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HALOGENATED PHTHALOCYANINE
DISULFONIC ACIDSAndré Pugin, Basel, Switzerland, assignor to J. R.
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The subject of this invention is halogenated phthalocyanin disulphonic acids containing heavy metals, particularly copper and nickel, which are distinguished from similar known compounds by an increased affinity to cellulose fibres, and also the manufacturing process therefor.

The production of sulphonated heavy metal-containing phthalocyanins of the benzene series which are derived from phthalonitrile is known. The copper and also the nickel compounds are chiefly distinguished from the various heavy metal compounds of the phthalocyanins which serve as starting materials for the sulphonation, by the valuable shades of their sulphonic acids. According to the kind of sulphonating agent, the duration of reaction and temperature, products are obtained on sulphonation which either contain altogether 4 sulphonic acid groups, i. e. possibly one in each benzene ring, or less, for example only 3, 2, or 1 sulphonic acid group. While the higher sulphonated products have no practical significance for the dyeing of textiles according to the usual methods, the disulphonic acids, particularly, possess the quality of dyeing cellulose fibres directly, and their alkali metal salts have sufficient water solubility for dyeing purposes. However, the copper phthalocyanin disulphonic acid for example, in comparison with the generally used direct cellulose dyestuffs shows only a limited affinity, poor take-up and very bad wet fastness properties. When employed according to the usual dyeing procedure for direct dyestuffs, i. e. by dyeing from a dye liquor containing Glauber's salt, up to 50% of dyestuff, according to the desired deepness of shade, is not taken up by the fibres. However, in spite of this, it has attained a great practical significance due to the very pure luminous sky blue nuance which can not be achieved in this purity and fastness to light with any of the known direct cellulose dyestuffs.

There has been no lack of endeavour to improve the bad take-up of these interesting metal-containing phthalocyanin sulphonic acids. These include, for example, the conversion of the sulphonic acid groups into sulphonate amino groups, their complete or partial substitution by carboxyl groups, or the use of diphenyl for building up the phthalocyanin sulphonic acids. However, none of these suggestions has been of practical significance, because either the small degree of improvement did not justify the greater expense or because undesirable changes, particularly an undesired alteration in the shade towards green, becomes apparent.

In contrast to this, it has now been found that it is possible with technically simple agents to convert the heavy metal, particularly copper and nickel, phthalocyanin disulphonic acid compounds derived from the benzene compounds into products of undoubtedly improved substantivity without an important alteration of the shade. This can be achieved by halogenating them in an alkali chloride or aluminium chloride melt at temperatures from 120–220° C. until at least 2 and at most 7, preferably 4–6 halogen atoms have entered the dyestuff molecule. Preferably temperatures of 140–180° C. are used if the halogenation is effected with compounds giving off halogen. The halogenated copper and nickel-containing phthalocyanin disulphonic acids or their alkali salts so obtained on comparison with the starting material while showing only an unimportant alteration in the shade and maintaining complete brilliance of the shade, are distinguished by an improved affinity to natural cellulose fibres, particularly to cotton fibres. This increased affinity is shown mostly by the improved take-up which results in better exhaustion of the dye baths and also by improved water and washing fastness properties of cotton piece dyeings. In comparison with those dyeings produced from unhalogenated metal phthalocyanin sulphonic acids, the dyeings produced from the corresponding halogenated compounds show a much smaller alteration of the nuance on wet treatment and smaller migration of the dyestuff on damp pressing. Also, they often show an improved fastness to light. The new dyestuffs can be called the first really substantive copper and nickel-containing phthalocyanin disulphonic acids derived from compounds of the benzene series and are a valuable addition to the group of direct-drawing cotton dyestuffs.

The structural composition of the new halogenated metal-containing phthalocyanin disulphonic acids cannot be given exactly because even the position of the two sulphonic acid groups in the starting material is not known exactly. Nevertheless, with regard to the position of the halogen atoms which have been introduced, it has been ascertained that chiefly unsymmetrical halogenation takes place, as a yield of tetrachlorophthalimide of about 80% of the theoretical can be obtained from a product according to this invention containing 5 chlorine atoms, by degradation with nitric acid.

