Patented Aug. 27, 1946 2,406,586

UNITED STATES PATENT OFFICE

2,406,586

DYESTUFF COMPOSITION

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No Drawing. Application August 13, 1943, Serial No. 498,575

14 Claims. (Cl. 8—70)

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This invention relates to dyestuff compositions, and particularly to improved dyestuff compositions containing a salt of an acid polybasic acid ester, especially an acid sulfuric acid ester, of a leuco compound of a vat dyestuff, or a mixture of such salts and to a process for coloring textile materials therewith.

Salts of acid polybasic acid esters of leuco compounds of vat dyestuffs of various classes (e. g., indigoid, thioindigoid, anthraquinone, etc.) are well known in the art. Usually they appear on the market in the form of sodium salts of acid sulfuric acid esters of leuco compounds of vat dyestuffs; but salts of other metals, especially alkali metals, and of ammonia and organic bases, and of acid esters of other polybasic acids (such as, phosphoric acid and maleic acid), are also known. For simplicity, they will be referred to hereinafter by the term "vat dyestuff ester salts," and those derived from sulfuric acid will be referred to by the term "vat dyestuff sulfuric ester salts."

The aforesaid ester salts are stable forms of leuco compounds of the vat dyestuffs from which they are derived. They are not reoxidized to the parent vat dyestuff upon exposure to air; they are relatively more soluble in water than the parent compounds, and form neutral aqueous solutions; and they are generally substantive toward animal fibers (e. g., wool, silk, nylon, casein wool). Their affinity for vegetable fibers is in general poor, although this affinity can be improved by the addition of an exhausting agent, e. g., Glauber's salt, and/or raising the temperature at which the fiber is impregnated with the ester salt. When subjected to mild oxidizing agents (such as nitrites, chromates, etc.) in dilute acid solution, a vat dyestuff ester salt of the aforesaid type is converted into the corresponding parent insoluble vat dyestuff. Accordingly, the use of these ester salts in coloring textile materials requires neither the strongly alkaline conditions nor the complicated compounding and control required for dyeing and printing with the ordinary vat dyestuffs.

For example, cotton, wool, silk, or rayon material can be colored by working it in a dye bath or padding bath consisting of an aqueous solution made by dissolving a vat dyestuff sulfuric ester salt in water, followed by treatment with an acid oxidizing solution (such as a dilute aqueous solution of sulfuric acid containing sodium dichromate dissolved therein; or the material can be printed or padded with a paste containing the vat dyestuff sulfuric ester salt and a thickener,

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with or without additional substances (such as sodium nitrite, sodium chromate, alcohols, glycerine, glycols, polyglycols, phenols, dioxydiphenyl sulfide, etc.), followed by an acid steaming treatment (so-called "acid ageing") or treatment with an acid oxidizing solution or both (cf. U. S. P. 1,575,958). In some cases the printing or padding paste contains substances which form an acid oxidizing medium during the steaming operation (such as, sodium chlorate, ammonium sulfocyanide and ammonium vanadate) thereby making unnecessary an acid oxidizing treatment. In general the dyed or printed material is further treated in a manner similar to that employed in coloring with vat dyestuffs; e. g., it is rinsed, soaped and finished.

The vat dyestuff ester salts of a number of vat dyestuffs of the indigo, thioindigo, and anthraquinone series have been found suitable for commercial application in coloring textile materials in the aforesaid manner. However, it has been found that printing pastes containing the said ester salts are generally unstable, their dye strength decreasing considerably on standing for appreciable periods of time. In commercial operations, where uniformity of printing is highly desirable, this characteristic renders the preparation of a large quantity of a printing paste for use over a considerable period of time impractical and wasteful. Moreover, ester salts of a number of vat dyestuffs are unsuitable for printing because of their poor solubility in aqueous media.

In accordance with the present invention, improved coloring compositions, containing salts of acid polybasic acid esters, and especially acid sulfuric acid esters, of leuco compounds of vat dyestuffs as coloring constituents, are obtained by incorporating into such coloring compositions a xanthinic base (for example, theobromine, caffeine). As employed herein, and in the appended claims, the expression "xanthinic base" refers to a xanthine base of truly basic character, i. e., yielding a solution in water having a pH value of more than 7.0.

