PATENT SPECIFICATION

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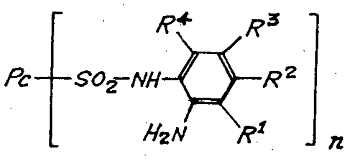
(54) PHTHALOCYANINE COMPOUNDS, PROCESS FOR THEIR PREPARATION AND THEIR USE AS DYESTUFFS

(71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt Main 80, Postfach 80 03 20, Federal Republic of Germany, 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 present invention relates to phthalocyanine compounds, a process for preparing them and their use as dyestuffs.

The present invention provides phthalocyanine compounds of the general formula (I)



(I)

in which Pc represents the copper, cobalt or nickel phthalocyanine radical which may be substituted by one or more substituents selected from halogen, such as chlorine and bromine, preferably chlorine, atoms, phenyl, sulfo, sulfanoyl and N-arylsulfonyl, such as N-phenyl-sulfanoyl group, mono and di-lower alkyl substituted sulfanoyl groups and N-arylsulfanoyl groups N-substituted by a lower alkyl group, R^1, R^2, R^3 and R^4, which may be same or different, each represents a hydrogen atom, a halogen, such as chlorine or bromine, atom, a lower alkyl group which may be substituted, for example by hydroxy, chlorine, carboxy, sulfo or sulfato, or represents an aryl, such as phenyl, radical, a lower alkoxy group which may be substituted in the alkyl radical, for example by lower alkoxy, or represents an aryloxy, such as phenoxy, group, a carboxy or carbamoyl group, a carbamoyl group which is mono- or di-lower alkyl substituted, a carbamoyl group which is mono amino substituted, an arylcarbamoyl such as phenylcarbamoyl, group, a cyano group, an alkoxycarbonyl group of 2 to 5 carbon atoms, an alkanoyl group of 2 to 5 carbon atoms, such as an acetyl or propionyl group, an alkanoyloxy group of 2 to 5 carbon atoms, a benzoyl or benzoyloxy group, a lower alkenylsulfonyl group, a lower alkylsulfonyl group which may be substituted in the alkyl radical, for example by chlorine, hydroxy, lower dialkylamino, sulfo, sulfato, phosphato or carboxy groups, or represents an arylsulfonyl, such as phenylsulfonyl, group, a sulfo or sulfanoyl group, a N-(lower alkyl)-sulfanoyl group which may be substituted in the lower alkyl radical, for example by chlorine, hydroxy, lower dialkylamino, sulfo, sulfato, phosphato or carboxy groups, or represents a N,N-di-(lower alkyl)-sulfanoyl group which may be substituted in one or both, preferably one, of the lower alkyl radicals, for example by chlorine, hydroxy, lower dialkylamino, sulfo, sulfato, phosphato or carboxy, or represents a N-methyl-N-phenyl-sulfanoyl group, a N-phenyl-sulfanoyl group, a trifluoromethyl or nitro group, a lower alkylsulfonylamino group which may be substituted in the lower alkyl radical, for example by chlorine, hydroxy, lower dialkylamino, sulfo, sulfato, phosphato or carboxy, or represents a N-(lower alkyl)-alkylsulfonylamino group which may be substituted in the lower alkyl radical which is present at the sulfonyl group, for example by chlorine, hydroxy, lower dialkylamino, sulfo, sulfato, phosphato or carboxy, or represents an alkanoylamino or alkenoylamino group having from 2 to 5 carbon atoms, a benzoylamino group which may be substituted by 1 or 2 substituents selected from chlorine atoms and lower alkyl, lower alkoxy, sulfo, sulfanoyl, carboxy, N-(lower alkyl)-sulfanoyl and N,N-di-(lower-alkyl)sulfanoyl groups, or represents an arylsulfonylamino, such as phenylsulfonylamino, group, or R^1 and R^4 are defined as above and R^2 and R^3 together represent the group —NH—CO—NH—, with the proviso that at least one, preferably two, especially three of four of R^1, R^2, R^3 and R^4 represents a hydrogen atom, and n is a number from 1 to 4, and salts thereof.

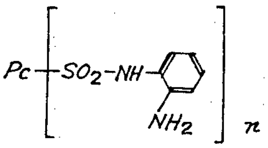
The term "lower" used in this specification means that the alkyl or alkenyl or alkylene radical contained in the group has from 1 to 4 carbon atoms.

If the compounds of the formula (I) contain anionic groups, they are present preferably in the form of their alkali metal salts, such as the sodium or potassium salts, or alkaline earth metal salts, such as calcium salts, or in the form of ammonium salts.

Preferred compounds are those of the formula (I), in which Pc represents the copper, cobalt or nickel phthalocyanine radical, especially the copper phthalocyanine radical, which compounds are unsubstituted in the phthalocyanine radical or substituted by sulfo in the 3- and/or 4-position of the respective aromatic carbocyclic ring in the phthalocyanine skeleton, in which n stands for a number of from 1.5 to 4 and R^1, R^2, R^3 and R^4 are identical or different and each is a hydrogen atom, a chlorine atom, a methyl, ethyl, methoxy, ethoxy, acetylamino, propionylamino, cyano, carboxy, ethoxycarbonyl, methoxycarbonyl, carbanoyl, N-methyl- or N-ethylcarbanoyl group, a N-phenylcarbanoyl group, a sulfanoyl, N-methyl-, N-ethyl-, N,N-dimethyl-; N,N-diethyl- or N-methyl-N-phenyl-sulfanoyl group, a methylsulfonyl, ethylsulfonyl, phenylsulfonyl, acetyl, propionyl, benzoyl, phenyl, β-hydroxy-ethylsulfonyl, β-chloro-ethylsulfonyl, β-sulfatoethylsulfonyl or β-sulfoethylsulfonyl group, a vinylsulfonyl group, a sulfanoyl group mono- or disubstituted at the nitrogen atom by a β-hydroxyethyl, β-sulfatoethyl or β-sulfoethyl group, or is an acetoxy, propionyloxy, benzoyloxy, phenoxy, trifluoromethyl, nitro, benzoylamino, methylsulfonylamino, ethylsulfonylamino or phenylsulfonylamino group or a phenylsulfonylamino group substituted in the nucleus by one or more, preferably 1 or 2, substituents selected from lower alkyl and lower alkoxy groups and chlorine atoms, with the proviso that at least 2, especially 3 or 4, of R^1, R^2, R^3 and R^4 each represents a hydrogen atom.

