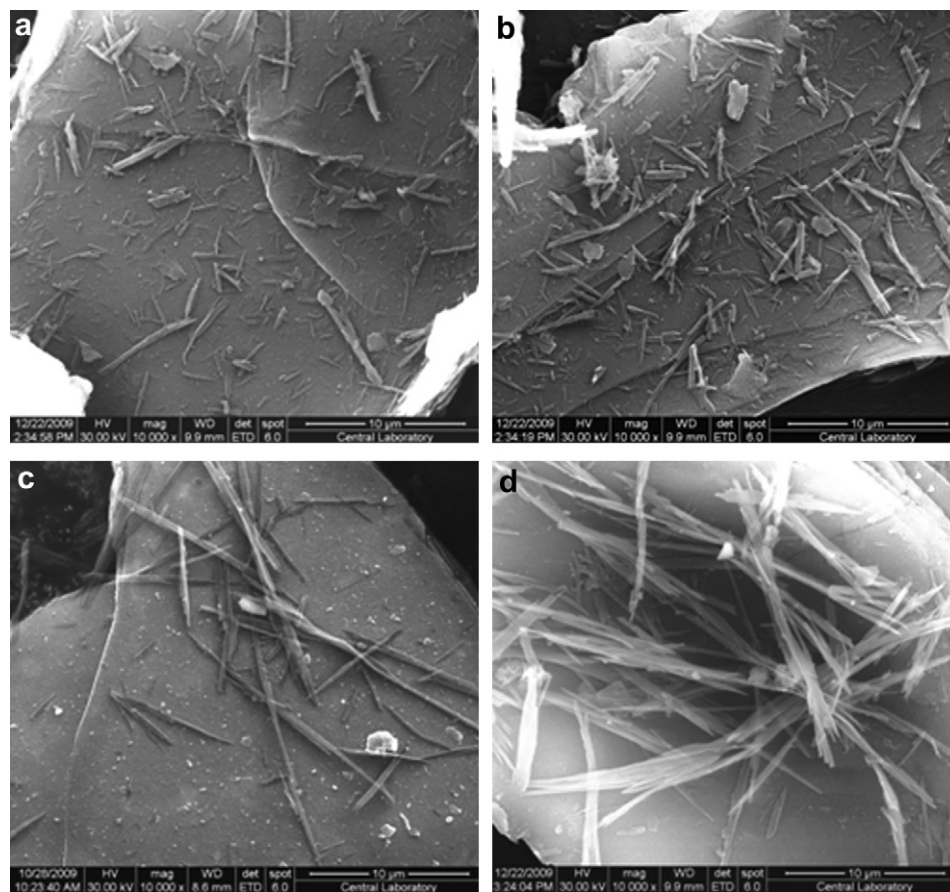


Fig. 3. SEM micrographs of CuPhM at (a) 25 °C, (b) 60 °C, (c) 90 °C, (d) 120 °C.

amount of deposition of TCuPh as a function of temperature was inconsistent (Table 2).

### 3.4. FT-IR spectra of combination pigments

The peaks appearing at  $1190\text{ cm}^{-1}$ ,  $941\text{ cm}^{-1}$ ,  $871\text{ cm}^{-1}$ ,  $864\text{ cm}^{-1}$ ,  $771\text{ cm}^{-1}$ , and  $723\text{ cm}^{-1}$  in the IR spectrum in Fig. 1 confirms that CuPh synthesized is in  $\alpha$ -phase [9]. However, peaks corresponding to the  $\beta$ -phase can also be seen with very small intensity at  $779\text{ cm}^{-1}$  and  $984\text{ cm}^{-1}$ . In the case of the CuPhM pigments, a peak shift was observed with increasing temperatures. Fig. 5 shows the FT-IR spectra of CuPh and CuPhM pigments in  $700\text{--}900\text{ cm}^{-1}$  range.

