

UNITED STATES PATENT OFFICE

2,613,128

VAT DYEING COMPOSITIONS, INCLUDING A MIXTURE OF COBALT PHTHALOCYANINE DYES

Fritz Baumann, Leverkusen-Bayerwerk, and Berthold Bienert, Leverkusen-Wiesdorf, Germany, assignors to Farbenfabriken Bayer, Leverkusen, Germany

No Drawing. Application March 11, 1949, Serial No. 81,025. In Germany October 29, 1948

2 Claims. (Cl. 8—28)

1

The present invention relates to new compositions of matter which are useful for dyeing textile fibers from the vat.

The phthalocyanines which are distinguished by clear shades and excellent fastness properties have been used as yet only for pigmenting, as substantive dyestuffs and as dyestuffs for lake-making. In British Patent No. 322,169 some indications are given of phthalocyanines being suitable for the dyeing from the vat. These indications refer both to unsulphonated and sulphonated products, specific mention being made of the copper, nickel and iron complex. In reality, unsulphonated copper and nickel phthalocyanines have no vatting properties. Sulphonation products thereof are capable of being vatted but do not dye the fiber from the vat to any material extent. Unsulphonated as well as sulphonated iron phthalocyanines are capable of use as vat dyes, also exhibit some affinity to the fiber, but yield unsatisfactory shades.

We have now found that cobalt phthalocyanines are far superior to all other phthalocyanines as far as vatting properties are concerned. Contrary to the unsubstituted copper and nickel complex the unsubstituted cobalt phthalocyanine is capable of use as a vat dye and, on dyeing from the vat, yields essentially clearer shades than the iron complex. Furthermore, in contrast to all other phthalocyanines as far as these are vatable at all, the vatted cobalt phthalocyanine is distinguished by excellent stability on dyeing from the hot vat. The property of vatting and yielding clear valuable dyeings on textiles from the vat is not restricted to the unsubstituted cobalt phthalocyanine. According to our present invention, the above properties to a larger extent are met with those substitution products of cobalt phthalocyanine the hydrophilic property of which has been increased by substitution. For accomplishing this effect, substituents of different kind may be used, for instance, sulphonic acid groups, sulphonamide groups (the nitrogen of which may be mono- or disubstituted by alkyl-, aryl- or aralkyl radicals), sulphinic acid groups, carboxylic acid groups, carboxylic amide groups, cyano groups, hydroxy groups, alkoxy groups, —SH groups, —S.alkyl groups, nitro groups, amino groups, or acylamino groups. These groups may be introduced into the cobalt phthalocyanine as usual, i. e. either subsequent to complex formation or in the course of preparing the complex by starting from phthalic acids, phthalonitriles etc. containing such substituents, e. g. 4-sulphophthalic acid, 4-methoxyphthalic

2

acid etc. As a matter of fact, besides such substituents as increase the hydrophilic property, the cobalt phthalocyanines may also contain substituents which exert the contrary effect, provided however, that there are sufficient hydrophilic substituents in order to accomplish at least a higher hydrophilic character than in the case of cobalt phthalocyanine. All these substitution products have generally better vatting properties than the unsubstituted cobalt phthalocyanine itself. This is true with the reservation that the number of hydrophilic groups must not be so high as to render the products easily soluble in water as otherwise the affinity to the fiber of the vatted product will be impaired. For this reason, it is advisable to substitute the dyestuffs with only a small number of strong hydrophilic groups, such as SO₃H-groups or COOH-groups.

Our present invention also comprises the application of cobalt phthalocyanines with increased hydrophilic properties in admixture with the unsubstituted cobalt phthalocyanine or with cobalt phthalocyanines containing other substituents. We have found that even small amounts of hydrophilic cobalt phthalocyanines will do to convert larger amounts of non-hydrophilic phthalocyanines with poor vatting properties into a state in which they exhibit excellent vatting properties. Such mixtures may be obtained in a simple manner, for instance, by starting on cobalt phthalocyanine synthesis from a preponderant amount of phthalic acid in admixture with a small amount of hydrophilic substituted phthalic acids. Another possibility of preparing such dyestuff mixtures consists in subsequently introducing small amounts of hydrophilic substituents into the phthalocyanine molecule.