Of these compounds, especially the copper phthalocyanine compounds are interesting, which contain the orthoaminophenylene-sulfonamide radical(s) preferably in the 3-position of the carbocyclic aromatic phthalocyanine nuclei and in which one of R^1, R^2, R^3 and R^4 represents the cyano, carboxyu or carbanoyl group and the other three each stand for hydrogen, or in which each of R^1, R^2, R^3 and R^4 represents a hydrogen atom, and n is a number of from 2 to 4.

Preference is given in particular to phthalocyanine compounds of the formula



in which Pc has one of the above-mentioned meanings and n is a number of from 2 to 4, of these especially the compounds in which Pc stands for the copper phthalocyanine radical having one of the above-mentioned meanings.

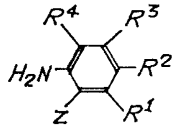
Particularly preferred are the compounds of Examples 3, 4, 20 and 23 with a sulfanoyl radical portion of 2 to 4.

Of all the above-specified compounds of the formula (I), preference is given especially to those which do not contain any anionic groups.

The present invention also provides a process for preparing a phthalocyanine compound of the general formula (I), which comprises reacting 1 mole of a phthalocyanine sulfochloride of the general formula (II)

$$Pc\text{-}(SO_2Cl)_m \qquad (II)$$

in which Pc is defined as above and *m* is a number of from 1 to 4 and is not less than *n*, as defined above, for the phthalocyanine compound, with *n* mole(s) of an amine of the general formula (III)



(III)

in which R^1, R^2, R^3 and R^4 are defined as above and Z represents an amino, lower alkanoylamino, benzoylamino or nitro group, and, 4 *m* is greater than *n* — simultaneously in this reaction or subsequently or, if Z has another meaning than the amino group, in one of the following process steps — hydrolyzing unreacted sulfonylchloride groups into sulfonic acid groups in a known manner; if Z represents one of the above-mentioned acylamino groups, the condensation product obtained is deacylated in a known manner, in which process sulfonylchloride groups which may still be present are simultaneously hydrolyzed into sulfo groups, or, if Z represents a nitro group, the condensation product obtained is reduced in a known manner to give the compound of the above-specified formula (I), in which process sulfonylchloride groups which may still be present are simultaneously or subsequently hydrolyzed to give sulfo groups.

The deacylation to be optionally effected is to be carried out while considering that the sulfanoyl bond having been formed in the preceding reaction, needs to be maintained; the deacylation is therefore carried out accordingly while applying analogous methods known for such cases, for example by heating with dilute aqueous sodium hydroxide solution at a pH value of from 8 to 10 and at a temperature in the range of from 30 to 50°C.

The reduction of the nitro group to be optionally carried out may also be effected in an analogous manner to known processes, for example by heating with sodium sulfide in a neutral or alkaline aqueous medium at a pH value of from 7 to 10 and at a temperature in the range of from 30 to 60°C.

The reaction of the phthalocyanine sulfochlorides of the general formula (II) with the amines of the general formula (III) may be carried out in an aqueous medium. However, the reaction can also be advantageously effected in an organic solvent, such as an organic solvent miscible with water, for example a lower alkanol, such as methanol or ethanol, in N-methylpyrrolidone, dimethylformamide or dimethylsulfoxide, or in an aqueous-organic medium, the organic solvent being a solvent miscible with water, for example one of the above-mentioned solvents.

The reaction of the compounds of formula (II) with the amines of the formula (III) is advantageously carried out at a temperature in the range of from −10°C to 110°C. In this connection it is advantageous, — depending on the reactivity and reaction rate of the sulfochloride groups — , to start the reaction at a low temperature, for example at a temperature of from −10°C to +20°C, especially at 0 to 10°C, to maintain the major part of this reaction proceeding in an exothermic manner, at this temperature and to subsequently heat up to a temperature of from 20 to 50°C or, if necessary, up to about 100°C, in order to complete the reaction.

If the reaction rate of sulfochloride groups or their number is small, it is also possible to carry out the reaction at a starting temperature of from 20 to 55°C. The process is then effected in dilute conditions or under strong cooling, or one of the reaction components is added to the other slowly.

Furthermore, it is advantageous to carry out the reaction of the phthalocyanine sulfochlorides with the amines of the formula (III) in the presence of an acid-binding agent, for example an alkali metal hydroxide, alkali metal carbonate, alkaline earth metal carbonate, alkali metal phosphate, alkali metal acetate or a tertiary organic amine, in order to bind the hydrogen chloride being set free. As acid-binding agents of this kind there are to be mentioned in particular: Sodium and potassium acetate, sodium and potassium bicarbonate, sodium and potassium carbonate, sodium-dihydrogen-phosphate, disodium-hydrogen-phosphate, trisodium phosphate or the corresponding potassium salts thereof. It is also possible, however, to use an excess amount of the amine of the formula (III) instead of one of the above-mentioned acid-binding agents. The use of an excess amount of an amine of the formula (III) is recommended in any case, if a complete reaction of all sulfochloride groups present in the compound of the formula (II) with the amine of the formula (III) is to be achieved.

The amines of the formula (III) are oxidation-sensitive. It is therefore recommended to carry out the reaction of these amines with the phthalocyanine sulfochlorides of the formula (II) with the exclusion of air by, for example, covering the reaction mixture with an inert gas, such as nitrogen. However, the reaction may also be carried out in the presence of small amounts of compounds acting as antioxidants, such as sodium dithionite or hydrazine.

