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3,320,020

COMPOSITION FOR AND DYEING CELLULOSE COPPER AND NICKEL TETRAZAPORPHIN-BETAINE DYE COMPOSITIONS AND REACTIVE DYEING CELLULOSE THEREWITH

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12 Claims. (Cl. 8—25)

This application is a continuation-in-part of our copending parent application, Ser. No. 160,935, filed Dec. 20, 1961, and now abandoned, the disclosure of which is incorporated herein by reference as fully as if it were included in its entirety.

This invention relates to new processes for dyeing and/or printing cellulosic textile materials with tetrazaporphin dyes of the general formula:

$$T—(CH_2—X)_n$$

in which T denotes the radical of a copper or nickel tetrazaporphin, $—CH_2—X$ denotes an amino acid internal salt group with X representing a nitrogen atom quaternized by a hydrocarbon structure which in turn bears at least one free or functionally modified sulphonic acid group or carboxylic acid group, and n denotes one of the whole numbers from 1 to 8. These dyes which are capable of forming an internal salt group are generally referred to hereinafter as "betaine" dyes because of their similarity in structure to the class of organic bases known as betaines. The invention also relates to alkaline dyeing or coloring compositions containing said "betaine" dyes and to cellulosic textile materials which have been dyed and/or printed by the new processes.

It is known fom the literature, for example from U.S. patent specification No. 2,599,371, that textile material or paper can be dyed or printed with so-called "onium" dyes—i.e. dyes which contain quaternary ammonium, tertiary sulfonium or isothiuronium salt groups attached to the aromatic nucleus of the dyes by way of methylene bridges—if the dyes are applied in the presence of weakly acid reacting agents and the textile material or paper is treated with alkaline reacting agents before, during or after such application, or if the dyes are used in the presence of a mixture of a weak acid or an acid salt and an alkali metal salt of a weak acid.

In this process, use of the dyes in the form of alkaline solutions is avoided, so-called buffer systems being used instead. Since "onium" dyes, even under these weakly acid conditions, become insoluble relatively quickly, there results a deposition of insoluble dye particles on the surface of the fibrous material and a corresponding substantial decrease in the fastness to rubbing and brilliance of the dyeings (cf. Textil-Rundschau, 10th year (1955), page 133).

A process, described in British patent specification No. 686,036 has been developed in which printing pastes of similar "onium" dyes are used wherein the most important components are non-volatile acids and hygroscopic solvents. According to this process, the steamed dyed material is aftertreated in various ways, for example with acidified aqueous alkali metal bichromate solutions. By this last-mentioned measure, the soluble portions of the dye which have remained unchanged after steaming are to be fixed in order to prevent bleeding of the dye into the white parts of the printed pattern (cf. Textil-Rundschau, 10th year (1955), page 133 and 11th year (1956), pages 136 to 144, especially page 141).

One object of the present invention is to provide new methods of dyeing or printing on cellulosic textile materials by using specific alkaline dyeing compositions capable of avoiding the problems of poor dye stability and lack of fastness properties evidenced by prior methods and compositions.

Another object of the invention is to provide stable alkaline dyeing compositions of a tetrazaporphin dye which can be used to advantage in combination with various known reactive dyes, discharge dyes, vat dyes, aniline black and naphthol dyes in otherwise conventional dyeing and/or printing procedures.

Still another object of the invention is to provide high quality cellulosic textile products which have been dyed and/or printed according to the processes described hereinafter in order to achieve dyeings or printed patterns which are fast to washing, soda boiling, or similar wet treatments, which are also fast to rubbing or bleeding and which are especially fast to chlorine.

These and other objects and advantages of the invention will become more apparent upon consideration of the following detailed description.

We have now found in accordance with the invention that textile materials, such as fibers, filaments, threads, flock, woven fabrics and knitted fabrics of native and/or regenerated cellulose, can be dyed and/or printed so as to achieve the above objects in an improved manner by applying to the cellulosic textile material an alkaline dyeing composition comprising (A) a tetrazaporphin dye of the formula:

$$T—(CH_2—X)_n$$

in which T, X and n have the meanings given above and (B) an alkaline-reacting agent, and then heating the treated material to temperatures between 50° and 150° C.

