UNITED STATES PATENT OFFICE

2,085,145

VAT DYE COMPOSITIONS

Paul Whittier Carleton, Penns Grove, N. J., and Arthur Lawrence Fox, Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application August 8, 1935, Serial No. 35,399

15 Claims. (Cl. 8—5)

This invention relates to new and improved vat dye compositions and a simplified method of dyeing which is especially useful in dyeing textile materials which cannot withstand the action of strong alkalis, such as, for example, wool, silk and other fibers of animal origin.

According to the usual method of dyeing cotton with vat dyes, it is customary to prepare the dye bath by reducing the vat dye, usually in the form of a paste, with a suitable reducing agent such as sodium hydrosulfite in the presence of a caustic alkali and water. Inasmuch as a relatively large amount of caustic alkali is ordinarily employed, the resultant dye bath is rather strongly alkaline. While cotton fibers, fabrics and yarns may be readily dyed in such a bath because they are not substantially acted upon by the alkali, great care must be taken in dyeing fibers, fabrics and yarns of animal origin such as wool and silk because the strong alkali tends to destroy such materials. For this reason, although vat dyes are the fastest type of dye known, they have presented special problems in the dyeing of wool, silk and similar materials. Thus, as pointed out by Whittaker, "Dyeing with Coal Tar Dyestuffs" (1920), pp. 118–124, while wool has been dyed with vat dyes from both fermentation vats and hydrosulfite vats, careful control is necessary. In both types of vats the amount of alkali is a controlling factor. The temperature must also be carefully regulated in order to avoid action by the alkali upon the wool. This is particularly true in the hydrosulfite vat which is the principal method of vat dyeing in this country.

It is an object of the present invention to provide a new and improved method of dyeing which is applicable to the coloring of all types of materials with vat dyes and which is especially useful in dyeing wool, silk and materials of animal origin which are adversely affected by strong alkalis. A more specific object is to provide a new and improved method of dyeing with indigoid dyes. A still more specific object is to provide a new and improved method of dyeing with thioindigoid dyes. Another object is the production of new and improved non-aqueous vat dye compositions, and particularly vat dye powders, which are directly adapted for use in the coloring of textile materials. An additional object is the production of new and improved thioindigoid dye powders. Other objects will appear hereinafter.

These objects are accomplished by the preparation of non-aqueous compositions comprising an intimate mixture of a water-insoluble metal leuco derivative of a vat dye other than an alkali metal derivative, and a water-soluble metal salt which forms a more insoluble salt with the metal of the said leuco derivative by double decomposition. Although it is not essential, it is preferable that these dye compositions also contain a dispersing agent. They may be prepared in powder or non-aqueous paste form and may contain other addition agents such as, for example, protective colloids and hydrotropic agents.

When a dye composition of the type above described is added to water, double decomposition occurs producing a dye bath containing the leuco compound in solution and the water-insoluble metal salt. The fiber, fabric or yarn to be dyed may be passed through the solution and subjected to oxidation by the usual methods to fix the dye to the fiber. The insoluble salt may be separated before or after the fabric is dyed. It causes no inconvenience if left in the dye bath. The dye bath may or may not contain an alkali, depending upon the material to be dyed and the conditions of temperature. The same is true of the non-aqueous dye composition originally employed. If the fiber to be dyed is of animal origin, it is preferable to effect the dyeing operation without an alkali or with a mild alkali. This may be done, for example, by choosing as the water-soluble metal salt in the preparation of the dyestuff composition a suitable neutral salt. Thus, the dye powder employed may consist of a mixture of the calcium leuco derivative of a vat dye and a neutral sulfate such as, for example, sodium sulfate, with or without a dispersing agent. When this is added to water, the normal leuco derivative is formed, together with insoluble calcium sulfate. Similar results are obtained with the barium leuco derivative. If the presence of an alkali is desired, a mild alkali such as an alkali metal carbonate may be added to the non-aqueous dye composition or to the dye bath.

While the invention is susceptible to considerable variation and modification in the manner of its practical application, the following examples, in which the parts are by weight, will serve to illustrate how it may be practiced.

