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To cite this version:

W. Wacawek, M. Kulesza, M. Zibkowska. METALLIC CONDUCTIVITY OF COPPER PHTHALOCYANINE - CARBON BLACK COMPOSITES. Journal de Physique Colloques, 1983, 44 (C3), pp.C3-673-C3-676. <10.1051/jphyscol:19833131>. <jpa-00222643>

HAL Id: jpa-00222643
https://hal.archives-ouvertes.fr/jpa-00222643
Submitted on 1 Jan 1983

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METALLIC CONDUCTIVITY OF COPPER PHTHALOCYANINE - CARBON BLACK COMPOSITES

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Résumé - On a mesuré la conductivité électrique et l'effet thermoélectrique pour les composites : phthalocyanine de cuivre et noir de carbone. Pour quelques composites le caractère métallique est confirmé.

Abstract - Electrical conductivity and thermoelectric power for copper phthalocyanine - carbon black composites were measured. For some composites metallic behaviour was found.

I - INTRODUCTION

There are several ways to obtain organic materials of high conductivity - some of them make use of phthalocyanines, which are close analogues of natural pigments: chlorophyll and hemin.

The direct way is to synthesize pure, low-molecular weight conducting compounds like bis(phthalocyaninato) neodymium complex /1/. Ukei /2/ obtained one-dimensional conductor by preparing lead phthalocyanine thin film samples in a special way (usually, lead phthalocyanine is a typical organic semiconductor).

Hamann /3/ and Füstös-Wegner /4/ revealed switching phenomenon for lead and metal-free phthalocyanine thin films. High conducting state for these samples can be obtained, if field strength of definite value is applied.

One can make conductivity higher by polymerization of monomeric phthalocyanine /5/ using a bidentate linear bridging ligand e.g. pyrazine, 4,4'-bipyridine, 1,4-diisocyanobenzene, oxygen, cyanide (CN⁻) or acetylide (C≡C⁻).

Partial reduction or oxidation also leads to preparation of highly conducting phthalocyanine derivatives. The best results are due to oxidation with iodine, single crystals of nickel phthalocyanine treated with iodine become even metallic conductors e.g. /6/.

It is interesting to note, that electrical conductivity of the oxidized polycrystalline material is lower than that of the single crystal and has thermally activated character.

In this laboratory treatment of phthalocyanines by iodine to produce highly conducting samples has been carried out for a couple of years /7/. We have doped copper, cobalt, nickel and lead phthalocyanines. Their conductivities rose many orders of the magnitude as compared with the undoped materials, but were still thermally activated. Moreover the materials prepared at room temperature are not stable because of iodine desorption.

In order to have thermally and chemically stable highly conductive materials we have prepared composites of copper phthalocyanine and acetylene carbon black of different compositions. The electrical properties of the composites have not been determined.
investigated yet, but in the case of polyester resin–acetylene carbon black composites metallic conductivity is observed /8/ in spite of the fact, that the material studied is noncrystalline.

II - EXPERIMENTAL

Copper phthalocyanine (denoted BSL) produced by Wola Krzysztoporska works (Poland) and acetylene carbon black were used for the investigation. The samples (of 0%, 0.1%, 1.0%, 2.4%, 3.0%, 6.0%, 8.3%, 10.0%, 17.0%, 20.0% and 30.0% wt of carbon black) were compressed (at pressure of 10^8Pa) to make pellets of 8 mm and 10 mm in diameter. Samples were prepared by grinding the components of known percentage in agate mortar. Silver paint (DAG 1415 Acheson, Holland) was used as contacting agent. The electrical conductivity and thermoelectric power were measured as a function of temperature using arrangement previously described /7,9/. For samples with evaporated silver electrodes an apparatus with pressing contacts was used. Measurements of electrical conductivity and thermoelectric power were carried out on electrometers Cary 401 (USA) and Keithley 616 (USA), Semi-automatic RLC bridge type E 314 (Meratronik, Poland) and Digital Voltmeter type V 534 (Meratronik, Poland). The ac conductivity was measured with bridges: 4270A (Hewlett Packard, USA), General Radio 1620 (USA) and Wayne Kerr E 602 (G.B).

III - RESULTS AND DISCUSSION

The electrical conductivity, $\sigma$, and thermal activation energy of conductivity, $E_a$, were found to be strongly dependent on acetylene carbon black content, $%C$, Fig. 1 and 2, respectively.

![Fig. 1](image1.png)  
*Fig. 1*  

![Fig. 2](image2.png)  
*Fig. 2*
Fig. 1 - Electrical conductivity, $\sigma_{25}$ (at 298,15 K) of the composites as a function of carbon black content, %C (in weight %).

Fig. 2 - Thermal activation energy, $E_a$, of the composites as a function of carbon black content, %C (in weight %).

The electrical conductivity dependence on carbon black content can be divided into the region in which conduction occurs via separate particles (up to 4%C) and the region typical for conduction through the adjacent carbon black particles. The shape of this curve changes sharply by using carbon black differing in grain size.

It is interesting to note the linear dependence of thermal activation energy of conductivity on carbon black content (Fig. 2). For all the samples studied Seebeck coefficient was positive, as for undoped copper phthalocyanine - indicating holes as dominant charge carriers.

For samples of the carbon black content higher than 10% wt electrical conductivity was nearly independent of temperature and for the content as high as 30% wt metallic behaviour occurs in spite of the fact, that electrical conductivity of the both components is thermally activated.

The metallic behaviour was in an accordance with the Seebeck coefficient dependence on temperature - for the samples with carbon black content of 17% wt and higher, it had small positive value which increased with temperature. However, for samples with evaporated silver electrodes the conductivity was slightly thermally activated even for samples with 30% wt of carbon black.

It should be noted, that electrical conductivity of the silver paint alone was measured and found to be independent of temperature. The investigations of the electrical conductivity as well as the mobility of charge carriers for the composites are in progress. The ac conductivity for samples with small content of carbon black was strongly dependent of frequency. Starting from 6% wt of carbon black the dependence became to be weaker and for the composition containing 10% wt of carbon black was nearly independent of frequency. This behaviour, it may be a sign of the presence of conducting paths in the materials.

There are some similarities between copper phthalocyanine doping with carbon black and oxidation with iodine: a big rise in conductivity which is greater than that of the components, and small positive Seebeck coefficient. Moreover for samples doped with carbon black no influence of iodine was found. That is why we propose to interpret the influence of phthalocyanine doping with carbon black as well as with iodine to have got similar molecular mechanism. Probably in both cases conduction process occurs via conducting paths formed between carbon black particles and iodine chains respectively, as one can conclude due to dc and ac conductivity data.
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