The tetrazaporphin "betaine" dyes of the invention in the alkaline composition may also be used together with vat dyes and the dye mixture then fixed by the methods usual for vat dyes.

Cellulosic textile material may also be dyed and/or printed fast to rubbing and wet treatment in a simple way by applying said tetrazaporphin "betaine" dyes together with other reactive dyes in the presence of the alkaline agent on the cellulosic textile material and fixing the resulting dye mixture in the way usual for reactive dyes.

The new process may also be used for discharge printing by printing dyes of the "betaine" type according to this invention in the presence of the alkaline agent and a conventional discharging agent onto cellulosic textile materia dyed with a dischargeable dye and then heating the material to temperatures between 98° and 106° C.

Dyes according to this invention may also be printed in the presence of an alkaline agent and a reducing agen onto cellulosic textile material which has previously been padded or impregnated with aniline black or treated according to the so-called naphthol process with compounds capable of being coupled, the material then heated at temperatures between 98° and 106° C., and the dyeings then finished off in the conventional way for resist printing beneath aniline black or naphthol paddings.

Conventional dyeing and printing methods are described in the literature, for example in "Lehrbuch der Textilchemie" by Hermann Rath (Springer-Verlag, Berlin/Göttingen/Heidelberg, 1952) on pages 362 to 407 and 459 to 462, in the book, "The Dyeing of Textile Fibers," by R. S. Horsfall and L. G. Lawrie (2nd edition London, 1949) on pages 60 to 70, and in the book "The Principles and Practice of Textile Printing" by Edmund Knecht and James Best Fothergill (4th edition, London 1952) on pages 17 to 85.

The conventional method of fixing vat dyes is described in the literature, for example in "Handbuch der

Zeugdrucks" by G. Georgievics, R. Haller and L. Lichtenstein (Leipzig, 1930) in volume 1 on pages 613 to 631 and in the above-mentioned book "The principles and Practice of Textile Printing" on pages 351 to 398.

Reactive dyes and the usual method of fixing them are described in the literature, for example in the article "Zur Kenntnis der Reaktivfarbstoffe" by J. Wegmann in the periodical "Textilpraxis," 13 (1958), on pages 936 to 940 and 1056 to 1061, in the article "Reactive Dyes for Cellulose Fiber Goods" by B. C. M. Dorset in the periodical "Textile Manufacturer" (1958) on pages 522 to 526 and in the particle "Chemismus der Reaktivfarbstoffe" by H. Zollinger in the periodical "Angewandte Chemie," 73 (1961) on pages 125 to 136.

Conventional discharging agents are specified in the literature, for example in the above-mentioned "Lehrbuch der Textilchemie" on pages 560 to 563 and in the above-mentioned book "The Principles and Practice of Textile Printing" on pages 1009 to 1012.

Dischargeable dyes are given in the literature, for example in the above-mentioned "Handbuch des Zeugdrucks" in volume II on pages 756 to 757, in the textbook "The Chemistry of Synthetic Dyes and Pigments" by H. A. Lubs (New York, 1955) on pages 134 to 141 and in the "Color Index" (2nd edition 1956) in volume II on pages 2001 to 2360 and 2569 to 2678.

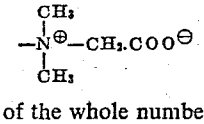
The finishing off of dyeings in the manner usual for resist prints beneath aniline black or naphthol paddings is described in the literature, for example in the above-mentioned "Handbuch des Zeugdrucks" in volume II on pages 803 to 810 and on pages 752 to 756 and in the above-mentioned book "The Principles and Practice of Textile Printing" on pages 751 to 753, on pages 759 to 766 and 771 to 772.