The most distinguishable peaks of CuPh corresponding to  $\alpha$ - and  $\beta$ -forms are at  $723$ , and  $729\text{ cm}^{-1}$ , respectively [9]. The CuPh is found to be in the  $\alpha$ -phase on mica-titania pigment when deposited at  $25\text{ }^{\circ}\text{C}$  as confirmed by the  $\alpha$ -peak at  $723\text{ cm}^{-1}$ . As the deposition temperature is increased to  $60\text{ }^{\circ}\text{C}$ , the peak at  $723\text{ cm}^{-1}$  broadened and created an additional peak at  $729\text{ cm}^{-1}$ . In fact, this broadened peak contains both  $\alpha$ - and  $\beta$ -peaks. In other words, both  $\alpha$ - and  $\beta$ -

forms of CuPh are deposited onto the substrate at  $60\text{ }^{\circ}\text{C}$ . At  $90\text{ }^{\circ}\text{C}$  and  $120\text{ }^{\circ}\text{C}$ , only  $\beta$ -peaks could be observed at  $729\text{ cm}^{-1}$ , and in addition, a  $\beta$ -peak at  $781\text{ cm}^{-1}$  was also present.

Fig. 6 shows the FT-IR of TCuM pigments synthesized at different temperatures. The peaks of TCuM were hardly distinguishable, because, very small amounts of TCuPh deposited on the substrates. The polymorphic form of TCuPh powder was found to be  $\alpha$ -phase which was confirmed by peaks at  $769\text{ cm}^{-1}$ , and  $723\text{ cm}^{-1}$ . The peak at  $723\text{ cm}^{-1}$  became significant when the broad peak at  $739\text{ cm}^{-1}$  was deconvoluted. The peaks observed at  $739\text{ cm}^{-1}$  and  $715\text{ cm}^{-1}$  belong to the out of plane deformation of the macrocycle. In TCuM pigments, no  $\alpha$  and  $\beta$  peaks of TCuPh were observed at the temperatures the experiments carried out. So it can be interpreted that the TCuPh formed an amorphous structure on the mica-titania substrate.

### 3.5. XRD analysis of combination pigments

In Fig. 7, the XRD peaks of CuPh located at  $2\theta = 6.86^{\circ}$ ,  $9.74^{\circ}$ , and  $15.6^{\circ}$  all belong to the  $\alpha$ -form. A small peak due to the  $\beta$ -form is present at  $2\theta = 9.16^{\circ}$ . At  $25\text{ }^{\circ}\text{C}$ , the CuPh pigment on the surface of the mica-titania showed pure  $\alpha$ -polymorphic phase with peaks at  $2\theta = 6.82^{\circ}$  and  $15.68^{\circ}$ . When the reaction temperature was increased to  $60\text{ }^{\circ}\text{C}$ , tiny peaks of  $\beta$ -phase were also observed in the pattern. This feature suggests that the CuPh on the mica-titania substrate begins to transform to the  $\beta$ -form at this temperature. In fact it was stated in the literature that the metastable  $\alpha$ -polymorph tends to transform to the stable  $\beta$ -form by thermal treatment or by exposure to some organic solvents [12]. When the

**Table 1**  
Average length of CuPh rods at different temperatures.

Sample	Average length of rods ( $\mu\text{m}$ )
CuPhM ( $25\text{ }^{\circ}\text{C}$ )	2.50
CuPhM ( $60\text{ }^{\circ}\text{C}$ )	3.63
CuPhM ( $90\text{ }^{\circ}\text{C}$ )	6.09
CuPhM ( $120\text{ }^{\circ}\text{C}$ )	10.94