Example I

An insoluble iron derivative of leuco 4:4′-dimethyl-6:6′-dichloro thioindigo may be prepared as follows:

Heat together 12 parts of 4:4′-dimethyl-6:6′-dichloro thioindigo, 2000 parts of water and 15 parts of a 40% sodium hydroxide solution to 90° C., and then add 13 parts of sodium hydrosulfite. When the pink color has completely gone, add 10 parts of concentrated hydrochloric acid to the solution, followed by a solution of 15 parts of $FeCl_2.4H_2O$ in 200 parts of water. Filter, wash and dry the heavy precipitate which forms. This may then be ground into a powder and separately mixed with sodium carbonate, potassium carbonate, and with trisodium phosphate in proportions chemically equivalent to the amount required to form the ferrous carbonate or phosphate by double decomposition.

Similar powders may be prepared with the addition of 1% to 10% of dextrine and/or a sodium salt of a naphthalene-sulfonic acid-formaldehyde condensation product in amount corresponding to about 1% to 10% by weight of the leuco vat dye.

Dye baths may be prepared by adding powders of the type above described in amounts sufficient to produce baths containing 0.05% dye. Cotton, wool, silk and cellulose acetate fabrics may be dyed a pink shade of excellent fastness by passing them through said baths and then oxidizing in the usual manner.

Example II

Heat together 100 parts of 2:1:2′:1′-naphthioindigo (21.5% paste), 2000 parts of water and 15 parts of 40% sodium hydroxide solution to 80° C. and add 15 parts of sodium hydrosulfite. When vatting is complete, add hydrochloric acid until turbidity first occurs, and to this solution add 20 parts of $FeCl_2.4H_2O$ in 200 parts of water. A gray precipitate forms at once and may be filtered, dried and ground.

The iron leuco derivative thus obtained may be made up into dye powders by intimately mixing therewith (1) two molecular proportions of potassium carbonate per mole of metal leuco derivative; (2) two molecular proportions of sodium carbonate per mole of metal leuco derivative; or (3) two-thirds molecular proportion of trisodium phosphate per mole of metal leuco derivative.

The dye powders thus prepared may be made up into dye baths by adding them to 400 parts of water. Cotton, wool and silk fabrics may be dyed by passing through the baths and subsequently oxidizing in the usual manner.

Example III

Heat to the boil 17 parts (or 100 parts 17% paste) of 3:3′-dichloro-N-dihydro-1:2:2′:1′-anthraquinone azine, 200 parts of water and 15 parts of 40% sodium hydroxide solution, and add 15 parts of sodium hydrosulfite. After vatting is complete, add 9.6 parts of concentrated hydrochloric acid followed by 15 parts of calcium chloride dissolved in 200 parts of water. Filter the precipitate which forms and wash with water.

Mix all of this precipitate with 3 parts of a 30% solution of the sodium salt of a naphthalene-sulfonic acid-formaldehyde condensation product and 18 parts of dextrine dissolved in 50 parts of hot water. After thoroughly mixing, dry the mixture at atmospheric or reduced pressures and at temperatures up to 100° C. The resultant dried mixture may then be ground and intimately mixed with the following salts in the proportions given:

		Parts of
(1)	Dry dye mixture	36
	Sodium sulfate	74
(2)	Dry dye mixture	36
	Sodium fluoride	74
(3)	Dry dye mixture	36
	Sodium oxalate	74
(4)	Dry dye mixture	36
	A sodium phosphate	74
(5)	Dry dye mixture	36
	Sodium carbonate	74
(6)	Dry dye mixture	36
	Sodium bicarbonate	74
(7)	Dry dye mixture	36
	Sodium sulfate	36
	Sodium carbonate	28

Alternatively, the proportions may be 36 parts of dry dye mixture, 50 parts of sugar and 24 parts of inorganic salt. All of the above make a 17% powder.

Dye baths may be prepared by adding 1 to 5 parts of any one of the above dye powders to 400 parts of water. Cotton, wool and silk may be dyed a blue shade from such baths.