Dyes of the type used according to this invention are obtained in a simple manner, for example according to the process disclosed in German patent specification No. 843,725 by the reaction of derivatives of copper or nickel tetrazaporphin containing halomethyl groups with tertiary amines which contain at least one free or functionally modified sulphonic acid group or carboxylic acid group. The tetrazaporphin dyes used according to this invention are preferably derivatives of tetrabenzotetrazaporphins, especially of copper phthalocyanine and its phenylated and advantageously low halogenated derivatives. Especially bright shades are obtained with these dyes. Other tetrazaporphins may however also form the basis of the "betaine" dyes used according to this invention.

It is especially advantageous to use for the purposes of this invention those dyes of the formula:

$$T-(CH_2-Y)_n$$

in which T denotes the radical of a copper or nickel tetrazaporphin, Y denotes the radical of the formula:



and *n* denotes one of the whole numbers from 1 to 8.

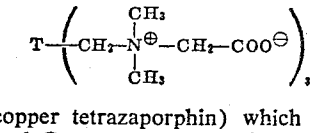
The alkaline dyeing composition of the invention includes as essential ingredients (A) a "betaine" dye as defined above and (B) an alkaline-reacting agent capable of fixing the dye under heat treatment to a cellulosic textile material. The alkaline dyeing composition may be in the form of a dye bath or a printing paste in which the ingredients are dispersed or dissolved in water. Other additives which are conventional for the preparation of aqueous baths or pastes of known dyes may also be included in the compositions of this invention, e.g. various known thickening agents, finishing agents or the like. However, it will be apparent that one must avoid the presence of acid-reacting agents such as the weakly acid agents required in the prior art for use with the so-called "onium" dyes, and the compositions of this invention therefore exclude such substances as formic acid, acetic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, diglycolic acid, citric acid, lactic acid, tartaric acid, maleic acid and oxalic acid, or acid-reacting salts such as sodium dihydrogen phosphate. In other words, such acid-reacting agents must not be present when the "betaine" dyes of the invention are applied to the cellulosic material.

Alkaline-reacting agents for this invention may be of an organic or inorganic nature, inorganic alkaline-reacting agents being preferred. Examples of organic alkaline-reacting agents are water-soluble aliphatic amines with a boiling point of, or advantageously above, 100° C., as for example 2-hydroxyethylamine, 2- or 3-hydroxypropylamine, tri-(2-hydroxyethyl)-amine, tri-(2- or 3-hydroxypropyl)-amine or triethylenetetramine. Examples of inorganic alkaline-reacting agents are hydroxides or carbonates of alkali metals or alkaline earth metal hydroxides, such as lithium hydroxide, rubidium hydroxide, rubidium carbonate, cesium hydroxide, barium hydroxide and preferably the hydroxides and carbonates of sodium and potassium which are especially economical and convenient to use. The alkaline-reacting agents can also be used in admixture with each other. Mixtures of two or more tetrazaporphin dyes of the above-mentioned "betaine" type and/or mixtures of two or more alkaline agents may also be used for the new compositions and processes.

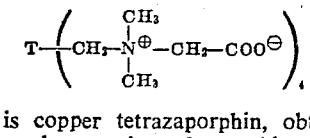
Dyeings and/or prints of the "betaine" dyes are fixed in the presence of the alkaline agent by heating for about 0.5 to 10 minutes at temperatures between 50° and 150° C., preferably between 98° and 106° C. according to the new process. Fixation may be carried out by dry heating or advantageously by steaming.

Dyeings and/or prints obtainable according to this invention have excellent fastness properties, especially very good fastness to washing and soda boiling, and prints do not exhibit any bleeding.

The use of the dye of the formula



(T being copper tetrazaporphin) which is described in Example 1 of German patent specification No. 843,725 and obtainable by reaction of tri-(chloromethyl)-copper phthalocyanine with dimethyl glycocoll potassium, and the use of the dye of the formula



wherein T is copper tetrazaporphin, obtainable in an analogous way by reaction of tetrachloromethyl copper phthalocyanine with dimethyl glycocoll potassium is of special technical interest because these dyes give dyeings and prints in outstanding chlorine-fast shades according to the new process.

