PATENT SPECIFICATION

NO DRAWINGS

Inventor: DR. HELMUT MOSER

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1,185,791

1,185,791

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No. 1546/68.
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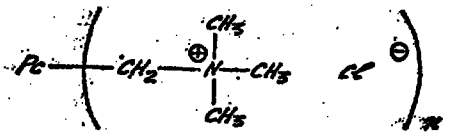
International Classification: —C 09 b 47/08

COMPLETE SPECIFICATION

The Use of Copper Phthalocyanines with Trimethyl-Ammonium-Methyl Groups as Paper Dyes

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:—

The compounds of formula

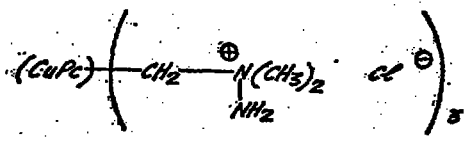


(I)

where Pc stands for the radical of a copper phthalocyanine free from sulphonic acid groups or containing an average of up to 0.5 sulphonic acid radicals in the molecule and n for 2 or 3, are known dyes. They are used for dyeing cotton and according to the literature these dyeings must be fixed with heat. It has been found that the compounds of formula (I) are particularly suitable for dyeing sized and unsized papers in the stock before sheet formation. The dyes are readily soluble in water. The dyed papers made from paper pulp dyed with a dye of formula (I) are of brilliant shade and outstandingly fast, with particularly good wet fastness. The light fastness is good and after a long period of exposure to light the shade fades tone-in-tone.

The dyes of formula (I) can be converted into concentrated aqueous dye solutions containing 25 to 55 parts of 100% dye of formula (I) in 100 parts of water. Alternatively the dye solutions may contain 25 to 120 parts of the 100% dye of formula (I) and 1 to 45 parts of a carboxylic acid amide in 100 parts of water. The amount of the carboxylic acid amide is chosen so that the dyes of formula (I) form solutions. Urea is the preferred carboxylic acid amide.

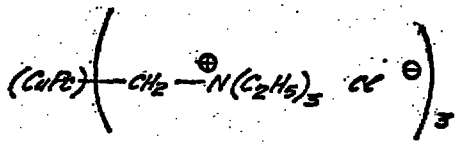
The use of the dye of formula



a)

for dyeing paper is known from French Patent 1,377,708. It was surprising that the dyes of formula (I) are more highly soluble in water than this dye, particularly at room temperature. Owing to this better solubility, the dyes of formula (I) can be marketed in the form of concentrated aqueous solutions (stock solutions), which is of great advantage for the continuous dyeing of paper. This also eliminates the troublesome dusting occurring in the weighing out of dyes in powder form.

In German Patent 812,945 the dye of formula



b)

is described as a dye not easily soluble in water. It was therefore particularly surprising that the dyes of formula (I) are readily soluble, even in cold water.

[*Price 5s. 0d.*]

SEE ERRATA SLIP ATTACHED

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The dyes of formula (I) can be produced, for example, in accordance with United States Patent 2,435,307 or German Patent 843,726 by chloromethylation of copper phthalocyanine which is either free from sulphonic acid groups or contains an average of up to 0.5 sulphonic acid groups per molecule and subsequent reaction with trimethylamine.

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

Example 1

70 parts of chemically bleached sulphite cellulose are mixed with 30 parts of chemically bleached birch cellulose and 0.2 parts of the dye bis-,trimethylammoniummethyl)-copper phthalocyanine chloride in aqueous solution. After 10 minutes the stock is formed into an absorbent sheet of paper. It is dyed in a turquoise shade of medium depth and although the paper contains no sizing or fixing agent the dye is so well fixed that the backwaters from the paper machine are colourless. The dyeing is wet-fast.

Example 2

100 parts of chemically bleached sulphite celluose are beaten in a beater, during which operation 2 parts of resin milk and shortly afterwards 0.5 parts of an aqueous solution of a mixture of the dyes bis- and tris-(trimethylammonium-methyl)-copper phthalocyanine chloride are added. After 10 minutes 3 parts of aluminium sulphate are added and after a further 10 minutes the paper sheet is formed. The paper is dyed in a bright turquoise shade of medium depth; the dyeing is fast to light and wet treatments.

Example 3

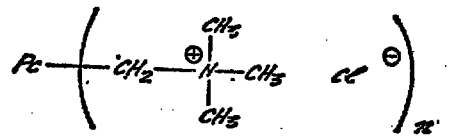
95 parts of tri-(chloromethyl)-copper phthalocyanine are added in small portions over 3 hours to a mixture of 230 parts of water and 76 parts of 32% aqueous trimethylamine solution at 40°. Stirring is continued for 5 hours to give a dye solution of thin consistency with a dye content of approximately 30%. The same procedure can be followed using 165 parts of water, on which a concentrated aqueous solution is obtained containing about 35% of 100% dye. The solution can thus be adjusted to any desired concentration by the addition of water, although concentrated solutions containing 25—55 parts of 100% dye in 100 parts of water are best.

Example 4

95 parts of tri-(chloromethyl)-copper phthalocyanine are added in small portions over 3 hours to a mixture of 95 parts of water and 76 parts of 32% aqueous trimethylamine solution at 40°. After stirring for 5 hours a highly viscous solution is obtained. On the addition of 10% urea, calculated on the total amount of the solution. It is converted into a dye solution of low viscosity with a dye content of approximately 40%.

WHAT WE CLAIM IS:—

1. A process for dyeing paper pulp with a dye of formula



(I)

where Pc stands for the radical of a copper phthalocyanine which is free from sulphonic acid groups or contains up to 0.5 sulphonic acid radicals in the molecule and n stands for 2 or 3.

2. A concentrated aqueous dye solution containing 25 to 55 parts of the 100% dye of formula (I) in 100 parts of water.

3. A concentrated aqueous dye solution containing 25 to 120 parts of the 100% dye of formula (I) and 1 to 45 parts of a carboxylic acid amide in 100 parts of water.

4. Paper pulp dyed with a dye of formula (I) according to claim 1 and paper made therefrom.

5. Solutions according to claim 3 containing urea as carboxylic acid amide.

6. A process for dyeing paper pulp with a dye of the formula (I) substantially as herein described and as illustrated in any of Examples 1 and 2.

7. The dyeing process conducted substantially as described in Examples 1 and 2 herein.

8. Concentrated aqueous dye solutions substantially as herein described and as illustrated in Example 3 or Example 4.

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ERRATUM

SPECIFICATION NO. 1,185,791

Page 1, Index at acceptance:- *for* "CH P" *read* "C4 P"

THE PATENT OFFICE,
6 May 1970

R 123995/14

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Example 3

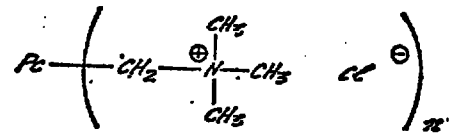
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