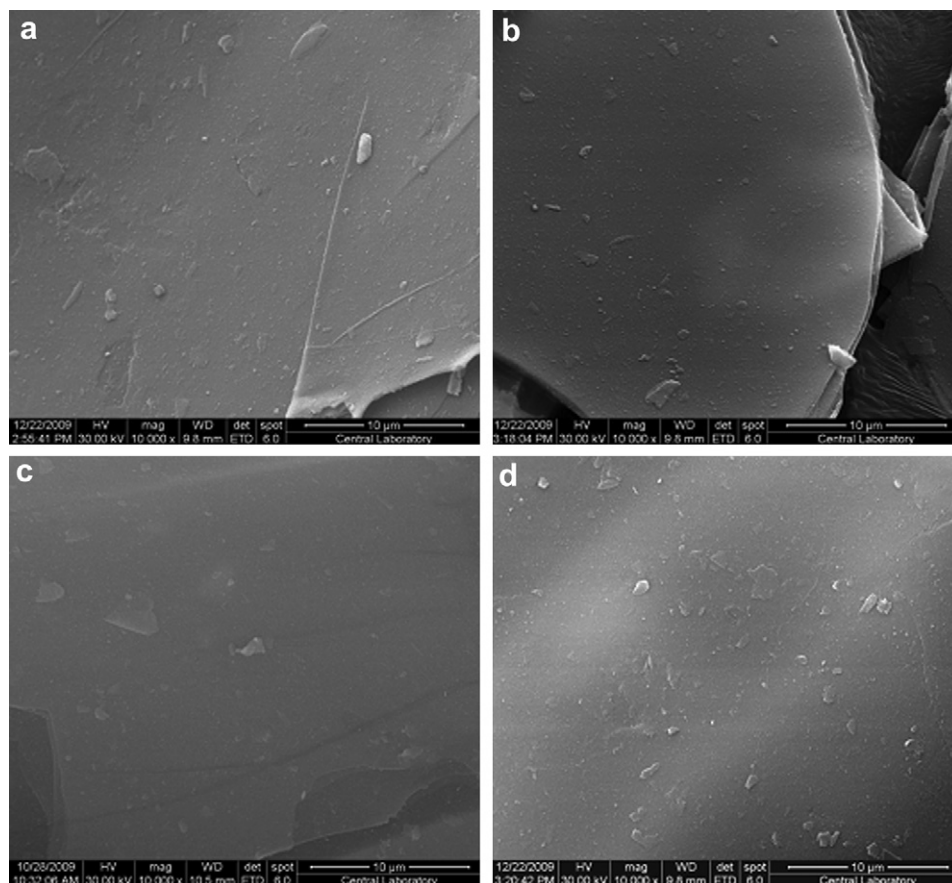


Fig. 4. SEM micrographs of TCuPhM at (a) 25 °C, (b) 60 °C, (c) 90 °C (d) 120 °C.

temperature was further increased to 90 °C, the peaks that are ascribed to the  $\alpha$ -crystalline form disappeared, and the  $\beta$ -peaks showed up distinctly at  $2\theta = 7.02^\circ$  and  $9.16^\circ$ . At 120 °C, the  $\beta$ -crystalline form is also identifiable at  $2\theta = 6.98^\circ$  and  $9.14^\circ$  from the precise analysis of data, as, these peaks cannot be clearly seen in Fig. 7.

The XRD patterns of TCuPh pigment show a structure similar to the  $\alpha$ -polymorphic form of CuPh and peaks appear at  $2\theta = 6.88^\circ$ ,  $7.22^\circ$ , and  $15.9^\circ$  as seen from Fig. 8. While the former one is identifiable, the latter two are less significant. Upon deconvolution of  $2\theta = 5^\circ$ – $10^\circ$  range, extremely broad and small peaks at  $2\theta = 6.88^\circ$  and  $7.22^\circ$  were identified. The most intense peak located at  $2\theta = 5.58^\circ$  corresponds to an interplanar spacing of  $d = 15.83 \text{ \AA}$ . This peak is the third peak that is obtained in the deconvolution of the  $2\theta = 5^\circ$ – $10^\circ$  range in the Peakfit software. It is thought to be the (200) plane of TCuPh. Such a peak is expected to appear at  $2\theta = 6.88^\circ$  which corresponds to a smaller interplanar spacing of

$d = 12.88 \text{ \AA}$ . A shift to the larger interplanar spacing between the (200) planes could be due to an increase of distance between TCuPh molecules affected by amide side groups.

When the XRD pattern of TCuPhM pigments was investigated, no peaks could be clearly detected. So, it is clear that the TCuPh deposited on mica-titania substrate had an amorphous structure at all deposition temperatures. This may be because the amide groups prevented ordering (stacking) of molecules as crystals on the

Table 2  
Mass percentages of CuPh and TCuPh pigments on mica-titania.