It is known from the literature, for example, from German patent specification No. 843,725, that dyes of the kind used according to this invention can be dyed onto textile materials from neutral solution. Dyeings which have only very poor wet fastness properties are obtained, however, so that hitherto these dyes have not been used in practice.

The "onium" dyes of the prior art, as described above in connection with U.S. Patent No. 2,599,371, for example the dyes known from U.S. Patent No. 2,464,806, cannot be suitably employed except in the presence of weakly acid agents and even then do not provide satisfactory dyes or printing pastes. These known dyes are especially unsuitable for combination with other types of dyes which require an alkaline medium during application or during aftertreatment such as fixing on the

fiber, because "onium" dyes are not stable in an alkaline medium.

It could not therefore have been foreseen that the "betaine" dyes used according to this invention, which differ from the "onium" dyes used in the above-mentioned dyeing and printing methods only in their capability of forming internal salts between the quaternized nitrogen atom and the sulphonic acid or carboxylic acid radicals, would have a substantially lower sensitivity to alkaline-reacting agents.

Alkaline solutions, padding liquors or prinitnig pastes containing the dyes used according to this invention are characterized as a rule on the one hand by high stability and do not deposit any insoluble constituents. On the other hand, the dyes characteristic of the present invention are completely converted into a water-insoluble form on the material to be dyed or printed in the presence of alkaline reagents by steaming or dry heating and thus fixed in the fibers in a manner fast to rubbing, washing and soda boiling. A special advantage of the new process is that the same results are obtained when different amounts or different kinds of alkaline-reacting agents are used. The new process is therefore of special importance for industry by reason of its simplicity.

Whereas copper phthalocyanine and nickel phthalocyanine are not vattable, various derivatives of these dyes, for example their sulphonic acids, can be reduced. It is known from the book "The Chemistry of Synthetic Dyes and Pigments," by H. A. Lubs (New York, 1955) page 621, last paragraph, that such reduction products are unstable and readily decomposable. It is therefore surprising that the "betaine" derivatives of copper of nickel tetrazaporphin used according to this invention can be fixed, even in the presence of vatting agents, without difficulty and without destruction of the dye onto cellulosic textile materials in an excellent way in the presence of alkaline-reacting agents.

The new process therefore permits the use of tetrazaporphin dyes of the above-mentioned "betaine" type together with van dyes for dyeing and/or printing cellulosic textile materials and the fixation of the dye mixtures in the way usual for vat dyes.

It should be especially emphasized that no special measures such as are described in British patent specification No. 638,124 have to be used. The said specification describes a combined process for dyeing with "onium" dyes and vat dyes. The fabric is treated with a suspension of a vat dye in an aqueous solution of an "onium" dye and the "onium" dye first fixed on the fibrous material, and only then is the vat dye reduced and reoxidized.

Since the dyes used according to this invention are stable to discharging, they are especially suitable for use in so-called discharge printing processes. In such processes a fabric, advantageously dyed with a dischargeable dye, is printed with a printing paste which contains, besides the usual printing auxiliaries, a dye of the kind used according to this invention, and an alkaline-reacting agent and one of the usual discharge agents, for example sodium formaldehyde sulphoxylate, and the material dried and steamed. The printed parts of the fabric are locally dyed, following this process, in the shade of the dye used according to this invention, whereas the remaining parts of the fabric have the shade of the dischargeable dye.

Conventional printing auxiliaries are described in the literature, for example in the above-mentioned textbook, "Lehrbuch der Textilchemie," on pages 556 to 563 and in the abovementioned book, "The Principles and Practice of Textile Printing," on pages 1009 to 1012.

The "betaine" dyes used according to this invention may also be used in so-called resist printing processes, either as resists under aniline black or as resists under naphthol dyeings.

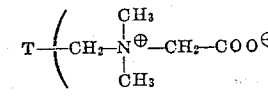
It is known that the dye aniline black is only developed by an acid reaction so that the parts of the fabric which have been treated with an alkaline printing paste containing one of the "betaine" dyes according to this invention prevent the formation of aniline black and these parts of the fabric are dyed exclusively in the shade of the "betaine" dye used.