Chlorine or bromine are the most suitable halogens to use in the present process, and the former is to be preferred on account of its cheap-

ness. As halogenating agents either the molecular halogens themselves or other compounds with a halogenating action, such as sulphuryl chloride, can be used. The desired degree of halogenation can easily be secured by employing an appropriate reaction temperature throughout the duration of action of the halogenating agent, which may be several hours. The halogen content of the product depends upon the reaction time and the reaction temperature. By halogen analysis of the final product and by carrying out a series of tests the most convenient time and temperature to give a product having a halogen content within the desired limits are determined.

A process is already known for halogenating metal-containing phthalocyanin sulphonic acids by means of halogenating agents in an alkali chloride-aluminium chloride melt, which, however, is expressly limited to such phthalocyanin sulphonic acids as contain at least 3, and preferably 4, sulphonic acid groups in the molecule whereby, however, it is stated that if required the sulphonic acid groups can be split off. Repetition of this process has now shown that in this way, for example, from copper phthalocyanin tri- or tetra-sulphonic acids, products result which, when the shade remains unaltered, show no good affinity to cellulose fibres. Halogenation, e. g. chlorination must take place to such a degree in these higher sulphonated starting materials that when a good cellulose affinity and a high halogen content are obtained an alteration of the shade towards green has already taken place. That the products produced according to this process have attained no practical significance is confirmed in British Intelligence Objective Subcommittee (B105) Report No. 690, page 37.

In contrast to this, the present process employs starting materials which differ from those mentioned above by containing only two sulphonic acid groups and the halogenation is accomplished without splitting off the sulphonic acid groups. As a result of the new process there is only slight alteration in the shade with no loss of brilliance but with considerably improved affinity to cellulose fibres whereas by the previously known process there was no significant improvement in the already bad affinity for cellulose fibres.

The following examples illustrate the invention without limiting it in any way. Parts are given by weight and temperatures are in degrees centigrade.

Example 1

70 parts of the sodium salt of copper phthalocyanin disulphonic acid are added to a melt of 400 parts of aluminium chloride and 70 parts of sodium chloride and 100 parts of chlorine are introduced over a period of 6 hours at 170-175°. Then the liquid reaction mixture is poured on to a diluted hydrochloric acid solution made of 1200 parts of water and 300 parts of concentrated hydrochloric acid. The precipitated dyestuff is filtered off, washed with dilute hydrochloric acid and dried. In this way 50 parts of the dyestuff are isolated, the analysis of which corresponds to dichloro copper phthalocyanin disulphonic acid. This dyestuff is soluble in alkali and colours cotton in luminous blue shades of improved fastness to water in contrast to the copper phthalocyanin disulphonic acid dyestuffs. In comparison with the starting product, the drawing power is also improved.

Example 2

70 parts of copper phthalocyanin disulphonic acid are added to a melt of 400 parts of aluminium chloride and 31 parts of triethylamine and 200 parts of chlorine are introduced over a period of 6 hours at 140-145°. The mixture is then poured into a diluted hydrochloric acid solution made up from 1200 parts of water and 300 parts of concentrated hydrochloric acid. The precipitated dyestuff is then filtered and washed with dilute hydrochloric acid and dried. In this way 73.7 parts of the dyestuff are isolated consisting of a mixture of hexachloro and heptachloro copper phthalocyanin disulphonic acid, according to analysis. This dyestuff is soluble in alkali and colours cotton in luminous blue-green shades of improved fastness to light and water. In contrast to the starting product, the drawing power is also improved.