Sample	Phthalocyanine (mass%)
CuPhM (25 °C)	4.26
CuPhM (60 °C)	7.30
CuPhM (90 °C)	8.12
CuPhM (120 °C)	7.76
TCuPhM (25 °C)	3.08
TCuPhM (60 °C)	0.71
TCuPhM (90 °C)	1.83
TCuPhM (120 °C)	1.92

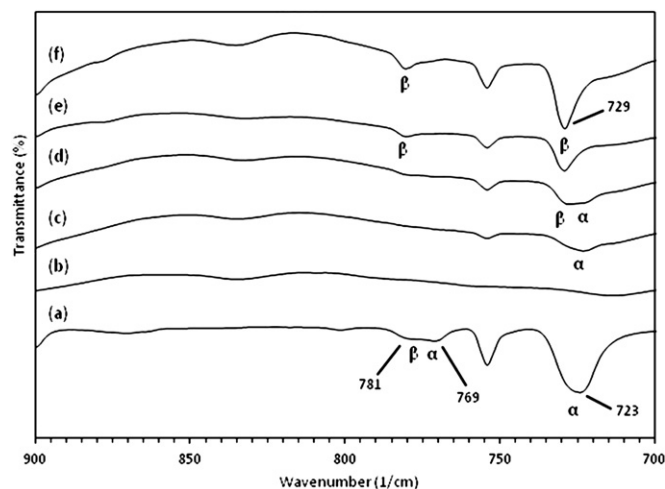


Fig. 5. FT-IR spectra of (a) CuPh, (b) Mica titania, CuPhM pigment at (c) 25 °C, (d) 60 °C, (e) 90 °C, (f) 120 °C.

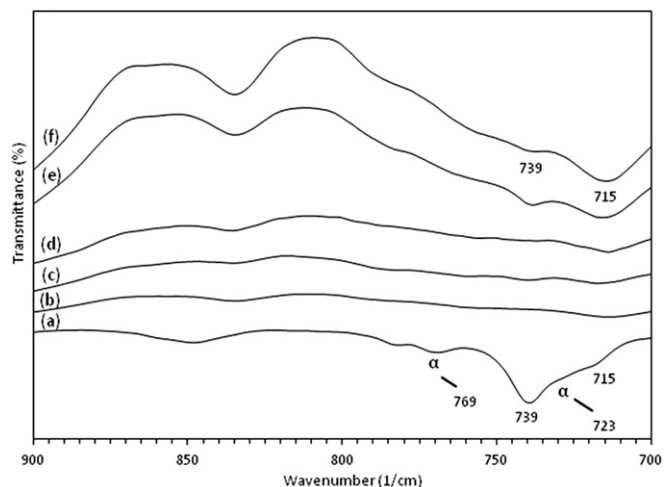


Fig. 6. FT-IR spectra of, (a) TCuPh, (b) Mica titania, CuPhM pigment at (c) 25 °C, (d) 60 °C, (e) 90 °C, (f) 120 °C.

substrate by increasing the distance between the molecules. On the contrary, the interaction between the TCuPh molecules and mica-titania substrate must have been greater than the interaction of TCuPh molecules among themselves. This would lead to higher adhesive force between the deposit and the substrate. Accordingly, deposition is expected to occur at a higher nucleation rate yielding an amorphous fine-grain structure in the growth stage.

### 3.6. Optical properties

CuPhM and TCuPhM pigments synthesized at 90 °C were used in an alkyd resin to study their optical behavior. The paint formulation was given in Section 2.4. The gloss values were measured at angles of 25°, 60°, and 85° which are the three basic angles used in the measurements. In order to examine the effect of process conditions on optical properties the amount of CuPh or TCuPh dissolved in DMF was varied. CuPh was changed between 0.005 and 0.040 g