In the case of naphthol dyeings, the resist action is based on the fact that after steaming a fabric which has been padded or impregnated with a coupling component usual for naphthol dyeing, as for example C. I. Azoic Coupling Component 2 (Colour Index, 2nd edition 1956, volume 3, page 3326, C. I. No. 37,705) and printed with an alkaline "betaine" dye according to this invention, no coupling takes place at the printed parts during treatment with a diazotized amine, for example C. I. Azoic Diazo Component B (Colour Index, 2nd edition 1956, volume 3, page 3321, C. I. No. 37,125), by reason of the alkali content and the reducing agent content of the printing paste. The printed parts of the fabric are therefore dyed only in the shade of the "betaine" dye and not in the shade of the azo dye to be formed.

The invention is illustrated by, but not limited to, the following examples in which parts and percentages are by weight.

Example 1

Cotton fabric is printed with a printing paste which contains, in 1000 parts, 40 parts of the aqueous dye paste described in Example 1 of German patent specification No. 843,725 and containing about 50% of the dye of the formula



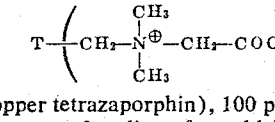
(T being copper tetrazaporphin), 600 parts of a 10% aqueous solution of starch ether, 60 parts of anhydrous sodium carbonate and 300 parts of water. The fabric is then dried, steamed for seven minutes at 102° C. and then soaped at the boil. Prints having excellent fastness properties are obtained in bright turquoise blue shades on a white ground.

Potassium carbonate, sodium hydroxide or potassium hydroxide may also be used instead of sodium carbonate, the procedure otherwise being as above.

If the corresponding nickel phthalocyanine dye is used instead of the copper phthalocyanine dye specified in the first paragraph of this example, a somewhat more greenish turquoise blue print is obtained.

Example 2

Cotton fabric dyed with 2% of the direct dye C.I. Direct Red 79 (Colour Index, 2nd edition 1956, volume 2, page 2103, C.I. No. 290,655) is printed with a printing paste which contains, in 1000 parts, 20 parts of the aqueous dye paste described in the second paragraph of this example and containing the dye of the formula



(T being copper tetrazaporphin), 100 parts of sodium carbonate, 60 parts of sodium formaldehyde sulphoxylate, 300 parts of a 10% wheat starch thickening, 300 parts of a 6% tragacanth mucilage and 220 parts of water. After the fabric has been dried, it is steamed in a rigid ager at 100° C. with air-free steam for five minutes. The fabric is then rinsed, soaped at the boil and dried. Bright turquoise blue prints are obtained on a red ground.

The dye paste used in the first paragraph of this example is prepared as follows: 100 parts of an aqueous filtered product containing 24 parts of tetrachloromethyl copper phthalocyanine, and a solution of 24 parts of dimethylglycocoll potassium in 38 parts of water are

stirred together for about one to two hours at 90° to 95° C., until a sample withdrawn and diluted with water is clearly soluble. The dye solution, which can easily be stirred while it is hot, becomes pasty when cooled.

Example 3

Spun rayon fabric is printed with a printing paste consisting of 40 parts of the blue dye paste used in Example 2, 300 parts of a 5% thickening or carob bean fluor ether, 400 parts of a 10% starch ether thickening, 40 parts of a 15% aqueous paste of the dye C.I. Vat Yellow 20 (Colour Index, 2nd edition 1956, volume 3, page 3527, C.I. No. 68,420) and 220 parts of water. After the fabric has been dried it is impregnated on a padding machine with a solution of 80 parts of sodium hydrosulphite and 90 parts of aqueous caustic soda solution of 38° Baumé strength in 1000 parts of water and then steamed for 30 seconds with air-free steam at 110° C. Since the blue "betaine" dye has fastness properties of a comparable standard to those of the yellow vat dye used, very fast prints in green shades are obtained.