Among the various combinations of cobalt phthalocyanines with hydrophilic groups and such without hydrophilic groups as described in the foregoing paragraph, mixtures of the unsubstituted cobalt phthalocyanine with low sulphonated cobalt phthalocyanine are of the greatest importance. On the preparation of such cobalt phthalocyanine sulphonic acids care must be taken that, in the first line, monosulphonic acids will be obtained. Such combinations may be prepared either by cautiously sulphonating cobalt phthalocyanine or by starting on phthalocyanine synthesis from a mixture of smaller amounts of sulphophthalic acid with larger amounts of phthalic acid. Combinations thus obtained may be blended with unsulphonated cobalt phthalocyanine so as to exhibit the

3

desired degree of solubility. The best results are obtained from combinations of cobalt phthalocyanine sulphonic acids and unsulphonated cobalt phthalocyanine in which the cobalt phthalocyanine sulphonic acids are present in an amount of 15-40% by weight (calculated as monosulphonic acid).

In these mixtures, sulphonic acid groups can be replaced with a similar effect by alkylsulfonamide groups.

Cobalt phthalocyanine and the various hydrophilic substitution products mentioned above as well as the combinations described in the foregoing will dye cellulose fibers according to the methods usually applied to vat dyestuffs. In general, the best affinity is reached when dyeing from the hot vat. Many cobalt phthalocyanines are capable of being vatted even in a weakly alkaline medium, for instance, in the presence of ammonia and, therefore, may also be used for dyeing animal fibers from the vat.

The following examples illustrate the invention without restricting it thereto, the parts and percentages being by weight if not otherwise stated.

Examples A-C describe various dyeing processes whereas Examples 1-22 refer to the preparation of various dyestuffs to be used for such dyeing processes.

Example A describes the vat dyeing with cobalt phthalocyanine vat dyestuffs on cotton:

100 parts by volume of a cobalt phthalocyanine paste (corresponding to 1 part of the 100% dyestuff) are added to 650 parts by volume of water and 7 parts by volume of concentrated caustic soda solution (38° Bé.) at 50° C. 40 parts by volume of sodium hydrosulphite solution (1:10 dissolved in water) are caused to react with the above mixture for 15 minutes at 50° C. 200 parts by volume of Glauber's salt solution (1:10 dissolved in water) are then added and 50 parts of cotton are dyed in the usual manner at 50° C. for one hour. After lifting the cotton is squeezed off and hanged in the air for 10 minutes; it is rinsed in cold water, the dyeing is treated with dilute sulphuric acid (2 parts by volume per 1000 parts by volume of water) and it is rinsed once more with water. The dyeing is then washed at the boil with Marseilles soap (2 parts per 1000 parts by volume of water), rinsed and dried. Full, blue to green, olive-green or grey shades are obtained.

Example B.—3 parts by volume of caustic soda solution of 38° Bé., 20 parts by volume of a paste of a cobalt phthalocyanine 1:100 (corresponding to 0.2 part of the 100% dyestuff) and 8 parts by volume of a sodium hydrosulphite solution (1 part dissolved per 10 parts by volume of water) are added to 170 parts by volume of water of 60° C. After 15 minutes 10 parts of cotton are dyed therein in the usual manner and, after hanging in the air, it is proceeded as described in Example A. That process can be modified by substituting 3 parts by volume of caustic soda solution by 4.5 parts by volume of caustic soda solution or by adding 40 parts by volume of Glauber's salt solution (1 part per 10 parts of water).