I have discovered that such a dyestuff composition, particularly one containing caffeine, is not subject to the aforesaid disadvantages, and that the presence of the xanthinic base in the said composition imparts various advantages to it. Thus I have found the incorporation of caffeine into a printing paste containing a vat dyestuff sulfuric ester salt imparts improved fixation properties to the ester salt, and results in prints which have greater tinctorial strength and

greater brilliancy and which are generally superior to those produced in the absence of caffeine or other xanthinic base.

Further, I have found that such printing pastes have greater stability when left standing in the paste form. Thus, I have found that the addition of caffeine to a printing paste of a vat dyestuff sulfuric ester salt improves the stability of the paste against decomposition of the ester salt upon standing, thereby permitting preparation of large uniform batches of the printing paste which may be kept without excessive loss of dye strength for longer periods of time than similar pastes which do not contain a xanthinic base.

I have also found that the xanthinic bases have a solubilizing effect upon relatively insoluble vat dyestuff sulfuric ester salts; that is, those having a solubility in water at 25° C. not exceeding 5% by weight. It is well known that the solubility in aqueous media of salts of acid sulfuric acid esters of leuco compounds of vat dyestuffs varies considerably with the nature of the parent vat dyestuff as well as with the nature of the cation of the salt. Thus, I have found by the addition of caffeine to the sodium salt of the acid sulfuric acid ester of the leuco compound of the blue-green vat dyestuff obtainable by thionation of 2-methyl benzanthrone (Color Index No. 1173), which salt has such a low solubility in water that it cannot be used commercially for printing textile fibers, the resulting composition has sufficient solubility in water and printing pastes to be useful in producing commercially acceptable prints in the ordinary printing processes.

Any member of the class of xanthinic bases may be employed according to this invention, for example, xanthine itself, 1-methyl xanthine, heteroxanthine (7-methyl xanthine), theophylline (1,3-dimethyl xanthine), paraxanthine (1,7-dimethyl xanthine), theobromine (3,7-dimethyl xanthine), 1-hydroxyethyltheobromine (1-hydroxyethyl-3,7-dimethyl xanthine), caffeine (1,3,7-trimethyl xanthine), and epiguanine (7-methylguanine). Those which are methyl derivatives of xanthine are preferably employed, and especially caffeine. Crude caffeine, such as is obtained as a result of the decaffeination of coffee, tea and the like, preferably after only a single recrystallization, and which is in a form comprising more than 90% by weight of caffeine in admixture with other xanthinic bases and/or other substances naturally occurring in coffee, tea and the like, is especially preferred in view of its relative cheapness and high effectiveness. It will be understood that, in speaking of caffeine in the specification and claims, the pure as well as the crude form is intended, unless otherwise indicated.

The amount of xanthinic base employed in accordance with the present invention may be varied considerably. In general, the optimum amount employed in a particular case will depend upon a number of factors, including the solubility of the vat dyestuff ester salt, the specific xanthinic base used, and the manner in which the vat dyestuff ester salt is to be employed. Thus, in the case of a vat dyestuff sulfuric ester salt which is relatively soluble in water and printing pastes, only sufficient xanthinic base need be included in a printing paste to produce improved prints or to impart desired stability to the printing paste. On the other hand, if the xanthinic base is employed for the purpose of imparting increased solubility in aqueous media to a relatively insoluble vat dyestuff sulfuric ester salt, a greater amount of the xanthinic base may be required. In general, the amount of xanthinic base should be at least one-quarter of the weight of the vat dyestuff equivalent of the salt of the acid sulfuric ester of the leuco compound of the vat dyestuff, and in some cases it may be 5 or more times the weight of the vat dyestuff equivalent of said salt. (The term "vat dyestuff equivalent," as employed herein, refers to the weight of unreduced vat dyestuff which is theoretically required to produce the given weight of vat dyestuff sulfuric ester salt. Thus, the vat dyestuff equivalent of 750 grams of the disodium salt of the acid sulfuric acid ester of the leuco compound of the blue-green vat dyestuff referred to above is 544 grams.) A greater amount of xanthinic base may be used; the excess acts as a diluent.

The addition of the xanthinic base to the compositions of the present invention can be made in any suitable manner and at any desired stage of the preparation of the final composition. Thus, an improved dyestuff composition can be produced by mixing the xanthinic base with the vat dyestuff ester salt in the dry form, for example, by mixing or grinding them together; or, in the preparation of a dye bath or padding bath or printing paste, the xanthinic base may be added before or after or together with the vat dyestuff ester salt. Dry compositions also can be prepared by adding the xanthinic base to a solution of the vat dyestuff ester salt and evaporating the solution to dryness.