The phthalocyanine compounds of the formula (I) of the invention may be isolated according to methods which are known to persons skilled in the art, for example by separation with filtration, if the reaction product is insoluble in the reaction medium, or by precipitation with water or an appropriate organic solvent, if the reaction product is soluble in the other solvent used, and/or by precipitation with acidification with a mineral acid and subsequent filtration. However, there is no need to isolate the reaction products if they are present in a dissolved form; they may be used in this form for further processing.

The phthalocyanine sulfonamide compounds thus obtained of the formula (I) may be isolated in the form of the free acid if they contain acid groups, and be converted in known manner into the salts thereof, preferably into their alkali metal salts, alkaline earth metal salts or ammonium salts.

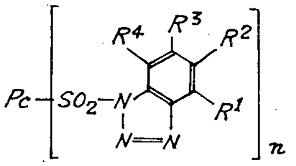
The phthalocyanine compounds of the formula (I) may also be present in the form of their acid salts of the amino group standing in ortho-position to the sulfanoyl groups, for example in the form of the hydrochlorides, sulfates or hydrogensulfates.

The compounds of the formula (I) are very suitable as dyestuffs according to the invention, especially for the dyeing and printing of natural and synthetic fibrous materials, such as natural cellulose, for example cotton, linen, hemp, of regenerated cellulose, of natural polyamide fiber materials, such as wool and silk, and of synthetic polyamide fiber materials, such as polyamide-6, polyamide-66, polyamide-11, of polyester fibers, for example polyesters from terephthalic acid and hexanediol, or of polyacrylonitrile fibers, as well as of mixtures of these types of fiber with each other.

In order to produce dyeings and prints by means of the compounds of the formula (I), said compounds are applied in usual manner, as it is known for dyeing and printing processes, from an aqueous or aqueous-organic medium onto the fibrous material, and may subsequently be exposed on the fiber to the action of nitrous acid. The application of the compounds of the formula (I) onto the various fibrous materials may be effected from an aqueous-alkaline, aqueous-neutral or aqueous-acid solution; the aqueous solutions may also contain an organic solvent miscible with water, for example methanol, ethanol, N-methylpyrrolidone. According to the methods usual for dyeing and printing processes it is also possible to add the usual auxiliary agents and manufacturing agents to the dyestuff solutions. The fibrous materials having been treated with these solutions or printing pastes of the dyestuffs of the formula (I) in the dye bath or preferably by padding or printing, are advantageously subsequently subjected to the action of nitrous acid; a drying process at a temperature in the range of from 30 to 80°C may optionally be interposed before the nitrous acid treatment.

The above process for fixing the compounds of the invention may be carried out by treating the pre-dyed fibrous material in an aqueous bath of an alkali metal nitrite, such as sodium nitrite, or by padding it over with an aqueous solution of this alkali metal nitrite; then optionally drying the material and treating it subsequently in an aqueous bath of an inorganic acid, such as hydrochloric, chloroacetic or sulfuric acid, preferably hydrochloric acid, the bath having a normality of from about 0.5N to 3N of this acid, at a temperature in the range of from 0 to 30°C, or by padding the material over with an acid solution of this kind. However, if the fibrous materials have been treated beforehand with alkaline solutions or printing pastes of the dyestuffs of the formula (I), an alkali metal nitrite, such as sodium nitrite, may already be added to these alkaline solutions or printing pastes, and the fibrous materials thus having been treated with the alkaline solutions or pastes are subsequently subjected, optionally after a drying process, to an acid treatment, for example in an acid bath, or by being padded over with an acid solution, for example an aqueous 0.5N to 3N hydrochloric, chloroacetic or sulfuric acid solution.

Under the action of the nitrous acid on the compounds of the formula (I) during the dyeing process, dyestuffs of the formula

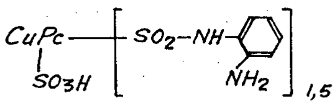


are most possibly formed by way of diazotization and cyclization, wherein Pc, R^1, R^2, R^3, R^4 and n are defined as above, which dyestuffs are no longer capable of forming alkali metal salts with the acid hydrogen atom, due to the lost sulfanoyl group. The compounds of the formula (I) therefore lose their solubility partially or entirely during the dyeing process and are thus fast-fixed on or in the fibrous material. In this manner, the compounds of the formula (I) of the invention yield dyeings or prints which are distinguished by a good fastness to washing, to water, to rubbing, to perspiration, to chlorine and to light.

The following Examples illustrate the invention. The parts and percentages are by weight, unless otherwise stated. Parts by volume are to parts by weight as is the kilogram to the liter. The formula symbols CuPc, NiPc and CoPc in the Examples represent the unsubstituted copper, nickel or cobalt phthalocyanine skeleton.

EXAMPLE 1.

10.8 Parts of 1,2-diaminobenzene are dissolved in 300 parts of water at 50°C. 16.5 Parts of a copper phthalocyanine-3-sulfochloride containing about 2.5 sulfochloride groups per molecule on average, are introduced into this solution in the form of a moist filter cake, while stirring thoroughly; subsequently 40 parts by volume of an aqueous saturated sodium carbonate solution are added, while maintaining a constant temperature of 50°C, and the reaction mixture is stirred at 50°C. Upon completion of the reaction the precipitated product is filtered off, is washed thoroughly with water and dried at 60°C in the drying cabinet. 18 Parts of a dark blue powder are obtained, the composition of which corresponds to the following formula

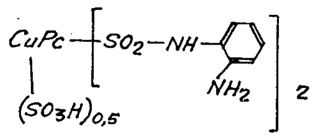


The compound of the invention thus obtained is soluble in water with the addition of sodium hydroxide solution.

