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PURIFYING METAL POLYPHTHALOCYANINES

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This invention relates to a method of removing excess metal from a metal polyphthalocyanine by electrolysis and this application is a continuation-in-part of copending application Serial No. 12,916, filed March 7, 1960 and now abandoned.

In copending application Serial No. 696,027, filed November 13, 1957 and now Patent No. 3,245,965, there is taught a method of making metal polyphthalocyanines comprising heating pyromellitonitrile in the presence of a metal salt. In this process a certain amount of unreacted metal salt will normally remain in the product metal polyphthalocyanine. This excess metal contaminant in the form of a metal salt is very difficult to remove from the product metal polyphthalocyanine by normal purification technique such as solvent extraction.

It has now been found that this metal contaminant and the anion with which it is combined in salt form can be removed from the metal polyphthalocyanine by a method of electrolysis to give a much purer metal polyphthalocyanine than is obtainable by conventional solvent extraction techniques. In this electrolysis method the metal polyphthalocyanine to be purified is inserted as an anode in the electrolyte of the electrolysis system. The direct current voltage in the electrolysis system or cell is adjusted to plate out the metal contaminant on the negative electrode of the system thereby removing it from the metal polyphthalocyanine.

It is a primary object of this invention to provide an improved method of purifying metal polyphthalocyanines.

These and other objects of the invention will become apparent as the detailed description of the invention proceeds.

In copending application S.N. 696,027, filed November 13, 1957, and now Patent No. 3,245,965, there is shown in detail the making of copper polyphthalocyanines. This same method is applicable to the making of other metal polyphthalocyanines, e.g., zinc, iron, cobalt, nickel, palladium, platinum, manganese, chromium, molybdenum, vanadium, beryllium, magnesium, silver, mercury, aluminium, tin, lead, antimony and cadmium polyphthalocyanines, etc. The method of this invention is applicable to the removal of excess metal from metal polyphthalocyanines wherein the metal does not react readily with water at ambient temperatures of about 20°–25° C., i.e. metals such as alkali metals, calcium and barium are excluded, since the water-reactive metals cannot be removed from the electrolysis bath by plating out on the cathode as can other metals.

The invention will be more clearly understood from the following detailed description of a specific example thereof:

Example 1

This example illustrates the preparation, purification and testing of a copper polyphthalocyanine.

In a bomb was placed 16 grams of pyromellitonitrile, 53 grams of cuprous chloride and 2 grams of urea. This mixture of materials was heated under 1,000 p.s.i.g. of nitrogen for 24 hours at 350° C. At the end of the 24 hour reaction period the material was taken from the bomb. Except for one piece of the material which was taken from the granular product, the balance of the material was ground to a powder using a motar and pestle. The powdered material was placed in a Soxhlet

apparatus and extracted with pyridine for 7 days, except that at the end of 3 days an intermediate treating step was used on the material, i.e., after 3 days the material was taken out of the Soxhlet apparatus, washed consecutively with dilute hydrochloric acid, water and pyridine, and put back in the extractor. At the end of the 7 day period of Soxhlet extraction the extracts were colorless. The solid material removed from the Soxhlet extractor was dried and reground. The reground material was next sublimed at 0.5 mm. of Hg and 300° C. for 24 hours. Very little, if any, material sublimed out. An elemental analysis of this residue product was as follows:

Calc'd for $C_{20}H_4N_8Cu$: C, 57.2%; H, 1.0%; N, 26.7%; Cu, 15.1%. Found: C, 43.6%; H, 1.8%; N, 19.9%; Cu, 20.4%; Cl, 7.5%; O, 6.8%.

A sample of the copper polyphthalocyanine product preparation of which is described in the previous paragraph was purified by electrolysis in the following manner: A solid chunk of the copper polyphthalocyanine was sawed to give a rectangular wafer having the dimensions 4 x 1.3 x 1.8 mm. A hole was drilled in one end of this wafer about one-third of the length thereof and a platinum wire was inserted therein forming a tight slip fit with the wafer. A portion of the wafer adjacent the platinum wire and a portion of the platinum wire was coated with polyethylene wax to insulate it electrically, thus forming the anode for an electrolytic cell. The cathode for the electrolytic cell was a rod of carbon which had a platinum lead attached thereto. A beaker was used as the container for the cell and a normal hydrochloric acid solution as the electrolyte therefor.