The xanthinic bases do not interfere with the inclusion in the compositions of other substances ordinarily forming a part of vat dyestuff ester salt compositions. Thus, in preparing dyestuff pastes, printing pastes, or powders of the vat dyestuff ester salts in accordance with the present invention, the xanthinic base may be used to replace a part of the water, diluent, or standardizing agent normally employed, if desired without otherwise changing the nature and proportions of the components of the pastes or powders. For example, additional substances having diluent, antifoaming, assisting, wetting, hygroscopic, catalytic, enolizing, or other desired action in the subsequent use of the compositions may be included in the compositions of the present invention. As indicative of the type of substances referred to, a number of which are known in the art, there may be mentioned inorganic salts (such as sodium carbonate, sodium sulfate, etc.) which serve as diluents or alkalinizing agents; solvents (such as alcohols, etc.); hygroscopic liquids (such as glycerine, glycol, diethylene glycol, etc.); organic salts (such as sodium naphthionate, which serves as a printing assistant, etc.); and organic fillers (such as dextrine, cerelose, etc.). In the preparation of printing pastes and related compositions, conventional thickeners are also included (such as gum tragacanth, locust bean gum, starch, dextrine, etc.).

The invention will be further described in connection with the following illustrative examples, wherein parts and percentages are by weight and temperatures are in degrees centigrade.

Example 1

A powder for use in textile printing, containing caffeine and the disodium salt of the acid sulfuric acid ester of the leuco compound of National Carbanthrene Blue Green FFB (Colour Index No. 1173), a blue-green vat dyestuff obtainable by thionation of 2-methyl-benzanthrone, is prepared by adding a wet filter-cake containing 233 parts

of the said disodium sulfuric ester salt (equivalent to 169 parts of the corresponding vat dyestuff: National Carbanthrene Blue Green FFB) to an aqueous caffeine solution which has been prepared by dissolving 9.6 parts of sodium hydroxide, 250 parts of caffeine, 57.5 parts of sodium carbonate and 360 parts of soluble dextrine in 1200 parts of water at 65° to 70°. Additional dextrine is added to the aqueous mixture in sufficient amount (about 90 parts) to bring the concentration of the disodium sulfuric ester salt in the mixture to about 23% of the total solids in the mixture (equivalent to a concentration of the corresponding vat dyestuff of about 15.5% of the total solids in the mixture). The liquid mass is dried, for example on a drum drier, and the product is ground to the desired degree of fineness.

EXAMPLE 2

Two similar printing pastes are prepared from the following dyestuff composition in the following manner:

Solution A

One part of a dyestuff composition containing, per hundred parts,

	Parts
The disodium salt of the acid sulfuric acid ester of the leuco compound of National Carbanthrene Blue Green FFB (equivalent to 20 parts of National Carbanthrene Blue Green FFB)	27.6
Sodium hydroxide	0.96
Sodium carbonate	5.75
Soluble dextrin	65.69

is mixed with 2.5 parts of denatured alcohol (U. S. Formula 2B) and 1 part of crude caffeine is added, followed by 5.5 parts of hot water (at 80°) and 2 parts of diethylene glycol.

Solution B

One part of the same dyestuff composition is mixed with 6.5 parts of the denatured alcohol, to which mixture is added 5.5 parts of hot water (at 80°) and 2 parts of diethylene glycol.

Each of the resulting solutions is mixed with 48 parts of a starch-tragacanth thickening (containing 6.2% of wheat starch, 2.9% of gum tragacanth, 1.44% of sodium benzoate, and 89.46% of water), and 4 parts of a neutral sodium chromate solution (prepared by dissolving 48 parts of sodium chromate: $Na_2CrO_4.4H_2O$ in 100 parts of water) are added to the resulting paste.

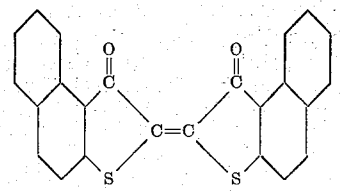
Cotton cloth is printed with a portion of each of the printing pastes as thus prepared. After drying, the printed cloth is subjected to an acid aging process by exposing it for about 3 minutes to the action of steam containing acetic and/or formic acid vapor (for instance, the vapor obtained by boiling a 25% aqueous solution of acetic acid). If the coloration is not fully developed, development can be completed by passing the material through an aqueous solution containing about 3.8% sulfuric acid and 5.0 grams of sodium bichromate ($Na_2Cr_2O_7.2H_2O$) per liter. When the development is complete, the material is rinsed, soaped and finished in the usual manner.