Example 4

Cotton fabric is padded with the following solution:

90 parts of aniline hydrochloride,
5 parts of aniline
150 parts of water
50 parts of starch-tragacanth thickening
70 parts of potassium hexacyanoferrate (II)
300 parts of water and
35 parts of sodium chlorate dissolved in
150 parts of water+
40 parts of 50% acetic acid+
5 parts of 85% formic acid+
105 parts of water

1000 parts

and dried. The fabric treated thus is printed with a printing paste prepared as in Example 2, dried and steamed for five minutes in a rapid steamer at 100° C. The fabric is then rinsed and soaped at the boil. A turquoise colored print on a black ground is obtained.

Example 5

A spun rayon fabric is impregnated with 2-hydroxy-napthalene-3-carboxylic acid anilide and then printed with a printing paste of the following composition:

40 parts of the dye specified in Example 1
30 parts of thiodiglycol
450 parts of starch-tragacanth thickening
75 parts of potassium carbonate
100 parts of sodium formaldehyde sulphoxylate
255 parts of water and
50 parts of aqueous potassium sulphite solution (45° Bé.)

1000 parts

After the fabric has been printed it is dried and steamed in a rapid ager for 5 minutes at 100° C. and then passed through a development bath containing diazotized 1-amino-3-nitro-4-methylbenzene. A red dyeing is thus produced on the parts of the fabric which have not been printed. The printed parts of the fabric on the other hand have a bright turquoise blue shade.

Example 6

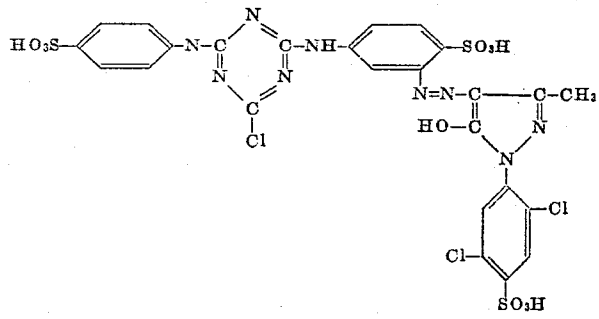
Cotton fabric is padded at 30° C. with an aqueous solution which contains per liter 20 grams of the dye described in Example 1 of German patent specification No. 843,725 in the form of an about 50% paste, 20 grams of anhydrous sodium carbonate and 50 grams of a 10% alginate thickening, and then dried at 50° to 60° C. The dyed fabric is then steamed for six minutes at 100° C. or subjected to a treatment with hot air at 150° to 160° C. The dyeing is then finished off as usual by rinsing, soaping and drying. Very fast dyeings in bright turquoise blue shades are thus obtained.

By using the corresponding nickel phthalocyanine dye instead of the said copper phthalocyanine dye, somewhat more greenish turquoise blue dyeings are obtained.

Example 7

Cotton fabric is printed with a printing paste of which each 1000 parts consists of:

30 parts of the yellow reactive dye of the formula



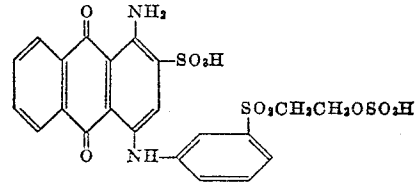
given in Example 1 of U.S. patent specification No. 2,945,021
40 parts of the turquoise blue dye described in Example 1 of German patent specification No. 843,725 in the form of an about 50% aqueous paste,
50 parts of sodium carbonate,
500 parts of 10% alginate thickening and
380 parts of water

The printed fabric is dried at 60° to 70° C. and steamed for five minutes at 100° to 103° C. After the usual rinsing, soaping and drying, bright green prints with very good fastness properties are obtained.