By means of the compound obtained above, a cotton dyeing may be prepared in the following manner: A cotton fabric is introduced into a solution of 1 part of the above dyestuff in 3 parts by volume of 1N-sodium hydroxide solution and 20 parts of water and is heated for 30 minutes at 90°C, while stirring constantly. Subsequently the fabric is rinsed for a short time with cold water, is introduced into an aqueous 40% sodium nitrite solution, is left there for 30 seconds, while stirring; then the excess nitrite solution is squeezed off and the fabric is treated for about 1 minute in an aqueous 1N-hydrochloric acid. The cotton fabric thus treated is thereafter rinsed with cold and hot water and is soaped at the boil. A strong turquoise blue dyeing is obtained which has good fastness properties.

EXAMPLE 2.

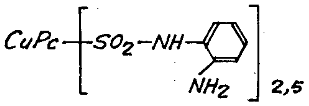
A solution of 81 parts of 1,2-diaminobenzene in 400 parts of methanol is placed under nitrogen in a closed vessel; 41 parts of a copper phthalocyanine-3-sulfochloride containing about 2.5 sulfochloride groups per molecule on average, are added to said solution in the form of a moist filter cake, the reaction mixture being maintained at a temperature of 20°C by cooling. When the addition of the sulfochloride has been finished, the mixture is further stirred for 15 hours at room temperature and is subsequently heated to 50°C. The reaction is completed, while stirring for 5 hours at 50°C. Subsequently the precipitated compound is filtered off, is washed thoroughly with methanol and dried. 47 Parts of a product are obtained which has the form of a dark blue powder and is soluble in water in the presence of sodium hydroxide solution with a turquoise blue color shade. The resulting compound corresponds to the following formula



It dyes a cotton fabric according to the dyeing process mentioned in Example 1 in turquoise blue color shades having good fastness properties.

EXAMPLE 3.

82 Parts of a copper phthalocyanine-3-sulfochloride containing about 2.5 sulfochloride groups per molecule on average, are slowly introduced in the form of a moist filter cake into a solution of 270 parts of 1,2-diaminobenzene in 300 parts of N-methylpyrrolidone under a nitrogen atmosphere and at a temperature of from 5 to 10°C. The reaction mixture is stirred for 5 hours at this temperature and subsequently for another 15 hours at a temperature of from 20 to 25°C. The solution is thereafter introduced into 2000 parts of n-butanol. The precipitated compound is filtered off, washed thoroughly with n-butanol and thereafter with methanol and dried. 100 Parts of a dark blue powder are obtained .which corresponds to a compound of the formula

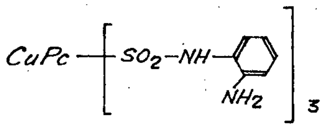


One part of the above dyestuff is dissolved in 20 parts of N-methylpyrrolidone, 7 parts of water and 3 parts by volume of 1N-hydrochloric acid. A cotton fabric is introduced into this dye bath and is treated therein for 30 minutes at 90°C. Subsequently the fabric thus obtained is rinsed for a short time with cold water, is introduced into an aqueous 40% sodium nitrite solution, and is moved therein for 30 seconds; then the excess nitrite solution is squeezed off, and the fabric is treated for about 1 minute with an aqueous 1N-hydrochloric acid.

The fabric thus dyed is then rinsed with cold and hot water and is soaped at the boil. A strong turquoise blue dyeing is obtained which has good fastness properties.

EXAMPLE 4.

5 Parts of sodium bicarbonate are added to a solution of 13 parts of 1,2-diaminobenzene in 70 parts of N-methylpyrrolidone under nitrogen, and the mixture is cooled to 5°C. Subsequently 17.5 parts of copper phthalocyanine-3-trisulfochloride are introduced in the form of a moist filter cake, while stirring thoroughly, in which process the temperature is not allowed to rise above 10°C. The reaction mixture is further stirred for about 5 hours, while cooling with ice; thereafter its temperature is allowed to rise to 20—25°C. Upon completion of the reaction the mixture is introduced into 500 parts of water. The precipitated product is filtered off with suction, is washed thoroughly with water and methanol and dried. 21 Parts of a dark blue powder are obtained which is soluble in water in the presence of alkali with a turquoise blue shade. It corresponds to the formula



and yields on cotton according to a dyeing process described in Example 1 or 3 turquoise blue dyeings having good fastness properties.

EXAMPLES 5 to 19.

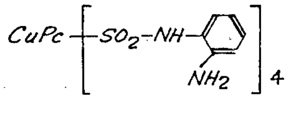
If the preparation of the compound is carried out in accordance with Example 4 above, however, while using equivalent amounts of a diamine of the formula (III) specified in the following Table 1, compounds of the invention are obtained which are also excellently suitable for the dyeing of cotton.

TABLE 1:

Example	R^1	R^2	R^3	R^4	Colour shade of the compound (I) obtained
5	H	H	CH_3	H	turquoise blue
6	H	OCH_3	CH_3	H	green
7	H	CH_3	H	CH_3	turquoise blue
8	H	H	CH_3	CH_3	turquoise blue
9	H	H	Cl	H	turquoise blue
10	H	H	OCH_3	H	green
11	H	H	OC_2H_5	H	green
12	CH_3	CH_3	H	H	turquoise blue
13	H	CH_3	CH_3	H	turquoise blue
14	H	CH_3	H	CH_3	turquoise blue
15	H	Cl	H	H	turquoise blue
16	H	Cl	Cl	H	turquoise blue
17	H	Cl	H	CH_3	turquoise blue
18	H	$-NH-CO-CH_3$	H	H	turquoise blue
19	H	$\underbrace{-NH-CO-NH-}$		H	green

EXAMPLE 20.

