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Optimization of the Electrical Conductivity of Copper Phthalocyanine Based Ink Applicable by Screen Printing on Textile Materials

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ABSTRACT

We report results on the conductivity of conductive ink based on copper phthalocyanine (CuPc), which contain different organic solvents, i.e. dimethylsulfoxide (DMSO) or Tetrahydrofuran (THF), and with different percentage of copper phthalocyanine. Conductive inks were prepared from the copper phthalocyanine by dispersion of the condcutive pigment in a screen printing paste. A variety of patterns have been developed with different percentages of CuPc on a cotton substrate using the screen printing technique. Simultaneously, the presence of solvent residue in the printed pattern also resulted in poor control of the morphology and the conductivity of the pattern. The solvent effect on copper phthalocyanine dispersion was studied by UV visible spectroscopy and the minimum resistance of printed circuit board was reached at about 3% of CuPc in THF and DMSO with 1 MΩ/cm and 1.8 MΩ/cm respectively.

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Introduction

Copper phthalocyanine and related macrocycles have attracted considerable attention as molecular materials that have exceptional electronic and optical properties. These electronic characteristics have driven the utilization of CuPc in many applications apart from pigmentation, ranging from gas sensing, to organic transistors, solar cells and organic light, using recent technology like screen and inkjet printings [1-4]. This type of techniques is usually used for printing electrical devices previously cited on several substrates including textiles to develop electronics materials, giving rise to the idea of electronic textiles. The progress of the current technology requires the application of printing technologies because of their low cost, environmental advantages as well as the possibility of large scale production. Several research works were interested in the formulation of conductive printing inks which shows the interest of the latter in the world of research and development. Different types of conductive inks based on nanomaterials have been developed for electronic and flexible applications. Among these types, graphene and silver nanoparticles based conductive inks are considered the most popular in the printing field [5, 6]. To the best of our knowledge, there is not much research work on the formulation of conductive inks based on conductive macromolecules. Copper phthalocyanine is among these types of compounds characterized by an attractive combination of electrical and thermal conductivity as well as chemical and thermal stability [7]. These characteristics show a significant sufficiency that make possible the use of phthalocyanine in printed electronics.

In the preparation of copper phthalocyanine conductive inks, solvents are necessary factors in with the aim to maintain the desired viscosity and dispersion of the fillers for each type of ink. Water and organic solvents such as, ethanol, N, N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP) and dimethylsulfoxide (DMSO) are widely used solvents for ink formulation [8]. These solvents are generally characterized by a high boiling point, i.e. > 150°C which limits their use in plastic and ceramic substrates. Therefore, dispersion of phthalocyanine in alternative low boiling solvents such as Tetrahydrofuran (THF) is favored to increase the applicability of copper phthalocyanine ink on temperature sensitive substrates such as textile fibers. Based on these explanations, the choice of dispersion solvent is a key parameter in ink formulation, as well as being a determining parameter to achieve the desired ink conductivity.

The purpose of this study was to examine the properties of conductive copper phthalocyanine inks prepared with different solvents and printed on a cotton substrate by screen printing technique. The conductive ink was annealed at 150°C for 3 minutes. Two solvents were used, namely THF and DMSO, in order to examine the effect of solvent on the dispersion of copper phthalocyanine and on the conductivity of conductive inks. In addition, the colorimetric properties of the conductive copper phthalocyanine pattern are provided in this study.

Experimental Work

Materials

A cotton-based fabric (100%) with a unit mass/area of 89.2g/cm^2 and a thickness of 0.04 mm was used as the textile substrate. The copper phthalocyanine ($C_{32}H_{16}N_8Cu$) is supplied by TIANKI. THF and DMSO used in this study, were obtained from Sigma-Aldrich. The screen printing paste was purchased from ARGOPRINT.

Methodology

For the preparation of screen printing ink based on copper phthalocyanine, different masses of CuPc were dispersed in THF and DMSO. The ultrasonic assisted dispersion process was used for the dispersion of CuPc. Table 1 shows copper phtalocyanine based conductive ink formulations.

Table 1: Copper Phthalocyanine Based Conductive Ink Formulations

Ink label	DMSO (ml)	Printing Paste (g)	CuPc (g)
I_1	10	30	0.25
I_2	-	-	0.75
I_3	-	-	1.25
I_4	-	-	1.75
I_5	-	-	2.5
Ink label	THF (ml)		
I_1'	10	-	0.25
I_2'	-	-	0.75
I_3'	-	-	1.25
I_4'	-	-	1.75
I_5'	-	-	2.5

Characterization

The study of the vibrational properties of chemical bonds constituting copper phthalocyanine was performed by RAMAN spectroscopy. The RAMAN spectra were recorded in the range of 200 to 3300 cm^{-1} using a Thermo Fisher DXR2 RAMAN spectrometer equipped with a helium-neon (He-Ne) laser source (λ= 633 nm; 8mW). The analysis of the dispersion of copper phthalocyanine under the effect of the solvent was carried out using a UV-vis spectrophotometer (Thermo Fisher Scientific TM Evolution TM 300) by scanning the absorption maxima solution at wavelengths between 300 and 700 nm. For the study and the characterization of cotton samples printed with copper phthalocyanine ink, the measurements are carried out with the DATACOLOR spectrocolorimeter and are systematically conducted in parallel with visual observations. The experimental results are then presented in tabular form. The electrical conductivity was measured according to the safety standard NF EN 61010-1 + NF EN 61010 2-030, relating to electronic measuring instruments using two points method with the Multimeter MTX 3292.