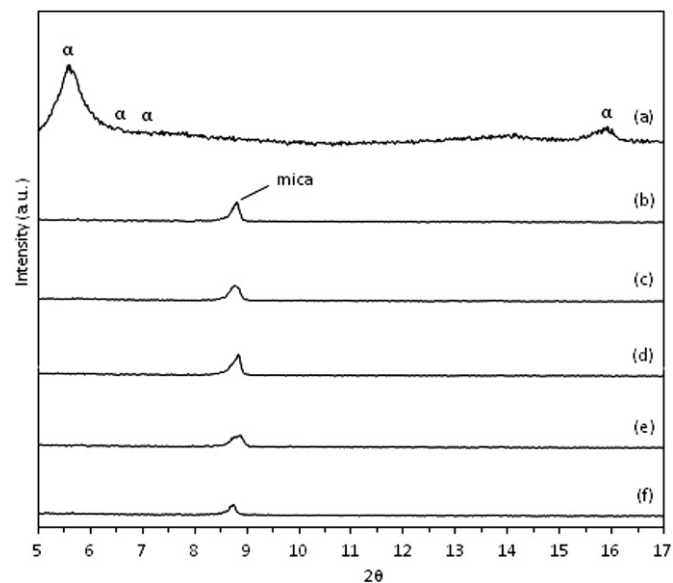


Fig. 8. XRD patterns of (a) TCuPh, (b) Mica titania, TCuPhM pigment at (c) 120 °C, (d) 90 °C, (e) 60 °C, (f) 25 °C.

whereas TCuPh was changed between 0.0065 and 0.052 g. In all the characterizations given above CuPhM specimen prepared by using 0.040 g CuPh and TCuPhM specimen prepared by using 0.052 g TCuPh were used (see Section 2.2.2.1).

The dependence of gloss on the initial amount of CuPh or TCuPh used in the synthesis of combination pigments is given in Table 3 where the numbers after the symbols indicate the initial amounts - used. Small quantities of CuPh (or TCuPh) increase the gloss of titania-mica pigment at all scattering angles. The increased amount of CuPh (or TCuPh) may cause absorption of light which in turn causes a decrease in gloss.

The  $L^*a^*b^*$  is an important parameter for the characterization of optical properties of the pigments; specifically,  $L^*$  is the lightness,  $a^*$  is red or green, and  $b^*$  is yellow or blue; that is,  $a^*$  and  $b^*$  are color opponent dimensions.  $dL^*$ ,  $da^*$  and  $db^*$  indicate how much a standard and a sample differ from one another in  $L^*$ ,  $a^*$  and  $b^*$ .  $dE^*$  represents the total color difference found from Euclidean distance, such that,

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

$\Delta E^* \approx 2.3$  corresponds to a noticeable difference. In Table 4,  $dL^*$ ,  $da^*$ ,  $db^*$  and  $dE^*$  values are given for each pigment. The increase of the initial amount of CuPh or TCuPh used in the synthesis increases the  $dL^*$ ,  $da^*$ ,  $db^*$  and  $dE^*$  values reaching the highest values at the highest amounts of CuPh and TCuPh, i.e. in CuPhM040 and

Table 3  
Gloss values of paints including CuPhM and TCuPhM pigments.

Specimen	25°	60°	85°
Mica-titania (Rutile)	48.5	75.7	75.8
CuPhM 005	58.7	79.6	80.8
CuPhM 010	56.7	78.9	78.8
CuPhM 020	50.7	78.5	77.6
CuPhM 040	49.8	78.0	77.2
TCuPhM 0065	59.8	84.9	87.6
TCuPhM 0130	48.0	75.2	58.0
TCuPhM 0260	47.3	74.8	50.1
TCuPhM 0520	45.9	74.0	45.3