The printing paste prepared from Solution A (containing caffeine) yields a blue-green print similar in shade to that obtained by employing the parent vat dyestuff. The print is stronger, greener, brighter and more level than that produced in the same manner with the printing paste prepared from Solution B (containing no caffeine).

Another portion of each of the printing pastes is permitted to stand for 3 days and then is employed for printing cotton cloth in the aforesaid manner. Very much stronger prints are obtained with the paste prepared from Solution A (containing caffeine) than with the paste prepared from Solution B (containing no caffeine).

EXAMPLE 3

A powder for use in textile printing, containing caffeine and the disodium salt of the acid sulfuric acid ester of the leuco compound derived from the naphthioindigo dyestuff having the following formula:



is prepared by intimately mixing in the dry form (e. g., by grinding together) 80 parts of a dry dyestuff composition containing 65.6 parts of the disodium salt of the acid sulfuric acid ester of the leuco compound of the aforesaid naphthioindigo (equivalent to 43.2 parts of the parent naphthioindigo) and 14.4 parts of water-soluble inorganic salts (associated with the ester salt, partly formed during the preparation thereof, and consisting essentially of sodium carbonate, trisodium phosphate, sodium sulfate and sodium chloride), with 15 parts of crude caffeine and 5 parts of 1,4-sodium naphthionate (containing about 10% of sodium sulfate). When used for preparing a printing paste which is printed on cotton, prints are obtained which are very much stronger than similar prints obtained in the absence of the caffeine.

EXAMPLE 4

Two similar printing pastes are prepared from the following dyestuff composition in the following manner:

Solution C

	Parts
A dyestuff composition containing, per 100 parts of composition	1.6
The disodium salt of the acid sulfuric acid ester of the leuco compound of the naphthioindigo of Example 3 (equivalent to 54 parts of the parent naphthioindigo)	82.1
Water-soluble inorganic salts	17.9

are mixed with 2.5 parts of denatured alcohol (2B), and 0.3 part of crude caffeine and 0.1 part of 1,4-sodium naphthionate (containing about 10% of sodium sulfate) are added, followed by 15.5 parts of hot water (at 80°) and 2 parts of diethylene glycol.

Solution D

A solution similar to Solution C is prepared from the same ingredients in the same manner as Solution C, except for the omission of the caffeine.

Each of the resulting solutions is mixed with 48 parts of starch-tragacanth thickening and 4 parts of a neutral sodium chromate solution (both of the type employed in Example 2).

Cotton cloth is printed with a portion of each of the printing pastes as thus prepared. After

drying, the printed cloth is subjected to acid aging for about 3 minutes in the vapor obtained by boiling a 25% aqueous solution of acetic acid. To complete color development, the material is passed through an aqueous solution of sulfuric acid and chromate of the type referred to above. The material is rinsed, soaped and finished in the usual manner.

The printing paste prepared from Solution C (containing caffeine) yields a brown print similar in shade to that obtained by employing the parent vat dyestuff. The print is stronger and more level than that produced in the same manner with the printing paste prepared from Solution D (containing no caffeine).

Another portion of each of the printing pastes is permitted to stand for 7 days and then is employed for printing cotton cloth as above described. The prints obtained with the paste obtained from Solution C (containing caffeine) showed the same superiority to the prints obtained with the paste prepared from Solution D (containing no caffeine) as the freshly prepared paste.

It will be realized by those skilled in the art that the invention is not limited to the foregoing examples and that changes can be made without departing from the scope of the invention.

Thus, instead of the salts of the acid sulfuric acid esters of the leuco compounds employed in the foregoing examples, salts of acid sulfuric acid esters of other vat dyestuffs may be employed; as for example, the sodium salts of the acid sulfuric acid esters of the leuco compounds of the following vat dyestuffs:

4,4'-dimethyl-6,6'-dibrom thioindigo,
5,5'-dichlor-6,6'-dimethyl thioindigo,
6,6'-diethoxy-thioindigo, or
3,4,8,9-dibenzopyrene-5,10-quinone.

