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DRAWINGS ATTACHED

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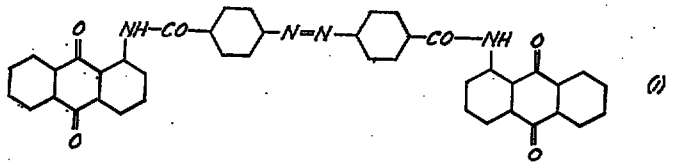
(72) Inventors DR. KLAUS EHRHARDT, DR. GEORGE GEIGER and DR.FRITZ KEHRER

(54) AN ANTHRAQUINONE PIGMENT AND THE PROCESS OF ITS PRODUCTION

(71) We, SANDOZ LTD. of Lichtstrasse 35, Basle, Switzerland, a Body Corporate organised according to the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the β-modification of 4,4'-bis-(α-anthraquinonylaminocarbonyl)-azobenzene, which in pigment applications, especially in the pigmentation of plastic materials, exhibits substantially better properties than the known α-crystal modification.

It has been found that the β-crystal modification of the pigment of formula



(I)

which is characterized by three specific lines in the X-ray spectrum (Cu-$K_{\alpha 1}$ radiation) at angles of diffraction of approximately 10.33°, 11.2° and 11.6° has considerably more valuable pigmentary properties than the known α-modification, which in Cu-$K_{\alpha 1}$ radiation has an X-ray spectrum showing a characteristic line at an angle of diffraction of approximately 8.4° (θ according to Bragg). The β-crystal modification lacks this characteristic line at angle of diffraction of approximately 8.4°.

The method of producing the α-crystal modification of the pigment of formula (I) is known and is described, inter alia, in United States Patent 2,228,455. The transformation of the α-modification thus formed into the β-crystal form of the present invention is effected by grinding at temperatures in excess of 100°C, preferably at 150° to 180°C.

The treatment is carried out preferably in the presence of grinding assistants, in particular inert inorganic salts, e.g. common salt, Glauber's salt, potassium ferrocyanide or calcium carbonate. On completion of grinding these assistants are washed out with water, if necessary in the presence of an acid. Any abraded iron present can be removed with a dilute acid. Grinding generally takes from 5 to 100 hours, or more particularly 40 to 60 hours, and can be carried out in any of the machines normally used for this purpose, including ball and roller mills and vibratory grinding equipment.

The pigment thus obtained, in comparison with the unground pigment and the same pigment ground at a lower temperature, is notable by reason of its enhanced brilliance and greater tinctorial strength. It is virtually insoluble in the commonly used organic solvents. Its rheological properties are very good. Applications for which it is suitable include the dyeing of paper in the stock, the pigmentation of plastics in the mass, by which are understood materials, which may be dissolved, containing plastics or synthetic resins, and of natural resins and rubber, and the printing of textiles and paper.

[*Price 25p*]

On these substrates, to which it is applied in accordance with the known methods, the pigment shows outstandingly good fastness to light, washing, chlorite, hypochlorite and peroxide bleaching, hydrosulphite, cross dyeing, blind vats, dry cleaning, rubbing, overlacquering and solvents. The heat stability and transparency are good.

In the following Examples the parts and percentages are by weight and the temperatures are given in degrees centigrade.

EXAMPLE 1

75 Parts of the pigment of formula (I), obtained in accordance with Example 1 of U.S. Patent 2,228,455, are entered, along with 600 parts of dry common salt, into an iron ball mill equipped with iron balls of about 2.5 cm diameter totalling 7000 Parts and an iron chain. In about 3 hours the mixture in the mill is raised to 150° by an external air bath and is then ground for 48 hours at about 90 r.p.m. and an air bath temperature of 150°. The iron balls are separated from the mixture and this is stirred into water, after which the pigment is filtered off and washed free of residual salt.

If an excessive amount of iron is ground off from the equipment during the process, it can be dissolved out of the aqueous pigment suspension with a hydrochloric acid solution of about 5% strength. For further purification the pigment can be treated with Javelle water in the normal way. After a final wash with distilled water, the pigment is vacuum dried at 60—90° and ground again, e.g. in a pin disk mill.

A pale yellow powder is obtained which pigments polyvinyl chloride in brilliant greenish yellow shades.

If the pigment of formula (I) obtained in accordance with Example 1 of U.S. Patent 2,228,455 is suspended in acetone and ground at room temperature it yields a pigment exhibiting duller and reddish yellow shades in polyvinyl chloride.