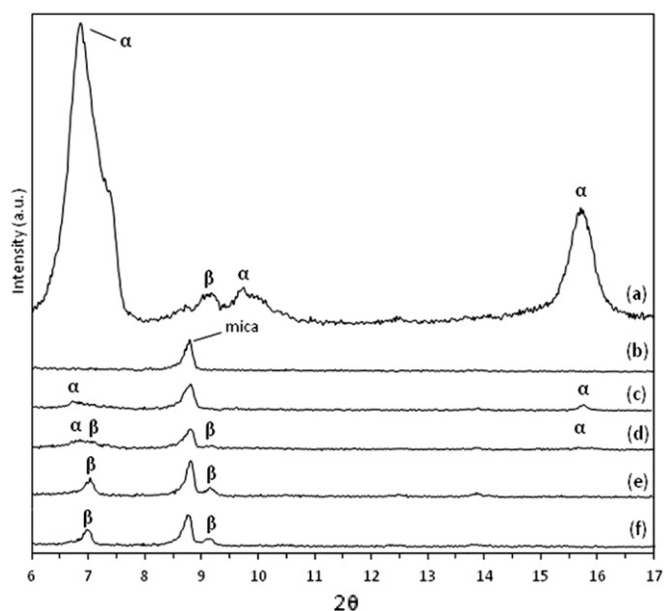
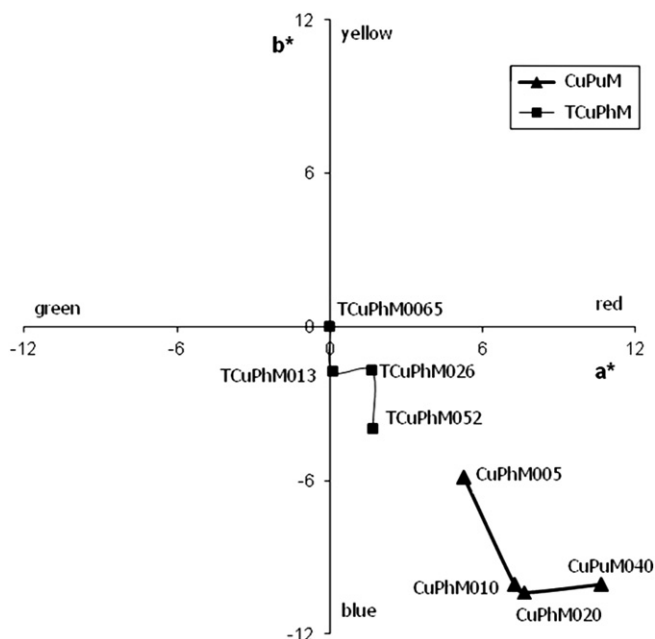


Fig. 7. XRD patterns of, (a) CuPh, (b) Mica titania, CuPhM pigment at (c) 120 °C, (d) 90 °C, (e) 60 °C, (f) 25 °C.

**Table 4**The  $dL^*$ ,  $da^*$ ,  $db^*$ , and  $dE^*$  values of paints containing combination pigments.

Specimen	$dL^*$	$da^*$	$db^*$	$dE^*$
TCuPhM0065 (standard)	0.00	0.00	0.00	0.00
TCuPhM0130	0.00	0.10	-1.73	1.74
TCuPhM0260	-2.13	1.65	-1.70	3.18
TCuPhM0520	-5.12	1.69	-3.97	6.00
CuPhM005	-3.80	5.26	-5.87	8.75
CuPhM010	-8.92	7.23	-10.07	15.28
CuPhM020	-11.48	7.61	-10.38	17.25
CuPhM040	-16.09	10.66	-10.06	21.77

**Fig. 9.** The comparative color properties of combination pigments based on different phthalocyanine deposition.

TCuPhM052, respectively. It is clearly seen that CuPhM040 has a much stronger effect on the change of color than TCuPhM040.

The change of comparative color properties can be better seen from Fig. 9 where the pigments were located on an  $a^*b^*$  diagram. In all of the foregoing characterizations the TCuPhM pigments are stationed around the origin whereas the CuPh pigments appear in the far blue–red zone of the diagram. In fact CuPh was a blue pigment whereas TCuPh was green. The carboxamide groups located on the phthalocyanine shifted the color from blue to green.

#### 4. Conclusions

Combination pigments were synthesized by depositing CuPh and TCuPh pigments onto mica–titania substrate. CuPh pigment crystallites formed on the mica–titania surface at all temperatures studied. The stable  $\beta$ -CuPh form was achieved on the surface of CuPhM pigment at deposition temperatures of 90 °C and 120 °C. On the other hand, amorphous TCuPh structure was obtained on the surface of TCuPhM pigment at all temperatures. The resulting

combination pigments depicted enhanced gloss especially at lower amounts of depositions.

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