Example IV

Heat together 70 parts of 4:4′-dimethyl-6:6′-dichloro thioindigo (18% paste) and 2000 parts of water to 90° C., and add 15 parts of 40% NaOH followed by 15 parts of sodium hydrosulfite. To the clear vat add 15 parts of dextrine and then just enough acid to neutralize the excess alkali. Cool this solution to 30° C. and add 15 parts of manganese sulfate dissolved in 200 parts of water. Filter the precipitate, wash as dry as possible and then make up into dye powders by drying, grinding and intimately mixing with the manganese leuco derivative in suitable proportions salts forming insoluble manganese compounds, as follows:

		Parts of
(1)	Manganese leuco compound	20
	Sodium acetate	80
(2)	Manganese leuco compound	20
	Ammonium phosphate	80
(3)	Manganese leuco compound	20
	Sodium carbonate	80
(4)	Manganese leuco compound	20
	Potassium oxalate	80
(5)	Manganese leuco compound	20
	Sodium phosphate	80

Alternatively, the dye powder may be prepared from 20 parts of the leuco compound, 60 parts of sugar and/or dextrine and 20 parts of the inorganic salt.

Dye baths may be prepared by adding 1 to 5 parts of the above described dye powders to 400 parts of water. Materials may be dyed by passing them through said baths and oxidizing the fabrics containing the solution of reduced vat dye, for instance, by boiling and soaping in the presence of air.

Example V

Heat together 100 parts of 5:7:5′:7′-tetrabromo indigo (10% paste), 2000 parts of water and 15 parts of 40% aqueous sodium hydroxide solution in a nitrogen atmosphere to 90° C. and then add 15 parts of sodium hydrosulfite. After vatting is complete, add 9.6 parts of concentrated hydrochloric acid and then 20 parts of $FeCl_2.4H_2O$ in 200 parts of water. The precipitate of the iron leuco compound which formed at once may be filtered, washed, dried and intimately powdered with water-soluble salts as follows:

		Parts of
(1)	Iron leuco derivative	12
	Sodium carbonate	88
(2)	Iron leuco derivative	12
	Sodium bicarbonate	88
(3)	Iron leuco derivative	12
	Potassium carbonate	88
(4)	Iron leuco derivative	12
	Trisodium phosphate	88

Alternatively, the dye powder may be prepared from 12 parts of the leuco derivative, 12 parts of inorganic salt and 76 parts of sugar and/or dextrine.

Dye powders may also be prepared by including with powders of the type above described 1% to 10% dextrine and/or the sodium salt of a naphthalene-sulfonic acid-formaldehyde condensation product.

Dye baths may be prepared by adding 1 to 5 parts of any of the above dye powders to 400 parts of water. Cotton, wool and silk materials may be dyed a blue shade from such baths.

Example VI

Heat 100 parts of dimethoxy-dibenzanthrone (20% paste), 2000 parts of water and 15 parts of 40% aqueous sodium hydroxide solution to 90° C., and add 15 parts of sodium hydrosulfite. When vatting is complete, add 9.6 parts of concentrated hydrochloric acid followed by 20 parts of $FeCl_2.4H_2O$ dissolved in 200 parts of water. The precipitate of the iron leuco salt may be filtered off, washed and dried.

Dye powders may be prepared by mixing together the iron leuco salt and the dimethoxy-dibenzanthrone and at least the theoretical proportions of an inorganic salt such as sodium carbonate, sodium bicarbonate, potassium carbonate and/or trisodium phosphate, to give the corresponding iron carbonate or phosphate by double decomposition.

Instead of the iron leuco salt, the chemical equivalent proportions of the aluminum leuco salt may be used in preparing vat dye powders as above described.

The aluminum leuco salt of the dimethoxy-dibenzanthrone may be prepared as follows:

Heat together at 80° C. about 100 parts of dimethoxy-dibenzanthrone (10% paste), 2000 parts of water and 15 parts of 40% sodium hydroxide solution. Then add 15 parts of sodium hydrosulfite. When vatting is complete, treat the resultant mixture with 9.6 parts of concentrated hydrochloric acid and then a solution of 15 parts of aluminum chloride ($AlCl_3$) in 200 parts of water. Filter the purple precipitate and make it up into a dye powder as before.

If desired, dextrine and/or sodium formaldehyde-naphthalene-sulfonate may be incorporated into the resultant dye composition before or after the addition of the inorganic salt in any suitable manner, and preferably in proportions corresponding to about 1% to 10% by weight of the mixture.