34 Parts of sodium hydrogencarbonate are added to a solution of 86 parts of 1,2-diaminobenzene in 350 parts of N-methylpyrrolidone, and the mixture is cooled to 5°C. 97 Parts of copper phthalocyanine-3-tetrasulfochloride are slowly introduced in the form of a moist filter cake, while stirring thoroughly, under a nitrogen atmosphere, the temperature being maintained in the range of from 5 to 10°C. The mixture is subsequently stirred for 3 hours at 10°C, and thereafter for 12 hours at a temperature in the range of from 20 to 25°C. The reaction mixture is then introduced into 3000 parts of water, while stirring, the precipitated product is filtered off with suction, is washed thoroughly with water and methanol and dried. 125 Parts of a compound are obtained which corresponds to the formula



The dark blue powder is soluble in dilute sodium hydroxide solution and yields on a cotton fabric according to the dyeing process described in Example 1 turquoise blue dyeings having good fastness properties.

EXAMPLE 21.

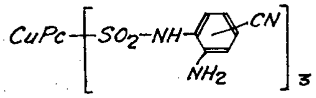
A compound which is suitable as a dyestuff and has good dyeing and fastness properties as those of the compound described in Example 20, however the shade being somewhat redder, is obtained if in Example 20 there is used, instead of the copper phthalocyanine-3-tetrasulfochloride, the same amount of copper phthalocyanine-3,4′,4″,4‴-tetrasulfochloride and the preparation process is carried out otherwise in the manner described in Example 20.

EXAMPLE 22.

Compounds of the invention which are also excellent as dyestuffs, but which have a greener shade than the dyestuff of Example 20, are obtained if instead of the copper phthalocyanine-3-tetrasulfochloride in Example 20 there is used an equivalent amount of a nickel phthalocyanine-3-tetrasulfochloride or a cobalt phthalocyanine-3-tetrasulfochloride.

EXAMPLE 23.

12.6 Parts of sodium hydrogencarbonate are introduced into a solution of 40 parts of 3,4-diaminobenzonitrile in 175 parts of N-methylpyrrolidone, the solution is placed under nitrogen in a closed vessel and is cooled to +5°C. Subsequently 43.6 parts of copper phthalocyanine-3-trisulfochloride are slowly introduced in the form of a moist filter cake, while stirring thoroughly, and the temperature is maintained in the range of from 5 to 10°C; thereafter the mixture is further stirred for 18 hours at 20°C. The reaction mixture is then introduced into 500 parts of water, the precipitated compound is filtered off, is washed thoroughly with water and methanol and dried. 57 Parts of a compound corresponding to the formula



are obtained in the form of a dark blue powder which is soluble in dilute sodium hydroxide solution and dyes cotton according to a dyeing process described in Example 1 or 3 in turquoise blue shades having good fastness properties.

EXAMPLES 24 to 58.

Compounds of the invention which have equally good dyestuff properties with regard to dyeing and also to the fastness of the dyeings prepared with them are obtained if in Example 23 an equivalent amount of a diamine specified in the following Table 2 corresponding to the formula (III), in which R^1, R^3 and R^4 are hydrogen in each case and R^2 is defined as in Table 2, is used instead of the 3,4-diaminobenzonitrile, and the process is carried out in accordance with the method of preparation described in Example 23.

TABLE 2

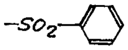
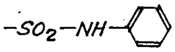
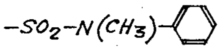
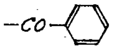
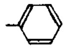
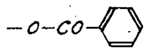
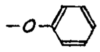
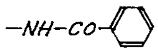
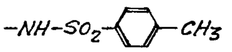
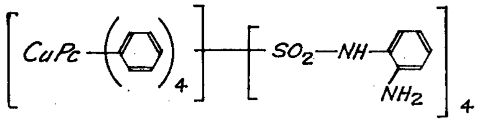
Example	R^2	Colour shade of the compound (I) obtained
24	$-COOH$	turquoise blue
25	$-COOCH_3$	turquoise blue
26	$-COOC_2H_5$	turquoise blue
27	$-CONH_2$	turquoise blue
28	$-CONH-NH_2$	turquoise blue
29	$-CO-NH-CH_3$	turquoise blue
30	$-SO_2-CH_3$	turquoise blue
31	$-SO_2-C_2H_5$	turquoise blue
32	$-SO_2-CH_2-CH_2-OH$	turquoise blue
33	$-SO_2-CH_2-CH_2-Cl$	turquoise blue
34	$-SO_2-CH_2-CH_2-OSO_3H$	turquoise blue
35	$-SO_2-CH=CH_2$	turquoise blue
36		turquoise blue
37	$-SO_2-NH_2$	turquoise blue
38	$-SO_2-NH-CH_3$	turquoise blue
39	$-SO_2-N(CH_3)_2$	turquoise blue
40	$-SO_2-N(C_2H_5)_2$	turquoise blue
41		turquoise blue
42		turquoise blue
43	$-SO_2-NH-CH_2-CH_2-OH$	turquoise blue
44	$-SO_2-NH-CH_2-CH_2-OSO_3H$	turquoise blue
45	$-SO_2-N(CH_2-CH_2-OH)_2$	turquoise blue
46	$-SO_2-N(CH_2-CH_2-OSO_3H)_2$	turquoise blue
47	$-CO-CH_3$	turquoise blue
48		turquoise blue

TABLE 2 (cont.)

Example	R²	Colour shade of the compound (I) obtained
49		blue green
50	–CO–CH$_3$	green
51		green
52		green
53	–CF$_3$	turquoise blue
54	–NO$_2$	blue green
55	–NH–CO–CH$_3$	turquoise blue
56		turquoise blue
57	–NH–SO$_2$–CH$_3$	turquoise blue
58		turquoise blue

EXAMPLE 59.

a) 16.8 Parts of sodium hydrogencarbonate are introduced into a solution of 43.2 parts of 1,2-diaminobenzene in 225 parts of N-methylpyrrolidone. After cooling to +5°C, 63.7 parts of tetraphenyl-copper phthalocyanine-tetrasulfochloride, the preparation of which is described below, are slowly added in the form of a moist filter cake under a nitrogen atmosphere, while stirring thoroughly, in the course of which the temperature of the reaction mixture is not allowed to rise above 10°C and is generally maintained in the range of from 5 to 10°C. The mixture is then further stirred for 3 hours at 10°C and subsequently for another 18 hours at a temperature of from 20 to 25°C. The compound formed is precipitated by adding 800 parts of water, is filtered off and washed thoroughly first with a mixture of 200 parts of N-methylpyrrolidone and 1000 parts of water and thereafter with water alone, until it is free from starting products. After drying, 75 parts of a compound in the form of a green powder are obtained, whose constitution corresponds to the formula