Example C describes the process of a vat dyeing on wool:

0.2 part of a cobalt phthalocyanine easily capable of being vatted (for instance the dyestuff obtained according to Example 22) is vatted by means of 2 parts by volume of concentrated ammonia (25%) and 0.75 part of sodium hydrosulphite in 120 parts by volume of water at about 75° C. The vat is then filled up to 500 parts by volume by adding water. 10 parts of wool are dyed in this liquor in the usual manner at 51-52°

4

C. for 1 hour. After lifting and wringing out the wool is hanged in the air for 20 minutes, rinsed with water and treated with dilute acetic acid (5 parts by volume of glacial acetic acid per 1000 parts by volume of water), rinsed and dried. Dyeings of good fastness properties are obtained.

Example 1 describes the preparation of a mixture easily capable of being vatted of a cobalt phthalocyanine sulphonic acid with cobalt phthalocyanine:

1.6 parts of cobalt phthalocyanine are gradually added while stirring into 20 parts of 10% fuming sulphuric acid at room temperature. The green solution thus obtained is heated for about 4 hours at 35-38° C. until a sample which has been washed neutral with water begins to dissolve on heating with pyridine water. This degree of sulphonation is reached when about 2.7-2.9% of sulphur have entered the molecule of the cobalt phthalocyanine. When this point is reached sulphonation is stopped and the solution is diluted below 40° C. with 36 parts of sulphuric acid of 66° Bé. When the solution shows only a small amount of free SO₃, 2.4 parts of cobalt phthalocyanine are added below 25° C. and, as soon as dissolution is completed, the whole is stirred into about 400 parts of ice water. The precipitated dyestuff is filtered off and washed with hot water. The product dyes cotton from olive colored vat full, clear greenish-blue shades which are distinguished by excellent fastness to light.

A vat dyestuff of equal dyeing properties is obtained by heating 20 parts of cobalt phthalocyanine in 150 parts of 10% fuming sulphuric acid at 45-48° C. for 2-3 hours until a sample which has been washed neutral with water can easily be vatted with sodium hydrosulphite and dilute caustic soda solution. If this is not the case, further 10-20 parts of 20% fuming sulphuric acid have to be added. The dyestuff is precipitated by stirring the solution into ice water and washing the precipitate with hot water.

Example 2 describes the preparation of a cobalt phthalocyanine with good vatting properties from phthalic acid anhydride and sodium 4-sulphophthalate:

A mixture of—

10.36 parts of phthalic acid anhydride
2.86 parts of sodium 4-sulphophthalate
3.74 parts of cobalt sulphate (83%)
2.34 parts of ammonium chloride
29.00 parts of urea and
0.34 part of ammonium molybdate

is gradually added to 20 parts by volume of nitrobenzene at 180° C. and the melt is further heated at 180° C. for about 6 hours. About 60 parts by volume of methanol are stirred into the melt while hot. The dyestuff thus obtained is sucked off and washed out with methanol. By boiling out with dilute hydrochloric acid, sucking off and washing with water the impurities are removed from the dyestuff. After drying about 10.8 parts of a cobalt phthalocyanine are obtained which, after redissolving from sulphuric acid monohydrate, dyes cotton from olive colored vat full, clear, blue shades of excellent fastness to light.

Example 3.—A mixture of—

4.44 parts of phthalic acid anhydride
2.26 parts of phthalimide-4-sulphonamide
1.55 parts of cobalt sulphate (83%)
1.18 parts of ammonium chloride
14.5 parts of urea and
0.18 part of ammonium molybdate

5

is gradually added to 14.5 parts of volume of trichlorobenzene and the melt is further heated at 180° C. for 5-6 hours. On processing as described in Example 2 a cobalt phthalocyanine with good vatting properties is obtained which dyes cotton full, very clear, blue shades of excellent fastness to light. The color of the vat is olive.

Example 4.—A mixture of—

11.1 parts of phthalic acid anhydride
6.1 parts of phthalimide-4-sulphomethylamide
4.7 parts of cobalt sulphate (83%)
2.5 parts of ammonium chloride
24.0 parts of urea and
0.4 part of ammonium molybdate

is gradually added to 30 parts by volume of trichlorobenzene of 180° C. and the melt is further heated at 180° C. for about 6 hours. On proceeding as described in Example 2 a cobalt phthalocyanine is obtained which after pasting from a mixture of sulphuric acid monohydrate and chlorosulphonic acid (5:1), dyes cotton from yellow-olive colored vat full, blue shades of good fastness to water and excellent fastness to light.