Example VII

The calcium salt of 6:6′-diethoxy thioindigo may be prepared as follows:

Heat together 12 parts of dry 6:6′-diethoxy thioindigo, 2000 parts of water and 15 parts of 40% sodium hydroxide solution at a temperature of 80° C., and add 15 parts of sodium hydrosulfite. When vatting is complete, add hydrochloric acid until turbidity just begins to appear. Then add a solution of 10 parts of calcium chloride in 100 parts of water and filter off the light tan-colored calcium leuco salt which precipitates.

A dye powder may be prepared from this dry leuco salt by mixing it with slightly in excess of equi-molecular proportions of sodium sulfate, and grinding.

In the preparation of powders useful for dyeing textile materials from dye baths, any one of the following substances or a mixture thereof may be incorporated in amounts varying from about 0% to 88% by weight of the total mixture of calcium leuco salt and sodium sulfate: dextrine, sodium salt of the condensation product of formaldehyde with naphthalene-sulfonic acid, and/or a mild inorganic base such as an alkali metal carbonate. If the dye composition is to be made up into a printing paste, substances such as glycerin, diethylene glycol, small amounts of alkali metal salts of anthraquinone-sulfonic acids and/or carboxylic acids together with a thickener such as customarily employed in the printing trade may be added.

The following composition is illustrative of a suitable printing paste prepared by mixing together:

	Parts of
Metal leuco derivative	20
Sodium sulfate	20
Potash	10
Diethylene glycol	10
Thickener	40

The thickener may be prepared by mixing together 1 part of wheat starch, 3 parts of British gum, 4 parts of water and 1 part of gum tragacanth (6% solution), and boiling the mixture for 10 to 15 minutes.

The paste prepared as above described may be printed on a textile material from an engraved metal roll, allowed to dry, aged from one to five minutes at about 214° F. to about 216° F., and the material then oxidized, rinsed, soaped, rerinsed and dried. In this manner prints have been obtained which were 10% stronger and noticeably brighter than those obtained from 6:6′-diethoxy thioindigo per se when printed in the normal manner with a reducing agent such as sodium formaldehyde sulfoxylate.

In preparing dye powders and printing pastes of the type above described, the neutral salt, sodium sulfate, may be replaced by other neutral salts which react with the calcium of the insoluble metal leuco derivative to form the corresponding insoluble calcium salt. The alkali metal carbonate such as potash or sodium carbonate is not essential but is desirable even in printing wool and silk. If desired, the neutral salt may be replaced entirely by the chemical equivalent amounts of alkali metal carbonate, particularly when printing on materials which are not affected by the alkali. In general, the proportions of inorganic salts such as sodium sulfate and sodium carbonate vary rather widely as long as the total amount of inorganic salt present is sufficient to react with the calcium of the leuco derivative.

Other substances may be employed instead of diethylene glycol, as, for instance, glycerin and other polyhydric alcohols or ether alcohols which are similarly employed in printing the dyestuffs per se. Printing assistants such as small amounts (say, 0.5% to 5.0%) of iron salts, for example, $FeCl_2.4H_2O$, and salts of organic acids such as the alkali metal salts of anthraquinone sulfonic and carboxylic acids may likewise be incorporated into the printing paste.

Example VIII

Dye powders and pastes may be prepared as in Example VII except that 15 parts of barium chloride ($BaCl_2$) are substituted for the 10 parts of calcium chloride. The resultant leuco derivative is the barium salt of 6:6′-diethoxy thioindigo. Prints with this salt are approximately equal in strength to those obtained from the original 6:6′-diethoxy thioindigo.

Example IX

In a manner similar to that described in Example VII the manganese salt of 6:6′-diethoxy thioindigo may be prepared by substituting 15 parts of manganese sulfate for the calcium chloride. Prints with this salt were close to those obtained from the original 6:6′-diethoxy thioindigo.

Example X

The magnesium salt of 6:6′-diethoxy thioindigo may be prepared by substituting 15 parts of magnesium chloride ($MgCl_2.6H_2O$) for the calcium chloride of Example VII. The methods of preparing dye powders and printing pastes are similar to those given in Example VII. Prints may be obtained with this salt which are 10% stronger than those from the original 6:6′-diethoxy thioindigo.