Example 3

180 parts of copper phthalocyanin disulphonic acid are added to a melt of 900 parts of aluminium chloride and 180 parts of sodium chloride, and 90 parts of chlorine are introduced over a period of 24 hours at 180-190°. The mixture is then poured into a dilute hydrochloric acid solution made up of 2900 parts water and 600 parts of concentrated hydrochloric acid. The precipitated dyestuff is then filtered off, washed with a dilute hydrochloric acid and dried. 184.7 parts of the dyestuff are isolated in this way which consists of trichloro and tetrachloro copper phthalocyanin disulphonic acid according to analysis. The dyestuff is soluble in alkali and dyes cotton in luminous blue-green shades of better light and water fastness than the dyeings from copper phthalocyanin disulphonic acid. It has a better drawing power in comparison to that of the starting material.

Example 4

50 parts of nickel phthalocyanin disulphonic acid are added to a melt of 300 parts of aluminium chloride and 60 parts of sodium chloride, and 150 parts of chlorine are introduced over a period of 8 hours at 160-165°. The mixture is then poured into a dilute hydrochloric acid solution made up of 1000 parts of water and 250 parts of concentrated hydrochloric acid. The precipitated dyestuff is then filtered off, washed with dilute hydrochloric acid and dried. 52.9 parts of the dyestuff are isolated in this way consisting, according to analysis, of a mixture of trichloro and tetrachloro nickel phthalocyanin disulphonic acid. This dyestuff is soluble in alkali and dyes cotton in greener shades than those obtained from copper phthalocyanin disulphonic acid. Here also, the drawing power and fastness to water are better than those of the starting product.

Example 5

50 parts of copper phthalocyanin disulphonic acid are added to a melt of 400 parts of aluminium chloride and 80 parts of sodium chloride, and 46 parts of bromine are dropped in over a period of 1 hour at 140-145°. The mixture is then heated for 5 hours at 140-145°. It is then poured into a dilute hydrochloric acid solution made up from 1200 parts of water and 300 parts of hydrochloric acid. The precipitated dyestuff is filtered off and washed with dilute hydrochloric acid and dried. 54.6 parts dyestuff are isolated in this manner, consisting chiefly of tribromo

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copper phthalocyanin disulphonic acid according to analysis. The dyestuff dissolves in alkali and has a better drawing power on cotton than the starting product.

Example 6

1 part of a mixture of 0.75 part of a chlorinated copper phthalocyanin disulphonic acid prepared according to Example 2 and 0.25 part of dehydrated sodium carbonate is dissolved in 100 parts of water. Then 2 parts of dehydrated sodium carbonate dissolved in 20 parts of water and 8 parts of sodium sulphate dissolved in 80 parts of water are added. The whole is then made up to 800 parts with hot water. 40 parts of cotton piece goods are then put into the dye liquor prepared in the above manner and are dyed for 1 hour at 90°. They are then rinsed in a salt solution made up from 5 parts sodium sulphate and 1000 parts of water and pressed. A pure blue-green dyeing is obtained with very good fastness to light and much improved wet fastness in comparison with the corresponding dyestuff containing no halogen. Also the drawing power on cotton piece goods is improved which is particularly shown on subsequent dyeings.

What I claim is:

1. A phthalocyanin dyestuff obtained from a halogen-free phthalocyanin disulfonic acid containing a metal selected from the group consisting of copper and nickel by reacting in an alkali chloride-aluminium chloride melt with a halogenating agent at a temperature between 120 and

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200° until from 2 to 7 halogen atoms have entered the dyestuff molecule.

2. A phthalocyanin dyestuff obtained from the copper compound of a halogen-free phthalocyanin disulfonic acid by reacting in an alkali chloride-aluminium chloride melt with a halogenating agent at a temperature between 120 and 200° until from 2 to 7 halogen atoms have entered the dyestuff molecule.

3. A phthalocyanin dyestuff obtained from the copper compound of a halogen-free phthalocyanin disulfonic acid by chlorinating in an alkali chloride-aluminium chloride melt at a temperature between 120 and 200° until from 2 to 7 chlorine atoms have entered the dyestuff molecule.

4. A phthalocyanin dyestuff obtained from the copper compound of a halogen-free phthalocyanin disulfonic acid by chlorinating in an alkali chloride-aluminium chloride melt at 170-180° until from 3 to 5 chlorine atoms have entered the dyestuff molecule.

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