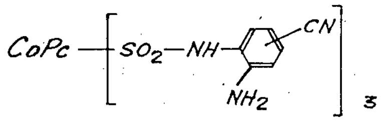
b) Application
A printing paste is prepared for the manufacture of a cotton print as follows: 10 parts of the above prepared dyestuff and 50 parts of urea are dissolved in 100 parts of water, while adding 14 parts of a 33% sodium hydroxide solution. 26 Parts of an aqueous 40% sodium nitrite solution are then added and, while stirring, 300 parts of a 4% sodium alginate thickener are introduced. A cotton fabric is then printed with the printing paste thus prepared. The print dried at 60°C is subsequently treated for 30 seconds, while being moved, with an aqueous 1N-hydrochloric acid at a temperature of from 20 to 25°C, and is then rinsed with cold and hot water and finally soaped at the boil. A brilliant bluish-green printing design is obtained which has good fastness properties.

c) Preparation of the starting sulfochloride
44 Parts of tetraphenyl-copper phthalocyanine are introduced slowly into 250 parts of chlorosulfonic acid; in the course of this process the temperature rises

up to 80°C. The mixture is then slowly heated to 100°C and is further stirred for 16 hours at this temperature. Subsequently the mixture is cooled to 90°C, and 100 parts of thionylchloride are added dropwise at a temperature in the range of from 80 to 90°C. Thereafter the reaction mixture is further stirred for 4 hours at 90°C. Subsequently it is cooled to room temperature, is stirrred onto ice, and the precipitated tetraphenyl-copper phthalocyanine-tetrasulfochloride is filtered off and is washed with ice water until neutral.

EXAMPLE 60.

25.2 Parts of sodium hydrogencarbonate are added to a solution of 79.8 parts of 3,4-diaminobenzonitrile in 350 parts of N-methylpyrrolidone, and the mixture is cooled to 5°C. 86.7 Parts of cobalt phthalocyanine-3-trisulfochloride are introduced in the form of a moist filter cake, while stirring thoroughly, under a nitrogen atmosphere, the temperature being maintained in the range of from +5 to +10°C; thereafter the mixture is further stirred for 3 hours at 10°C and then for 18 hours at a temperature in the range of from 20 to 25°C. It is then introduced into water; the precipitated compound is filtered off with suction, is washed at first with a mixture of 50 parts of N-methylpyrrolidone and 1000 parts of water and thereafter with water alone until it is free from starting products. After drying, 112 parts of a dark blue powder of a compound are obtained which corresponds to the formula



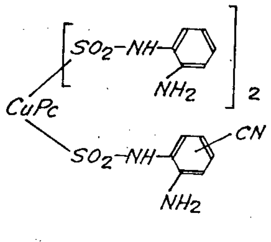
The product is soluble in dilute sodium hydroxide solution and yields on cotton fabric according to the printing process indicated in Example 59 turquoise blue prints having good fastness properties.

EXAMPLE 61.

If a compound according to the invention is prepared in the manner described in Example 60, however while using instead of the cobalt phthalocyanine-3-trisulfochloride an equivalent amount of nickel phthalocyanine-3-trisulfochloride, the corresponding nickel phthalocyanine dyestuff is obtained which is also excellently suitable for the dyeing of cotton and which yields blue green dyeings and prints with good fastness properties.

EXAMPLE 62.

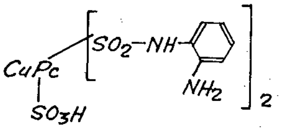
If a compound according to the invention is prepared in the manner described in Example 4, however while using instead of 13 parts of 1,2-diaminobenzene 5.1 parts of 3,4-diaminobenzonitrile and 8.6 parts of 1,2-diaminobenzene, and the product is worked up as has been described, for example, in Example 4, 19 parts of a compound are obtained which has most probably the following constitution:



This compound of the invention is soluble in dilute sodium hydroxide solution and yields on cotton fabric — for example according to the printing process described in Example 59 — turquoise blue prints having good fastness properties.

EXAMPLE 63.

12.6 Parts of sodium hydrogencarbonate are added to a solution of 32.4 parts of 1,2-diaminobenzene in 175 parts of dimethylformamide, the solution is placed under nitrogen and cooled to 5°C. 43.6 Parts of copper phthalocyanine-3-trisulfochloride are introduced in the form of a moist filter cake, while stirring thoroughly, the temperature being maintained at 5 to 10°C. The mixture is further stirred for 3 hours at a temperature of 10°C and then for 18 hours at 20 to 25°C. In order to precipitate the compound formed, 600 parts of water are added to the reaction mixture, the product filtered off with suction and is washed at first with a mixture of 175 parts of dimethylformamide and 1000 parts of water and then with water alone until the product filtered off is free from starting products. After drying, 41 parts of a compound are obtained which has the following constitution:



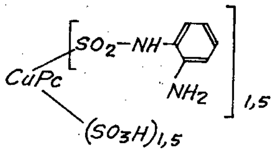
The compound is soluble in dilute sodium hydroxide solution and yields on a cotton fabric — for example according to the printing process described in Example 59 — turquoise blue prints having good fastness properties.

The same compound of the invention is obtained, if instead of the 175 parts of dimethylformamide used as solvent in this example in the sulfanoyl reaction, there is used the same amount of dimethylsulfoxide.

EXAMPLE 64.