Similarly other salts of the above or other acid sulfuric acid esters of leuco compounds of other vat dyestuffs of the anthraquinone, indigoid and thioindigoid series may be employed in accordance with the present invention.

In the foregoing description the use of the compositions in the dyeing or printing of textile materials has been stressed, since these are the more important applications of the compositions. It will be understood, however, that the compositions also may be used in the coloring of other substances wherein vat dyestuff sulfuric ester salts are applicable. It will also be understood, that this invention can be applied to dyestuff compositions comprising salts of leuco esters of vat dyestuffs derived from other polybasic acids, both inorganic and organic, e. g., phosphoric acid and maleic acid.

I claim:

1. A dyestuff composition comprising a salt of an acid polybasic acid ester of a leuco compound of a vat dyestuff, and caffeine.

2. A dyestuff composition comprising a salt of an acid sulfuric acid ester of a leuco compound of a vat dyestuff, and a xanthinic base.

3. A dyestuff composition comprising an alkali metal salt of an acid sulfuric acid ester of a leuco compound of a vat dyestuff and a xanthinic base, said salt having a solubility in water at 25° C. not exceeding 5 per cent by weight.

4. A dyestuff composition comprising a salt of an acid sulfuric acid ester of a leuco compound of a vat dyestuff, and caffeine in an amount equal to at least one-fourth of the weight of the vat dyestuff equivalent of said salt.

5. A dyestuff composition comprising a sodium salt of an acid sulfuric acid ester of a leuco compound of a vat dyestuff and caffeine in an amount equal to one-fourth to 5 times the weight of the vat dyestuff equivalent of said salt, said salt saving a solubility in water at 25° C. not exceeding 5 per cent by weight.

6. A printing paste comprising a salt of an acid sulfuric acid ester of a leuco compound of a vat dyestuff, caffeine, and a thickener.

7. A dyestuff composition comprising an alkali metal salt of an acid sulfuric acid ester of a leuco compound of a vat dyestuff, and caffeine in an amount equal to one-fourth to 5 times the weight of the vat dyestuff equivalent of said salt, said salt having a solubility in water at 25° C. not exceeding 5 per cent by weight.

8. A dyestuff composition comprising the sodium salt of the acid sulfuric acid ester of the leuco compound of the blue-green vat dyestuff obtained by thionation of 2-methyl-benzanthrone, and caffeine in an amount equal to one-fourth to five times the weight of the vat dyestuff equivalent of said salt.

9. A process for the coloration of textile materials, which comprises applying thereto a salt of an acid polybasic acid ester of a leuco compound of a vat dyestuff together with a xanthinic base, and developing the dyestuff by oxidation on the material in an acid medium.

10. A process for the coloration of textile materials, which comprises applying thereto a salt of an acid sulfuric acid ester of a leuco compound of a vat dyestuff together with caffeine, and developing the dyestuff by oxidation on the material in an acid medium.

11. A process for printing textile material, which comprises applying thereto a printing paste containing a sodium salt of an acid sulfuric acid ester of a leuco compound of a vat dyestuff, a thickener, and caffeine in an amount equal to at least one-fourth of the weight of the vat dyestuff equivalent of said salt, and developing the dyestuff by oxidation on the material in an acid medium.

12. A process for printing textile materials, which comprises applying thereto a printing paste containing the sodium salt of the acid sulfuric acid ester of the blue-green vat dyestuff obtained by thionation of 2-methyl-benzathrone, together with a thickener, and caffeine in an amount equal to one-fourth to 5 times the weight of the vat dyestuff equivalent of said ester salt, and developing the dyestuff by oxidation on the material in an acid medium.

13. A dyestuff composition comprising the sodium salt of the acid sulfuric acid ester of the leuco compound of 6,6'-diethoxy-thioindigo, and caffeine.

14. A dyestuff composition comprising the sodium salt of the acid sulfuric acid ester of the leuco compound of 3,4,8,9-dibenzopyrene-5,10-quinone, and caffeine.

EARL W. CLARK.

Certificate of Correction

Patent No. 2,406,586; August 27, 1946.

EARL W. CLARK

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 6, line 71, after "of" insert *a*; column 7, line 62, claim 1, strike out "caffeine" and insert instead *a xanthinic base*; and line 65, claim 2, strike out "a xanthinic base" and insert instead *caffeine*; column 8, line 11, claim 5, for "saving" read *having*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of October, A. D. 1946.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.