Example XI

By substituting 15 parts of aluminum chloride ($AlCl_3$) for the 10 parts of calcium chloride in Example VII, the aluminum leuco derivative of 6:6′-diethoxy thioindigo may be prepared. Suitable dye compositions may be prepared from this derivative as described in Example VII.

Example XII

The cobalt leuco derivative of 6:6′-diethoxy thioindigo may be prepared by carrying out Example VII with the substitution of 15 parts of cobalt chloride for the 10 parts of calcium chloride. Dye powders and printing pastes may be prepared from the cobalt derivative as described in Example VII.

Example XIII

The calcium salt of 6:6′-diethoxy thioindigo was prepared by heating together 12 parts of 6:6′-diethoxy thioindigo, 2000 parts of water and 15 parts of 40% NaOH to a temperature of about 80° C. Fifteen (15) parts of sodium hydrosulfite were then added. When vatting was complete, hydrochloric acid was added until the mixture became turbid. Then 10 parts of calcium chloride in 100 parts of water were added, and the light tan-colored calcium leuco salt filtered off and washed with cold water to remove inorganic salts. To the resultant paste 14 parts of dextrine were added and a slurry was made by mixing with a rapid mixer. Usually, the addition of the dextrine causes the wet cake to thin out, but a small amount of 30% sodium formaldehyde-naphthalene sulfonate may be added. When a smooth slurry is obtained, it may be dried in a vacuum oven or on a drum drier. The material thus obtained contains 50% color and may be diluted to standard strength (11%) by making any of the following compositions:

		Parts of
(A)	50% calcium salt of 6:6′-diethoxy leuco thioindigo	22
	Anthraquinone-2-sodium sulfonate	1
	Sugar	77
		100

		Parts of
(B)	50% calcium salt of 6:6′-diethoxy leuco thioindigo	22
	Silver salt (anthraquinone-beta-sodium sulfonate)	1
	Sodium sulfate (anhydrous)	10
	Sugar	50
	Dextrine	17
		100

		Parts of
(C)	50% calcium salt of 6:6′-diethoxy leuco thioindigo	22
	Anthraquinone-beta-sodium sulfonate	1
	Sodium carbonate (anhydrous)	10
	Sugar	50
	Tetra-hydronaphthalene-sodium sulfonate	17
		100

		Parts of
(D)	50% calcium salt of 6:6′-diethoxy leuco thioindigo	22
	Anthraquinone-beta-sodium sulfonate	1
	Isopropyl sulfate sodium salt	25
	Sugar	52
		100

		Parts of
(E)	50% calcium salt of 6:6′-diethoxy leuco thioindigo	22
	Anthraquinone-2:6-disulfonic acid	1
	Sodium benzene sulfonate	50
	Sugar	27
		100

		Parts of
(F)	50% calcium salt of 6:6′-diethoxy leuco thioindigo	22
	Anthraquinone 2:6-disulfonic acid	1
	Isobutyl sulfate (Na salt)	50
	Sugar	27
		100

These mixtures are converted to powders by some ordinary form of pulverizing and mixing such as ball milling, rod milling, etc. These powders are then suitable for printing.

Example XIV

Powders prepared as described in Example XIII may be made up into printing pastes of the usual type containing gums, starches, potassium carbonate and sodium formaldehyde sulfoxylate. However, it has been found that excellent prints result when pastes containing greatly reduced quantities of sulfoxylate are used. Inasmuch as the dye in these powders is already reduced, it is probable the only function of sulfoxylate is to prevent oxidation when the alkali metal salt of the leuco is formed.

A typical printing paste is as follows:

	Parts of
One of the above printing powders	20
A printing gum	80
	100

The above printing gum may be made by any of the following formulae or any other standard formula.

K-10-Na-1 printing gum

800 parts of S. B. G. thickener
Heat to 180° F. and dissolve
100 parts of potassium carbonate
Cool to 140° F., add
61 parts water
29 parts sodium hydroxide (flakes)
10 parts glycerin
Stir until smooth.