Example 5.—A mixture of—

8.88 parts of phthalic acid anhydride
5.08 parts of phthalic acid-4-sulphodimethylamide
3.74 parts of cobalt sulphate (83%)
2.34 parts of ammonium chloride
29.00 parts of urea and
0.34 part of ammonium molybdate

is gradually added to 20 parts by volume of nitrobenzene of 180° C. and the melt is further heated at 180° C. for about 6 hours.

On proceeding as described in Example 2 a cobalt phthalocyanine is obtained which, after pasting from a mixture of sulphuric acid monohydrate and chlorosulphonic acid (5:1), dyes cotton from yellow-olive colored vat full, greenish-blue shades of excellent fastness to light and good fastness to water.

Example 6 describes the preparation of a dyestuff with good vatting properties from cobalt phthalocyanine and phosgene:

10 parts of cobalt phthalocyanine are added at 120-130° C. to 100 parts of a mixture of aluminum chloride and sodium chloride (7:1). Phosgene is introduced at 150-155° C. As soon as a sample of the mix is capable of being readily vatted but not yet soluble in dilute caustic soda solution or only slightly soluble, the reaction is stopped and the dyestuff is isolated as usual. The dyestuff may either directly be used for vat dyeing or, after drying and pasting from sulphuric acid, in the presence of the same amount of cobalt phthalocyanine. In the latter case, somewhat redder and fuller shades are obtained.

Example 7.—A mixture of—

5.55 parts of phthalic acid anhydride
0.53 part of trimellitic acid
1.87 parts of cobalt sulphate (83%)
1.177 parts of ammonium chloride
14.5 parts of urea and
0.17 part of ammonium molybdate

is gradually added to 14 parts by volume of nitrobenzene of 180° C. The melt is further heated at 180° C. for 6 hours while stirring and it is proceeded as described in Example 2. The dyestuff thus obtained dyes cotton from olive-colored vat full, clear, blue shades of good fastness to water and excellent fastness to light.

6

Example 8 describes the preparation of a dyestuff with good vatting properties from cobalt phthalocyanine and phthalic acid anhydride:

A mixture of—

1 part of cobalt phthalocyanine
2 parts of water-free aluminum chloride and
10 parts of phthalic acid anhydride

is heated up to 210° C. for about 45 minutes until the reaction product exhibits good vatting properties.

The working up of the mixture can be performed either in an acid or in an alkaline medium. The dyestuff dyes cotton from the vat full, greenish-blue shades.

Example 9.—A mixture of—

8.5 parts of 4-bromophthalic acid anhydride
3.05 parts of phthalimide-4-sulphomethylamide
2.35 parts of cobalt sulphate (83%)
1.25 parts of ammonium chloride
12.00 parts of urea and
0.2 part of ammonium molybdate

is gradually added while stirring to 15 parts by volume of trichlorobenzene of 180° C. and the melt is further heated at 180° C. for about 6 hours.

On proceeding as described in Example 2 a cobalt phthalocyanine is obtained which after pasting dyes cotton from olive-colored vat full, greenish shades.

Example 10.—If phthalimide-4-sulphomethylamide (cf. Example 3) is replaced by an equivalent amount of 4-nitrophthalic acid there is obtained a dyestuff which dyes cotton from the vat full, greenish-blue shades of good fastness to water and very good fastness to light.

Example 11.—A mixture of—

16.9 parts of 4-nitrophthalic acid
3.1 parts of cobalt sulphate (83%)
2.35 parts of ammonium chloride
29.0 parts of urea and
0.35 part of ammonium molybdate

is gradually added while stirring to 29 parts by volume of trichlorobenzene at 180° C. and the melt is further heated at 180° C. for 6-7 hours.