The pigment ground under the action of heat, i.e. the β-crystal modification, is distinguished from the unground pigment and the α-crystal modification formed by grinding at room temperature, by the presence of three specific lines in its X-ray spectrum (Cu-$K_{\alpha 1}$ radiation) at an angle of diffraction of 10 to 12°, viz. at angles of diffraction of approximately 10.33°, 11.2° and 11.6°. The unground pigment and the pigment ground at ambient temperature do not differ from each other in their X-ray spectra, each having a line at a diffraction angle of approximately 8.4°, which is absent in the spectrum of the pigment modification of this invention.

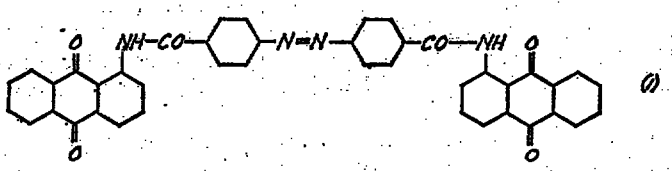
EXAMPLE 2

A mixture of 10 g. of the starting pigment as used in Example 1 and 100 g. of dry common salt is charged on to an iron triple roll mill of about 1.2 litres capacity, each of the three rolls being about 4 cm. in diameter and weighing about 1.3 kg. After an air bath has raised the mixture to 180° it is ground at this temperature for 60 hours at approximately 85 r.p.m. and subsequently it is worked up as described in Example 1. A pale yellow powder is obtained which has exactly the same properties as the final pigment of Example 1.

Figure 1 shows the X-ray spectrum of the β-modification and Figure 2 that of the α-modification. The intensity of the lines is plotted on a relative scale and the Bragg angle of deflection θ is given in degrees.

WHAT WE CLAIM IS:—

1. The β-crystal modification of the pigment of formula



which lacks the characteristic X-ray spectrum (Cu-$K_{\alpha 1}$ radiation) for the corresponding α-crystal modification at an angle of diffraction of approximately 8.4° and which is characterized by three specific lines in the X-ray spectrum (Cu-$K_{\alpha 1}$ radiation) at angles of diffraction of approximately 10.33°, 11.2° and 11.6°.

2. A process for the production of the β-crystal modification of the pigment of formula

On these substrates, to which it is applied in accordance with the known methods, the pigment shows outstandingly good fastness to light, washing, chlorite, hypochlorite and peroxide bleaching, hydrosulphite, cross dyeing, blind vats, dry cleaning, rubbing, overlacquering and solvents. The heat stability and transparency are good.

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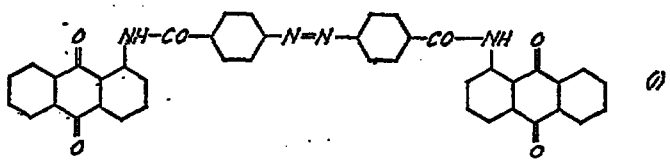
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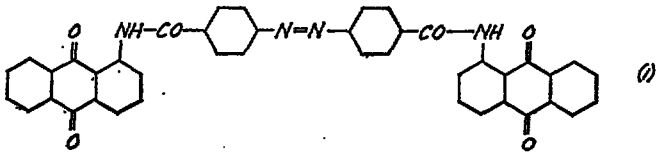


(I)

which lacks the characteristic X-ray spectrum (Cu-$K_{\alpha 1}$ radiation) for the corresponding α-crystal modification at an angle of diffraction of approximately 8.4° and which is characterized by three specific lines in the X-ray spectrum (Cu-$K_{\alpha 1}$ radiation) at angles of diffraction of approximately 10.33°, 11.2° and 11.6°.

2. A process for the production of the β-crystal modification of the pigment of formula

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(I)

which is characterised by submitting the α-crystal modification of the pigment of formula (I), produced in accordance with the known process, to grinding at temperatures above 100°C.

3. A process according to claim 2 substantially as herein described and exemplified.

4. The product of a process according to claim 2 or claim 3.

5. A dyeing or printing process in which a pigment according to claim 1 or claim 4 is used to dye paper in the stock, to pigment plastics in the mass or natural resin or rubber, or to print textiles or paper.

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Chartered Patent Agents,
70—72 Chancery Lane,
London, W.C.2.,
Agents for the Applicants.

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