Example 8

Cotton fabric is printed with a printing paste which contains, in 1000 parts:

60 parts of the turquoise blue dye used in Example 1
10 parts of the blue reactive dye of the formula



described in Example 4 on page 6 of British patent specification No. 867,546
20 parts of sodium carbonate
10 parts of aqueous caustic soda solution (38° Bé.)
500 parts of 10% alginate thickening and
400 parts of water

The printed fabric is then dried and steamed for five minutes at 100° to 103° C. The printed fabric is then rinsed, soaped and dried. Wet fast prints are obtained in bright bluish torquoise shades.

Example 9

20 parts of the yellow reactive dye used in Example 7
40 parts of the dye suspension described in the second paragraph of this example
50 parts of urea and
50 parts of sodium carbonate

are dissolved in 1000 parts of water. Cotton fabric is impregnated with this solution by means of a padding machine, the liquor take-up being 80%. The fabric is then dried by means of a hot-air dryer at 80° C. and

then steamed for five minutes at 100° to 103° C. After the dyed fabric has been rinsed and soaped as usual, a bright green dyeing with very good wet fastness properties is obtained.

The dye suspension used in the first paragraph of this example is prepared as follows: 50 parts of an aqueous filtered product containing 10 parts of a mixture of trischloromethyl and tetrakischloromethyl copper phthalocyanine, 10 parts of dimethylglycocoll sodium and 5 parts of water are stirred together for about two to three hours at 90° to 95° C. until a sample of the reaction product is clearly soluble in water. The mobile dye suspension thus obtained is used for dyeing in the way specified in the first paragraph of this example.

Example 10

Cotton fabric is printed with a paste which in 1000 parts contains 20 parts of the dye prepared as described in the following paragraph, 600 parts of an about 10% aqueous solution of starch ether, 50 parts of anhydrous potassium carbonate and 330 parts of water. After drying the fabric is steamed for 10 minutes at 102° C., soaped at the boil and rinsed, blue prints having good fastness properties being obtained.

20 parts of trichloromethylmonoaza copper phthalocyanine, made up with water into an about 30% paste, are stirred with a solution of 16 parts of sodium dimethylaminoacetate in 40 parts of water at 90° C. Dye formation is complete after about two hours. The mixture is allowed to cool and ethanol is added while stirring until the dye has completely settled out. It is then filtered off by suction and dried in the air. The blue dye obtained in an amount of about 30 parts is readily soluble in water.

Example 11

Cotton batiste is printed with a printing paste made up of 40 parts of the dye paste used in Example 1, 600 parts of a 10% aqueous solution of starch ether, 160 parts of triethylenetetramine and 200 parts of water. The fabric is dried, steamed at 102° C. for 8 minutes, soaped at the boil and rinsed, brilliant turquoise blue prints of good fastness properties being obtained on white grounds.

Similar results are obtained when triethanolamine or n-propanolamine are used instead of triethylenetetramine.

Example 12

Cotton batiste is printed in conventional manner with a printing paste which in 1000 parts contains 25 parts of the dye prepared as described in this example, 550 parts of a starch-tragacanth thickening, 45 parts of anhydrous sodium carbonate, 15 parts of potassium hydroxide of 33° Bé. and 365 parts of water. The fabric is then dried, steamed at 102° C. for 8 minutes, soaped at the boil, rinsed and again dried, brilliant greenish blue prints on white grounds being obtained.

A similar result is obtained when 15 parts of sodium hydroxide of 38° Bé. or 10 parts of lithium hydroxide are used instead of 15 parts of potassium hydroxide of 33° Bé.

The dye herein used is prepared in the following manner:

15 parts of tetrazaporphin obtained by cocondensation of 1 mol of 3,6-dichlorophthalic acid, 3 mols of phthalic acid and parts nickel chloride in molten urea in the presence of ammonium molybdate as catalyst are fed into a solution of 100 parts of chlorosulphonic acid, 50 parts of sulphuric acid monohydrate and 26 parts of paraformaldehyde and the mixture is heated for 7 hours at 95° C. After cooling the mixture is stirred into a mixture of 1000 parts of ice and 500 parts of water and the residue is filtered off and washed neutral with water.