On proceeding as described in Example 2 there is obtained 4,4',4''-tetranitro-cobalt phthalocyanine in a good yield which dyes cotton from yellow-colored vat very full, olive-green shades, the nitro groups being converted thereby into amino groups. The dyeings which are distinguished by very good fastness to light can be diazotized on the fiber and can be reacted in the usual way with coupling components, very full, olive-green to dark green dyeings of very good fastness to light and excellent fastness to water being obtained thereby.

Example 12.—A mixture of—

6.00 parts of 4-acetylamino phthalic acid
1.26 parts of cobalt sulphate (83%)
0.78 part of ammonium chloride
9.8 parts of urea and
0.11 part of ammonium molybdate

is gradually added while stirring to 18 parts by volume of nitrobenzene at 180° C. and the melt is further heated while stirring at 180° C. for 6 hours. On proceeding as described in Example 2 a cobalt phthalocyanine is obtained which, after pasting, dyes cotton from olive-green colored vat bluish-green shades of excellent fastness to light.

Example 13.—A mixture of—

7.36 parts of 4-methoxyphthalic acid
1.87 parts of cobalt sulphate (83%)
1.17 parts of ammonium chloride
0.17 part of ammonium molybdate and
14.5 parts of urea

is gradually added while stirring to 15 parts by volume of trichlorobenzene at 180° C. Thereupon, it is proceeded as described in Example 2.

4,4'.4''.4'''-tetramethoxy cobalt phthalocyanine thus obtained dyes cotton from yellow-olive colored vat full, clear turquoise blue shades of excellent fastness to light and very good fastness to water.

Example 14 describes the preparation of a dyestuff with good vatting properties from cobalt phthalocyanine and sulphur chloride:

Starting at 50° C., 4 parts of cobalt phthalocyanine are added to a mixture of 12 parts of water-free aluminum chloride and 24 parts of sulphur chloride, the temperature being raised thereby to 60° C. Temperature is kept at 60° C. until a sample treated with sodium hydrosulphite and dilute caustic soda solution yields a clear, olive-brown vat, this stage being achieved after about 3 hours. The greenish-blue vat dyestuff can be separated, for instance, by introducing the reaction mixture into dilute hydrochloric acid, sucking off and afterwashing with water.

For further purification the paste of the crude dyestuff is extracted with sodium sulphide solution a small amount of a greenish-blue dyestuff being dissolved thereby besides sulphur. The insoluble blue dyestuff is filtered off, washed with water and dried, and can directly be used for dyeing from the vat.

Example 15.—A mixture of—

13.32 parts of phthalic acid anhydride
6.33 parts of 4-nitrophthalic acid
5.6 parts of cobalt sulphate (83%)
3.51 parts of ammonium chloride
43.5 parts of urea and
0.51 part of ammonium molybdate

is added while stirring to 44 parts by volume of nitrobenzene at 180° C. and the whole is further heated while stirring at 180° C. for 5-6 hours. On proceeding as described in Example 2, 4-mononitro-cobalt phthalocyanine is obtained which, in the usual way, is converted on reduction with sodium sulphide into 4-mono-amino cobalt phthalocyanine and, at last, into 4-mono-mercapto-cobalt phthalocyanine by diazotizing and treating the diazonium compound with potassium thiocyanate and saponifying. 4-monomercapto cobalt phthalocyanine dyes cotton from yellow-olive colored vat full, green to blue shades of excellent fastness to light.

Example 16.—On processing according to Example 15 starting, however, from 8.88 parts of phthalic acid anhydride and 12.66 parts of 4-nitrophthalic acid, 4,4-dimercapto cobalt phthalocyanine is obtained which dyes cotton from the vat full, blue to green shades.

Example 17.—On processing according to Example 15 starting, however, from 4.44 parts of phthalic acid anhydride and 18.99 parts of 4-nitrophthalic acid, 4,4'.4''-trimercapto cobalt phthalocyanine is obtained which dyes cotton from yellow-olive colored vat bright, full, bluish-green shades of excellent fastness to light.