12.6 Parts of sodium hydrogencarbonate are added to a solution of 45 parts of 2-aminoacetanilide in 175 parts of N-methylpyrrolidone, the solution is placed under nitrogen and is cooled to 5°C. 43.6 Parts of copper phthalocyanine-3-trisulfochloride are added in the form of a moist filter cake, while stirring thoroughly, and the temperature is maintained at +5 to +10°C. Subsequently the reaction mixture is further stirred for 3 hours at +10°C and for 18 hours at a temperature of from 20 to 25°C. The reaction mixture is then mixed with 400 parts of water, and the precipitated compound is filtered off, is washed first with a mixture of 175 parts of N-methylpyrrolidone and 500 parts of water and then with water alone until it is free from starting products.

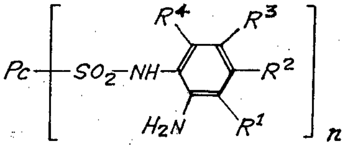
Subsequently the moist filter cake is boiled with 200 parts by volume of 2N-sodim hydroxide solution for 2 hours. The mixture is then neutralized at 20°C with hydrochloric acid, in which process the compound of the invention precipitates. It is filtered off with suction, washed thoroughly with water and dried. 45 Parts of a dark blue powder of a compound are obtained which corresponds to the formula



It is soluble in dilute sodium hydroxide solution and yields on cotton fabric, — for example according to the printing process described in Example 59 or according to the dyeing process described in Example 1 —, turquoise blue prints or dyeings which have good fastness properties.

WHAT WE CLAIM IS:—

1. A phthalocyanine compound of the formula (I)



(I)

wherein Pc represents a copper, cobalt or nickel phthalocyanine radical which may be substituted by one of more substituents selected from halogen atoms, phenyl, sulfo, sulfamoyl and N-arylsulfamoyl groups, mono- and di-lower alkyl substituted sulfamoyl groups and N-arylsulfamoyl groups N-substituted by a lower alkyl group, R^1, R^2, R^3 and R^4, which may be the same or different, each represents a hydrogen or a halogen atom, a lower alkyl group which may be substituted, a lower alkoxy group which may be substituted, an aryl, aryloxy, carboxy or carbamoyl group, a carbamoyl group which is mono- or di-lower alkyl substituted, a carbamoyl group which is mono amino substituted, an arylcarbamoyl group, a cyano group, an alkoxycarbonyl group having 2 to 5 carbon atoms, an alkanoyl or alkenoyloxy group having 2 to 5 carbon atoms, a benzoyl or benzoyloxy group, a lower alkenylsulfonyl group, a lower alkylsulfonyl group which may be substituted in the alkyl radical, an arylsulfonyl, sulfo or sulfamoyl group, a N-(lower alkyl)-sulfamoyl group which may be substituted in the lower alkyl radical, a N,N-di-(lower alkyl)sulfamoyl group which may be substituted in one or both lower alkyl raadicals, a N-methyl-N-phenyl-sulfamoyl group, a N-phenyl-sulfamoyl group, a trifluoromethyl or nitro group, a lower alkylsulfonylamino group which may be substituted in the lower alkyl radical, a N-(lower alkyl)-alkylsulfonylamino group which may be substituted in the lower alkyl radical present at the sulfonyl group, an alkanoylamino or alkenoylamino group having 2 to 5 carbon atoms, a benzoylamino group which may be substituted by 1 or 2 substituents selected from chlorine atoms and lower alkyl, lower alkoxy, sulfo, sulfamoyl, carboxy, N-(lower alkyl)-sulfamoyl and N,N-di-(lower alkyl)-sulfamoyl groups, or an arylsulfonylamino group, or R^1 and R^4 are defined as above and R^2 and R^3 together represent the group —NH—CO—NH—, with the proviso that at least one of R^1, R^2, R^3 and R^4 represents a hydrogen atom, and *n* is a number from 1 to 4, or a salt thereof.

2. A compound as claimed in claim 1, wherein, for R^1, R^2, R^3 and R^4, a substituted lower alkyl group is a lower alkyl group substituted by a chlorine atom or a hydroxy, carboxy, sulfo or sulfato group; a substituted lower alkoxy group is a lower alkoxy group substituted by a lower alkoxy group; and a substituted lower alkylsulfonyl, N-(lower alkyl)-sulfamoyl, N,N-di-(lower alkyl)-sulfamoyl, lower alkylsulfonylamino or N-(lower alkyl)-alkylsulfonylamino group is a group substituted as indicated in claim 1 by a chlorine atom or a hydroxy, lower dialkylamino, sulfo, sulfato, phosphato or carboxy group.

3. A compound as claimed in claim 1 or claim 2, wherein a halogen atom substituent of Pc is a chlorine atom and a N-arylsulfamoyl substituent of Pc is a phenylsulfamoyl group.

4. A compound as claimed in any one of claims 1 to 3, wherein, for R^1, R^2, R^3 and R^4, a halogen atom is a chlorine or bromine atom; an aryl, aryloxy, arylcarbamoyl, arylsulfonyl or arylsulfonylamino group is a phenyl, phenoxy, phenylcarbamoyl, phenylsulfonyl or phenylsulfonylamino group respectively; or an alkanoyl group is an acetyl or propionyl group.