K-4-2 printing gum

800 parts of S. B. G. thickener
Heat to 180° F. and dissolve
40 parts of potassium carbonate
Cool to 140° F. and add
130 parts of water
20 parts of sodium sulfoxite
10 parts of glycerin
Stir until smooth.

K-8-6 printing gum

800 parts of S. B. G. thickener
Heat to 180° F., then dissolve
80 parts of potassium carbonate
Cool to 140° F., then add
50 parts of water
60 parts of sodium sulfoxite
10 parts of glycerin
Stir until smooth.

The S. B. G. thickener used in making up the above printing gums is made as follows:

	Parts of
Wheat starch	100
British gum	300
Water	550
Glycerin	50

These are mixed and boiled ten minutes.

In a similar manner, water-insoluble metal leuco derivatives of other vat dyestuffs may be prepared and made up into marketable dye compositions in accordance with the present invention. Further examples of dyes which may be treated in this manner are 2-indol-3-indolindigo and derivatives thereof, 3:3'-bis-indolindigo and derivatives thereof, 2-thionaphthene-2-indolindigo and derivatives thereof, 2-thionaphthene-3-indolindigo and derivatives thereof, 2-indolacenaphthene-indolindigo and derivatives thereof, 2-thionaphthene-acenaphthene-indigo and its derivatives, quinone-indolindigos and quinone-thionaphthene-indigos and their derivatives.

The preferred dyes which are converted to water-insoluble metal leuco derivatives and made up into dye compositions in accordance with the invention are the thioindigoid dyes in which the 6-position is occupied by a substituent group as, for instance, 6:6'-diethoxy thioindigo, 4:4'-dimethyl-6:6'-dichloro thioindigo, and 6:6'-dichlorothioindigo. Within this preferred class of dyes, moreover, the metal leuco salts of metals of Group II*a* of the Periodic System, particularly calcium and magnesium, are preferred because it has been found that these metal salts of this particular class of dyes give improved results in printing.

In the preparation of the dye powders by mixing the water-insolube metal leuco salts and the inorganic salt, or salts, it will be recognized that the choice of inorganic salt will depend upon the particular metal of the metal leuco derivative and the choice is always made so that the inorganic salt is one which will react with the metal leuco derivative by double decomposition to form a more insoluble inorganic salt with the metal of the metal leuco derivative. Ordinarily, the inorganic salt which is mixed with the metal leuco derivative is an alkali metal salt, because this type of salt has the advantage of being soluble and therefore will react immediately by double decomposition as soon as the dye powder is added to water.

The proportions of metal leuco compound and inorganic salt are not particularly important as long as a sufficient amount of the inorganic salt is present to react by double decomposition with all of the metal leuco compound.

As indicated by the examples, auxiliary agents such as dextrine, alkali metal salts of formaldehyde condensation products of sulfonic acid derivatives of naphthalene and other materials having similar characteristics may be incorporated into the dye powder. In general, the auxiliary agents may include wetting agents, dispersing agents, protective colloids and similar materials of a type which are well known in the art. Where the salt which is employed to react with the metal leuco derivative is a neutral salt, a mildly alkaline reacting salt may also be added, as, for instance, mixtures of alkali metal sulfates and alkali metal carbonates when the metal leuco derivative is that of an alkaline earth metal or other metal which forms insoluble sulfates and carbonates.

If the mixture of water-insoluble metal leuco derivative and inorganic salt is to be made up into a printing paste, printing assistants such as anthraquinone-sulfonic acids, anthraquinone-carboxylic acids, salts thereof, and/or small amounts of inorganic iron salts may be added. Substances such as glycerin, diethylene glycol and thickening agents may also be employed. Reducing agents such as sodium formaldehyde-sulfoxylate are not essential but may be added if desired.