Example 18.—On processing according to Example 15 leaving out, however, phthalic acid anhydride and using 25.32 parts of 4-nitrophthalic

acid, 4,4'.4''-tetranitro-cobalt phthalocyanine is obtained. 4,4'.4''-tetramercapto-cobalt phthalocyanine obtainable therefrom dyes cotton from olive colored vat greyish-green shades which, on aftertreating with bichromate in acetic acid, turn fully, grey, the fastness to water being very good.

Example 19.—A mixture of—

4.84 parts of diphenyl-3,4-dicarboxylic acid
4.80 parts of phthalimide-4-sulphomethylamide
1.84 parts of cobalt sulphate (83%)
0.98 part of ammonium chloride
9.44 parts of urea and
0.16 part of ammonium molybdate

is introduced while stirring into 12 parts by volume of trichlorobenzene at 180° C. and it is proceeded as described in Example 2. The cobalt dyestuff thus obtained dyes, after pasting from ethyl sulphuric acid, cotton from yellow-olive colored vat full, greenish-blue shades.

Example 20.—A mixture of—

3.68 parts of 4-methoxyphthalic acid
4.84 parts of diphenyl-3,4-dicarboxylic acid
1.87 parts of cobalt sulphate (83%)
1.17 parts of ammonium chloride
14.5 parts of urea and
0.17 part of ammonium molybdate

is introduced while stirring into 15 parts by volume of trichlorobenzene at 180° C. and the melt is further heated while stirring at 180° C. for 5-6 hours. On proceeding as described in Example 2 a cobalt phthalocyanine is obtained which, after pasting from ethyl sulphuric acid, dyes cotton from yellow-olive colored vat clear, full, greenish-blue shades of good fastness to water and excellent fastness to light.

Example 21.—A mixture of—

49.0 parts of benzophenone
4.53 parts of anthraquinone-2''-carbonyl-4'-amino-3,4-dicyanodiphenyl (prepared from 4'-amino-3,4-dicyanodiphenyl and anthraquinone-2-carboxylic acid chloride)
3.84 parts of phthalodinitrile and
1.62 parts of dehydrated cobalt chloride

is heated after adding a small amount of pyridine at 240-245° C. for about 3-4 hours. After cooling down to about 80-90° C. the melt is diluted with 98 parts by volume of methanol and the separated dyestuff is sucked off. By washing with methanol, boiling out with dilute hydrochloric acid and boiling out with o-dichlorobenzene the dyestuff is obtained in a pure state. The dyestuff dyes cotton from yellow-brown colored vat clear, blue-green shades of good fastness to water.

Example 22 describes the preparation of a dyestuff especially suitable for wool vat dyeing.

A mixture of—

22 parts of urea
18 parts of the condensation product of 4-amino-phthalimide and beta-indichloride
2.8 parts of cobalt sulphate (83%)
1.8 parts of ammonium chloride
0.25 part of ammonium molybdate and
2.2 parts of benzamide

is introduced at 180° C. into a stirring vessel and the melt is stirred at 180-185° C. for 2-3 hours. The melt being still in a warm condition is diluted with 440 parts by volume of water, acidified with hydrochloric acid and the dyestuff thus obtained is salted out by adding 880 parts by volume of common salt solution. The dyestuff can be purified by dissolving once more in dilute hydro-

9

chloric acid and salting out with common salt and is soluble in dilute mineral acids with a bluish-green color.

We claim:

1. A vat dyeing composition comprising a 5
cobalt phthalocyanine free from hydrophilic groups, a cobalt phthalocyanine monosulphonic acid, sodium hydrosulphite, water, and caustic soda.

2. A vat dyeing composition comprising a mixture of 60-85% of a cobalt phthalocyanine free from hydrophilic groups and of 15-40% of cobalt phthalocyanine monosulphonic acid, sodium hydrosulphite, water, and caustic soda. 10

FRITZ BAUMANN. 15
BERTHOLD BIENERT.

10

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,133,340	Bienert -----	Oct. 18, 1938

FOREIGN PATENTS

Number	Country	Date
322 169	Great Britain -----	Nov. 18, 1929