Results and Discussion

Before proceeding with the formulation, the properties of copper phthalocyanine employed in the present study are listed in Table 2.

Table 2: Physical Properties of CuPc

Density (g/cm^3)	1.7
Moisture (%)	≤1.0
Water Soluble Matter	≤1.5
Oil Absorption (ml / 100g)	35-45
Electric conductivity (µS/cm)	≤500
Residue on 325 mesh sieve (Wet method)PPM	≤80
Magnetic on 325 mesh sieve (Wet method)PPM	≤8
PH Value 7-9	7-9

RAMAN spectroscopy analysis was performed to study the chemical structure, as well as any vibrational properties potentially in copper phthalocaynine. As CuPc is formed by four isoindole rings, its Raman spectrum (Figure 1) is mainly characterized by macrocycle vibrational peaks up to 1000 cm^{-1} correspond to the vibrations of the isoindole moieties and pyrrole groups (between 1200 and 1600 cm-1), while the peak at 1522 cm^{-1} which is caused by the displacement of the C-N-C bridge bond corresponds to the copper metal ion of the Pc molecule [9].

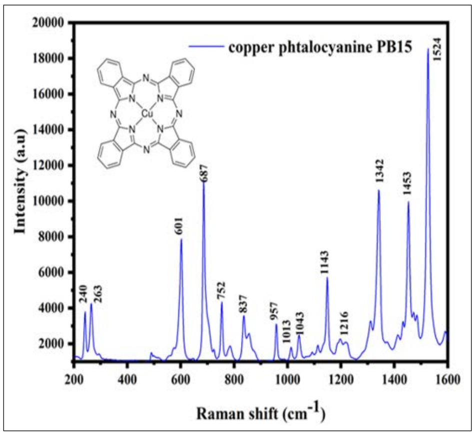

Figure 1: RAMAN Spectrum of CuPc

The dispersion quality of phthalocyanine was analyzed by UV-vis spectroscopy, in order to choose the suitable solvent to use for its dispersion. The solvents that were used in this analysis are DMSO and THF. The UV-visible spectrum obtained (Figure 2) shows the appearance of a wider band in the range of 300 to 500 nm for CuPc dispersed in DMSO, while CuPc dispersed in THF represents a less wide and more intense peak in the same wavelength range located precisely at 340 nm. In this case, they are B bands located in the near ultraviolet region representing the CuPc orbital transition [10]. The spectrum also shows the appearance of other bands in the range of 600-700 nm for both solvents. These bands correspond to the Q-type absorption bands that result from the π-π* transition [11]. It is also observed that in this region the solvent DMSO represents a single characteristic peak located at 660 nm whose intensity is low. However, THF represents two characteristic peaks the first one is located at 590 nm and the second one at 660 nm, the latter being the most intense, therefore, it can be concluded that the best solvent to be used for dispersing CuPc is THF. These results were also confirmed by calculating the molar absorption coefficient of different solvents studied from the Beer-Lambert law (Table 3).

Table 3: ε values of the solvents used

Solvants	[CuPc] (mol/l)	Absorbance	ε (l mol^{-1} cm^{-1})
DMSO	$1.7*10^{-3}$	0.26	152.94
THF	$1.7*10^{-3}$	0.82	482.35

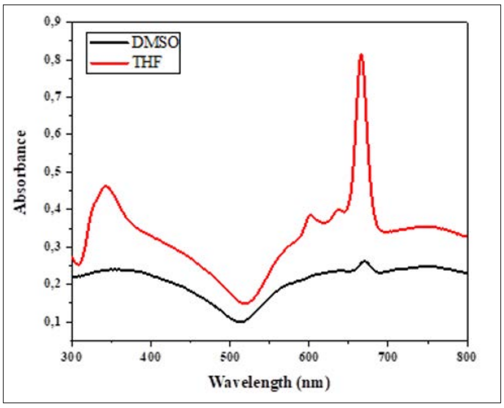

Figure 2: UV-Visible Spectrum of CuPc

The spectropolarimeter permitted us to identify the parameters L*, a* and b* of the printed samples. Knowing the properties L*, a* and b* which correspond to the two samples, it is possible to evaluate the difference between color 1 and color 2 as below:
ΔL* = L*(CuPc/THF) - L*(CuPc/DMSO)
Δa* = a*(CuPc/THF) - a*(CuPc/DMSO)
Δb* = b*(CuPc/THF) - b*(CuPc/DMSO)
$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1\backslash 2}$

The significance of the color differences is shown in (Table 4) [12].
In our case, the reference sample is cotton printed by CuPc dispersed in DMSO (Table 5).