The invention is advantageous in that it provides a new type of vat dye powder which is generally useful in dyeing with vat dyes and, in some cases, produces unusually good results when made up into printing pastes and used in printing. One advantage of the invention is that it enables the printing and dyeing of vat dyes without the use of reducing agents. It is particularly advantageous in dyeing and printing wool and silk fabrics because strong alkalis such as sodium hydroxide are not required to reduce the dye to its soluble form. In printing wool and silk, this is an important factor because such fibers, and animal fibers generally, are acted upon by strong alkalis and ordinarily very careful control of the alkali must be maintained if these materials are to be dyed with vat dyes. By enabling the printing to be carried out without a reducing agent, the invention is of value in printing vat dyes in the same pattern with some types of azo dyes. Thus, water-soluble diazoimino compounds when printed in the same pattern with vat dyes and sodium formaldehyde sulfoxylate according to the usual methods are adversely affected by the formaldehyde vapors given off in the ager. The present invention avoids this disadvantage.

So much of this application as relates specifically to printing pastes and a process of printing certain of the preferred metal leuco derivatives herein described is claimed in a co-pending application, Serial No. 35,400 filed of even date herewith.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as set forth in the appended claims.

We claim:

1. A non-aqueous dye composition comprising an intimate mixture of a water-insoluble metal leuco derivative of a vat dye and a water-soluble metal salt which yields an anion and which forms a salt with the metal of the said leuco derivative by double decomposition in the presence of water which is more insoluble than the metal leuco derivative.

2. The composition of claim 1 in which the water-soluble metal salt is a neutral salt.

3. A vat dye powder comprising an intimate mixture of a water-insoluble metal leuco derivative of a vat dye and a water-soluble metal salt which yields an anion and which forms a salt with the metal of the said leuco derivative by double decomposition in the presence of water which is more insoluble than the metal leuco derivative, said water-soluble metal salt being present in at least the theoretical proportions required for said double decomposition.

4. The composition of claim 3 which contains dextrine.

5. The composition of claim 3 which contains an alkali metal salt of a condensation product of a naphthalene-sulfonic acid with formaldehyde.

6. A non-aqueous vat dye composition comprising an intimate mixture of an alkaline earth metal leuco derivative of a vat dye and an alkali metal sulfate.

7. A composition according to claim 6 which also contains an alkali metal carbonate.

8. A non-aqueous vat dye composition comprising a metal leuco derivative of a metal of Group II*a* of the Periodic System and a thioindigoid dye containing in the 6-position of its aromatic nucleus a radical selected from the group consisting of halogen and alkoxy, and a water-soluble metal salt which yields an anion and which forms a salt with the metal of the said leuco derivative by double decomposition in the presence of water which is more insoluble than the metal leuco derivative, said water-soluble metal salt being present in at least the theoretical proportions required for said double decomposition.

9. A vat dye powder comprising an intimate mixture of the calcium leuco salt of 6:6'-diethoxy thioindigo and at least the theoretical proportions of an alkali metal sulfate required to form the alkaline earth metal sulfate by double decomposition with the leuco derivative.

10. In a process of coloring textile materials with vat dyes, the step which comprises preparing a dye bath by adding a water-insoluble metal leuco derivative of a vat dye and a water-soluble metal salt which yields in aqueous solutions an anion and which forms a salt with the metal of the said leuco derivative which is more insoluble than said metal leuco derivative to water whereby double decomposition occurs to form a water-soluble metal leuco derivative of a vat dye and a water-insoluble metal salt.

11. The process of claim 10 in which the water-soluble metal salt is a neutral salt.

12. The process of claim 10 in which the water-soluble salt is a mixture of a neutral salt and a mildly alkaline reacting inorganic salt, each of which yields in aqueous solution an anion which forms a more insoluble salt with the metal of the metal leuco derivative than said metal leuco derivative.

13. In a process of coloring wool, silk and fibers of animal origin, the step which comprises bringing together a water-insoluble metal leuco derivative of a vat dye and a neutral water-soluble metal salt yielding in aqueous solution an anion which forms a more insoluble salt with the metal of said leuco derivative by double decomposition than said metal leuco derivative, and water, whereby said double decomposition occurs, and treating the animal fiber with the resultant mixture.

14. The process of claim 13 in which a mildly alkaline reacting inorganic salt is also present.

15. The process of claim 13 in which the metal leuco derivative is an alkaline earth metal leuco derivative of 6:6'-diethoxy thioindigo, and the neutral salt is an alkali metal sulfate.

PAUL W. CARLETON.
ARTHUR L. FOX.