5. A compound as claimed in claim 1, wherein Pc represents a copper, cobalt or nickel phthalocyanine radical which is unsubstituted or is substituted by a sulfo group in the 3- and/or 4-positions of the aromatic carbocyclic ring in the phthalocyanine skeleton, R^1, R^2, R^3 and R^4, which may be the same or different, each represents a hydrogen or chlorine atom, a methyl, ethyl, methoxy, ethoxy, acetylamino, propionylamino, cyano, carboxy, ethoxycarbonyl, methoxycarbonyl, carbamoyl, N-methyl-carbamoyl, N-ethylcarbamoyl, N-phenylcarbamoyl, sulfamoyl, N-methyl-, N-ethyl-, N,N-dimethyl-, N,N-diethyl- or N-methyl-N-phenyl-sulfamoyl, methylsulfonyl, ethylsulfonyl, phenylsulfonyl, acetyl, propionyl, benzoy, phenyl, β-hydroxy-ethylsulfonyl, β-chloro-ethylsulfonyl, β-sulfato-ethylsulfonyl, β-sulfoethylsulfonyl or vinylsulfonyl group, a sulfamoyl group mono- or di-substituted at the nitrogen atom by a β-hydroxyethyl, β-sulfatoethyl or β-sulfoethyl group, an acetoxy, propionyloxy, benzoyloxy, phenoxy, trifluoromethyl, nitro, benzoylamino, methylsulfonylamino, ethylsulfonylamino or phenylsulfonylamino group, or a phenylsulfonylamino group substituted in the nucleus by one or more substituents selected from lower alkyl and lower alkoxy groups and chlorine atoms, with the proviso that at least two of R^1, R2, R^3 and R^4 each represents a hydrogen atom, and *n* is a number from 1.5 to 4.

6. A compound as claimed in claim 5, wherein a substituted phenylsulfonylamino group has 1 or 2 substituents.

7. A compound as claimed in claim 5, wherein R^1, R^2, R^3 and R^4, which may be the same or different, each represents a hydrogen or chlorine atom or a methyl, ethyl, methoxy, ethoxy, acetylamino, cyano, carboxy, carbamoyl, sulfamoyl, methylsulfonyl, ethylsulfonyl or trifluoromethyl group.

8. A compound as claimed in any one of claims 1, 3 and 5, wherein R^1, R^2, R^3 and R^4 each represents a hydrogen atom and *n* is a number from 2 to 4.

9. A compound as claimed in any one of claims 1 to 8, wherein Pc represents a substituted or unsubstituted copper phthalocyanine radical.

10. A compound as claimed in any one of claims 1, 3 and 5, wherein Pc represents a substituted or unsubstituted copper phthalocyanine radical, one or R^1, R^2, R^3 and R^4 represents a cyano, carboxy or carbamoyl group and the others each represent a hydrogen atom, and *n* is a number from 2 to 4.

11. A compound as claimed in any one of claims 1 to 10, wherein the phthalocyanine radical which is unsubstituted.

12. A compound as claimed in claim 8, or claim 9, wherein the phthalocyanine radical is unsubstituted.

13. An alkali metal, alkaline earth metal or ammonium salt of a compound as claimed in any one of claims 1 to 12, which contains one or more anionic groups.

14. A sodium, potassium, calcium or ammonium salt as claimed in claim 13.

15. A compound as claimed in any one of claims 1 to 12, which is free from anionic groups.

16. A compound as claimed in claim 1 and described herein.

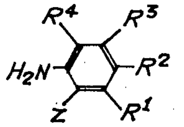
17. A compound as claimed in claim 1 and described in any one of Examples 3, 4, 20 and 23.

18. The compound as claimed in claim 1 and described in Example 4.

19. A process for the preparing a phthalocyanine compound as claimed in claim 1, which comprises reacting 1 mole of a phthalocyanine sulfochloride of the formula (II)

$$\text{Pc}\text{-}(\text{SO}_2\text{Cl})_m \qquad \text{(II)}$$

in which Pc is defined as in claim 1, and *m* is a number from 1 to 4 and is not less than *n*, as defined in claim 1, for the phthalocyanine compound, with *n* mole(s) of an amine of the formula (III)



(III)

in which R^1, R^2, R^3 and R^4 are defined as in claim 1 and Z represents an amino, lower alkanoylamino, benzoylamino or nitro group, and, if *m* is greater than *n*, simultaneously or subsequently hydrolyzing the unreacted sulfonylchloride groups into sulfo groups, and/or, if Z represents a lower alkanoylamino, benzoylamino or nitro group, deacylating a lower alkanoylamino or benzoylamino group represented by Z or reducing a nitro group represented by Z.

20. A process as claimed in claim 19, wherein the reaction of the compounds of the formulae (II) and (III) is carried out at a temperature in the range of from −10° to +110°C.

21. A process as claimed in claim 19 or claim 20, wherein the reaction of the compounds of the formulae (II) and (III) is carried out in an organic solvent selected from methanol, ethanol, N-methylpyrrolidone, dimethylformamide and dimethylsulfoxide, and/or water.

22. A process as claimed in any one of claims 19 to 21, wherein the reaction of the compounds of the formulae (II) and (III) is carried out in the presence of an acid-binding agent.

23. A process as claimed in any one of claims 19 to 22, wherein a subsequent deacylation is carried out by heating with dilute aqueous sodium hydroxide solution at a pH in the range of from 8 to 10 and at a temperature in the range of from 30 to 50°C.

24. A process as claimed in any one of claims 19 to 22, wherein a subsequent reaction is carried out by heating with sodium sulfide in an aqueous medium at a pH in the range of from 7 to 10 and at a temperature in the range of from 30 to 60°C.

25. A process as claimed in any one of claims 19 to 24, wherein the reaction of the compounds of the formulae (II) and (III) is carried out in the presence of an excess of the compound of the formula (III).

26. A process as claimed in any one of claims 19 to 25, wherein the reaction of the compounds of formulae (II) and (III) is carried out under an inert gas atmosphere and/or in the presence of an antioxidant.

27. A process as claimed in claim 19, conducted substantially as described herein.

28. A process as claimed in claim 19, conducted substantially as described in any one of Examples 1 to 4, 20, 23, 59, 60, 63 and 64.

29. A compound as claimed in claim 1, whenever prepared by a process as claimed in any one of claims 19 to 28.

30. A dyeing or printing process wherein a compound as claimed in any one of claims 1 to 18 and 29 is used.

31. A dyeing or printing process as claimed in claim 30, conducted substantially as described herein.

32. A dyeing or printing process as claimed in claim 30, conducted substantially as described in any one of Examples 1, 3 and 59.

33. A dyeing or printing preparation which contains a compound as claimed in any one of claims 1 to 18 and 29.

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