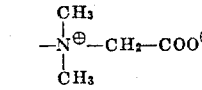
The moist filtrate is stirred with a solution of 20 parts of dimethyl glycocoll potassium in 50 parts of water and the mixture is heated to 90 to 95° C. Dye formation is complete after a few hours. A sample diluted with water dissolves completely. The dye is precipitated by stirring the cold dye paste into ethanol, filtered off by suction and dried. It is obtained in an amount of about 23 parts and is soluble in water.

The invention is hereby claimed as follows:

1. A process for dyeing and printing cellulosic textile material, which comprises applying to said textile material a composition comprising (A) a tetrazaporphin dye of the formula

$$T—(CH_2—Y)_n$$

in which T denotes a member selected from the class consisting of copper tetrazaporphin and nickel tetrazaporphin, Y denotes the radical of the formula



and *n* denotes one of the whole numbers from 1 to 8 and (B) an alkaline-reacting agent, and then heating the material thus treated at a temperature between about 50 and 150° C.

2. A process as claimed in claim 1 wherein the alkaline composition of said tetrazaporphin dye is applied to said textile material together with a vat dye and the material thus treated is heated in the presence of said alkaline-reacting agent and a vat dye reducing agent.

3. A process as claimed in claim 1 wherein the alkaline composition of said tetrazaporphin dye is applied to said textile material together with another reactive dye, and both dyes are then fixed to said material by heating in the presence of said alkaline-reacting agent.

4. A process as claimed in claim 1 wherein the alkaline composition of said tetrazaporphin dye is printed together with a discharge agent onto textile material dyed with a dischargeable dye and the textile material is then heated to a temperature between about 98° and 106° C.

5. A process as claimed in claim 1 wherein the alkaline composition of said tetrazaporphin dye is printed onto cellulosic textile material together with a reducing agent, said textile material having been previously impregnated with aniline black, and the textile material is then heated to a temperature between about 98° to 106° C.

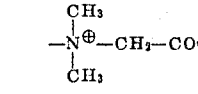
6. A process as claimed in claim 1 wherein the alkaline composition of said tetrazaporphin dye is printed onto cellulosic textile material together with a reducing agent, said textile material having been previously treated according to the naphthol process with compounds capable of coupling, and the textile material is then heated to a temperature between about 98° and 106° C.

7. The colored cellulosic textile material obtained by the process of claim 1.

8. A coloring composition comprising a tetrazaporphin dye of the formula

$$T—(CH_2—Y)_n$$

in which T denotes a member selected from the class consisting of copper tetrazaporphin and nickel tetrazaporphin, Y denotes the radical of the formula

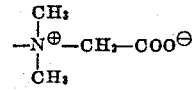


and *n* denotes one of the whole numbers from 1 to 8, and an alkaline-reacting agent.

9. A coloring composition comprising a tetrazaporphin dye of the formula

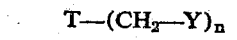
$$T—(CH_2—Y)_n$$

in which T denotes a member selected from the class consisting of copper tetrazaporphin and nickel tetrazaporphin, Y denotes the radical of the formula

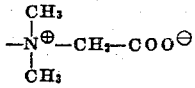


and *n* denotes one of the whole numbers from 1 to 8, a vat dye and an alkaline-reacting agent.

10. A coloring composition comprising a tetrazaporphin dye of the formula

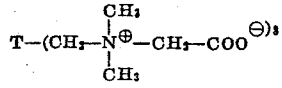


in which T denotes a member selected from the class consisting of copper tetrazaporphin and nickel tetrazaporphin, Y denotes the radical of the formula



and *n* denotes one of the whole numbers from 1 to 8, a reactive dye and an alkaline-reacting agent.

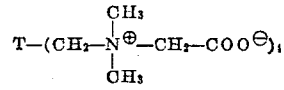
11. A coloring composition as claimed in claim 7 wherein the tetrazaporphin dye has the formula



wherein T is copper tetrazaporphin.

12. A coloring composition as claimed in claim 7

wherein the tetrazaporphin dye has the formula



wherein T is copper tetrazaporphin.

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