The platinum lead of the copper polyphthalocyanine anode and the platinum lead of the carbon cathode were connected to a battery source. With the anode and cathode inserted in the electrolyte, voltage was applied to the cell of about three to four volts varying the voltage to maintain the current flowing through the cell between about 10 and 30 milliamperes. The voltage source as has been indicated by the labeling of the electrodes was connected with the positive terminal being connected to the copper polyphthalocyanine anode or positive electrode and the negative terminal to the carbon cathode or negative electrode. Electrolysis was carried on for about 64 hours at room temperature, i.e. about 20–25° C. It was noted that copper plated out on the carbon. The weight of the copper polyphthalocyanine wafer before electrolysis was 3.275 grams; however, the weight was not determined after electrolysis. The weight of the copper plating out on the carbon electrode was 0.702 gram.

A sample of the electrolyzed copper polyphthalocyanine was treated in the following manner to prepare it for analysis and electrical testing: The sample was washed thoroughly with water, then with acetone. The material was then dried and extracted in a Soxhlet extractor for two days with acetone followed by extraction for two days with water. In each of these extractions a small amount of copper salt was removed as detected with dilute ammonium hydroxide. Also in these extractions, some almost colorless cream-colored material was removed. The sample was then dried and subjected to vacuum sublimation at 300° C./0.07 mm. of Hg for three days. In the sublimation treatment a small amount of white material was removed. The residue product from the sublimation treatment was now a purple color. An elemental analysis of this purple product was as follows:

Calc'd for $C_{20}H_4N_8Cu$: C, 57.2%; H, 1.0%; N, 26.7%; Cu, 15.1%. Found: C, 50.9%; H, 2.6%; N, 19.4%; Cu, 12.2%; Cl, 0.3%.

A sample of the material prepared as described in the paragraph immediately above was next subjected to electrical testing as follows: A sample (1.4 mm. in depth) of the material in powdered form was placed in an up-

right hollow cylindrical quartz cell having an inner diameter of about ¾". The quartz cell was resting in an upright position on a platinum plate which acted as a seal for the lower end of the cylinder. After the powdered sample had been added to the cylinder, a cylindrical slug of platinum was placed on top of the powder within the quartz cylinder. Pressure was exerted via the platinum slug to the extent of 900 grams/square centimeter on the powdered material. To make the electrical measurements at various temperatures heat was applied by conduction through the bottom platinum plate to the powdered sample. Electrical connections were made to the platinum plate and platinum slug and resistance measurements were made across the cell at the various temperatures.

The following is a summary of the electrical characteristics of the sample showing resistivity vs. temperature and 1000/T.

Temp. (T), ° C.	1000/T	Resistivity, ohm-cm.
280	1.81	5.6×10^{3}
259	1.88	8.0×10^{3}
245	1.93	1.0×10^{4}
235	1.96	1.1×10^{4}
221	2.02	1.3×10^{4}
210	2.07	1.4×10^{4}
200	2.11	1.6×10^{4}
190	2.16	1.7×10^{4}
180	2.21	1.9×10^{4}
170	2.26	2.2×10^{4}
160	2.31	2.4×10^{4}
150	2.36	2.8×10^{4}
140	2.42	3.2×10^{4}
130	2.48	3.6×10^{4}
120	2.55	4.4×10^{4}
110	2.61	5.2×10^{4}
100	2.68	6.4×10^{4}
90	2.76	7.8×10^{4}
80	2.83	9.8×10^{4}
70	2.92	1.3×10^{5}
60	3.00	1.6×10^{5}

The purified metal polyphthalocyanines which are products of the process of the invention are useful as semiconductors in thermoelectric devices, photoelectric devices, point contact rectifiers, thermistors, resistors, infrared detectors, power rectifiers, transistors, etc.

Although the invention has been described in terms of a specified embodiment which is set forth in considerable detail, it should be understood that this is by way of illustration only and that the invention is not necessarily limited thereto, since alternative embodiments and operating techniques will become apparent to those skilled in the art in view of the disclosure. Accordingly modifications are contemplated which can be made without departing from the spirit of the described invention.

What is claimed is:

1. A method of removing excess metal which does not react readily with water from a metal polyphthalocyanine comprising electrolyzing said metal polyphthalocyanine as a positive electrode in an electrolysis system using an applied direct current voltage sufficient to cause the metal to plate out on the negative electrode.

2. The method of claim 1 wherein said metal polyphthalocyanine is copper polyphthalocyanine.

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