Table 4: Color Differences Interpretation

Color Differences	Positive	Negative
ΔL*	The sample is clearer	The sample is darker
Δa*	The sample is redder or less green	The sample is greener and less red
Δb*	The sample is yellower or less blue	The sample is yellower or less blue

The color differences (Tables 6) of the samples show that the samples printed by CuPc dispersed in THF are darker than the samples printed by CuPc dispersed in DMSO (Figure 3). These results indicate that CuPc is well dispersed in THF.

Table 5: Color Differences Obtained for Cotton Printed by CuPc/DMSO and CuPc/ THF Formulated Paste

CuPc/ DMSO	Parameters			CuPc/THF	Parameters		
	L*	a*	b*		L*	a*	b*
I1	68.54	-14.01	-21.71	I_1'	56.97	-12.01	-24.39
I2	55.70	-15.37	-32.44	I_2'	47.50	-12.32	-26.94
I3	55.93	-15.98	-29.22	I_3'	28.43	0.42	-23.52
I4	60.48	-15.61	-23.86	I_4'	32.48	-2.37	-24.40
I5	60.05	3.02	-22.26	I_5'	30.28	-1.82	-24.50

Table 6: Comparison Between Cotton Printed by CuPc/DMSO and CuPc/ THF Formulated Paste

Differences	ΔL*	Δa*	Δb*	ΔE
Value	Negative	Positive	Negative	Positive
Comment	- ΔL* < 0 The cotton printed by CuPc dispersed in THF is darker than that printed using CuPc in DMSO	- Δa* > 0 The sample containing CuPc dispersed in THF is redder than the one containing CuPc dispersed in DMSO	- Δb* < 0 The sample screened by CuPc dispersed in THF is bluer than the one screened by CuPc dispersed in DMSO	- ΔE shows that the cotton whose screen paste contains CuPc dispersed in THF is darker than the sample containing the same concentration of CuPc dispersed in DMSO

From the results obtained, it can be seen that the cotton samples printed by CuPc dispersed in THF are darker than those printed by CuPc dispersed in DMSO for all concentrations used. These results confirm the UV-visible spectroscopy results obtained earlier regarding the choice of the proper solvent to be used for CuPc dispersion and therefore it can be deduced that THF is the proper solvent for CuPc dispersion.

In order to study the variation of the resistance of cotton samples printed by screen printing pastes containing as filler CuPc dispersed in DMSO and THF respectively with different mass of CuPc, resistance measurements were performed. The results were presented in a table that groups the resistance values for all the formulations (Table7). For the CuPc dispersed in DMSO, it can be seen that the resistance is inversely proportional to the weight of CuPc, this is apparently due to the conductivity of the filler contained in the paste. Concerning the CuPc dispersed in THF we observe that the resistance decreases until a certain value of weight of the CuPc which is equal to 1,25 g then it stabilizes at 1 MΩ/cm. This can be explained by the fact that when the value of the weight of the charge reaches a threshold value, the dispersion of the CuPc becomes random which consequently causes a disturbance in the mobility of the electronic charge carriers. This disturbance is manifested by a stability or a decrease of the conductivity when the amount of charge increases [13].

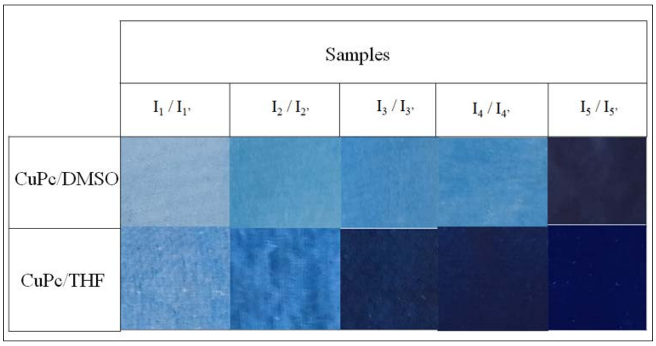

Figure 3: Optical Images of Printed Samples

Table 7: Resistance Values for the Different Types of Formulation

Ink label	Resistance (MΩ/cm)	Ink label	Resistance (MΩ/cm)
I_1	6,28	I_1'	1,67
I_2	4	I_2'	1,5
I_3	3,83	I_3'	1
I_4	2,28	I_4'	1
I_5	1.8	I_5'	1

Conclusion

In this study, conductive inks based on copper phthalocyanine were fabricated by dispersing CuPc in two different solvents. The conductive inks based on CuPc dispersed in THF showed better dispersion than that dispersed in DMSO. The electrical resistance decreased with increasing mass of CuPc. These results indicate that the conductive copper phthalocyanine ink dispersed in THF used by screen printing method can be applied more effectively on textile due to the low boiling temperature of THF. Our future work focuses on the elaboration of composite ink based on copper phthalocyanine and other conductive element to make different conductive patterns which can be used more effectively to make different flexible electronic patterns on textile substrates.

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