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ART OF DYEING WITH VAT DYES

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This invention relates to the art of dyeing and to dyeing compositions and their application to textile fibers. It relates especially to a new class of assistants for the dyeing of textile fibers and especially those of the vegetable type such as cotton, regenerated cellulose and the like, with vat dyes by a process in which a leuco compound of a vat dye is formed by the reduction of a vat dye in the presence of the fiber to be dyed, as for example a printing process or a pad-jig dyeing process.

As is well known, vat dyes are solid substances which are insoluble in water. In order to render them useful in the dyeing of textile fibers they are converted to a water soluble form, in which form they are taken up by the fiber, and then the fiber is subjected to an oxidizing or fixing treatment whereby the vat dyestuff is again rendered insoluble. One general method of application of vat dyes to the dyeing of textile fibers involves application of the dye in the unreduced form to the material to be dyed, subjecting the resulting material to a reducing treatment whereby the dye is converted to the soluble form in the presence of the fiber and is taken up by the fiber, and then subjecting it to oxidation and/or other finishing treatments to fix the dye on the fiber and complete the finishing of the material. In dyeing with vat dyes by this general method one of two procedures is usually followed, it depending upon whether the textile material is to be dyed a uniform or so-called "solid" color, or is to be dyed in accordance with a pattern or design in one or more colors. If the material is to be dyed a solid color, the so-called "pigment padding" or "pad-jig" process may be employed. If the material is to be dyed in accordance with a pattern or design, the so-called "printing" process is generally utilized.

The pad-jig process of dyeing with vat dyes generally involves passing the textile material to be dyed through an aqueous suspension or so-called "padding" bath containing the unreduced vat dye in finely divided form suspended in a suitable suspension medium (such as water, which may or may not also contain a gum or thickener and other substances, such as an assistant, sodium sulfide, disodium phosphate, etc.) whereby the fiber mechanically picks up the particles of insoluble dye; subsequently working the textile material having the particles of dye mechanically attached thereto, in a reducing bath whereby the dye is reduced to the soluble form and is taken up (absorbed and/or adsorbed) by the fiber; and finally subjecting the material to oxidation and finishing treatments to reconvert the dye to the insoluble form and fix it on the fiber, and further complete the finishing of the material.

The printing process of dyeing textile fabrics generally involves applying a so-called "printing" paste to the fabric in the form of a design (for example, by means of a screen, a stencil or an engraved roll), and then subjecting the printed fabric to further treatment to fix the dye. In general, vat dye printing pastes contain, in addition to the unreduced vat dye, substances which in themselves do not reduce the vat dye under the conditions of the printing operation but which in the subsequent operations (such as application of heat and/or steam) react with the dye to reconvert it to the soluble form (such as sodium formaldehyde-sulfoxylate and potassium carbonate), other substances or assistants which promote the reduction of the dye and/or absorption of the reduced compound by the fiber, and suitable gums or thickeners. In some cases, as in printing with difficultly reducible vat dyes, the vat dye in the printing paste is subjected to a preliminary partial reduction before applying the printing paste to the fabric. The fixing treatment usually comprises subjecting the printed fabric to a short treatment with wet steam while excluding air (so-called "steaming" or "aging") whereby the vat dye is reduced (for example, by the action of the sodium-formaldehyde-sulfoxylate and potassium carbonate), or its reduction is rendered more complete, and the reduced dye is taken up by the fiber, and then subjecting the fabric to oxidizing, washing and other finishing treatments.

Vat dyes, when applied to fabric by a padding process or when printed on fabrics with the aid of alkalies, as for example alkali metal carbonates or alkali metal bicarbonates, frequently fail to yield full color value. This may be attributed to improper fixation of the dye on the fiber because of variable aging conditions or variable physical conditions of the vat dye padding liquors or printing paste.

Various assistants heretofore have been proposed with the object of improving the dyeings obtained with vat dyes by pad-jig and printing processes but they are all subject to various disadvantages. For example, various monohydric alcohols have been proposed as assistants in vat dye printing in view of their solvent action on the leuco compounds of the vat dyes of the indigoid and thioindigoid classes. Low boiling alcohols, however, are objectionable in vat printing pastes, inasmuch as they evaporate prior to the aging

step and even before application to the fiber, thus causing partial drying out of the paste and premature loss of assistant, resulting in uneven prints. (A vat dye assistant, to be most effective, should be present during the reducing or aging step.) The use of higher boiling monohydric alcohols has the objections that they are insufficiently soluble in water, and especially in printing pastes, to yield good homogeneity, and they impair the good working properties of vat dyestuff printing pastes. In general the assistants heretofore proposed further suffer from the fact that they produce little or no improvement in prints of light shades.

The use of dispersing agents has also been proposed in the dyeing with vat dyes by the pad-jig process, but they are open to the objection that they act mainly during the padding operation and do not assist in the absorption or adsorption of the leuco compound of the vat dye in the reducing or "jigging" step.

The present invention is based upon the discovery that the soluble salts of the acid reaction products resulting from the interaction of an aliphatic alcohol containing less than 6 carbon atoms with a polybasic inorganic acid or suitable derivative thereof possess a combination of properties which render them of particular value for use as assistants in the dyeing of textile fibers, and especially those of the vegetable type, such as cotton, rayon (regenerated cellulose) and the like, by a process in which a leuco compound of a vat dye is formed by reduction in the presence of the fiber to be dyed, and especially by pad-jig and printing processes, as well as in the preparation of printing pastes and padding liquors for dyeing textile fibers with vat dyes. Thus the soluble salts of the acid reaction products of sulfuric acid or chlorsulfonic acid upon the aliphatic monohydric alcohols which contain 5 or less carbon atoms, which products are considered to be acid alkyl sulfates corresponding with the formula $ROSO_3H$ (in which R is a hydrocarbon radical containing not more than 5 carbon atoms), as well as others of the hereinafter-described soluble salts of acid alkyl esters of inorganic polybasic acids, have the faculty of rapidly entering into solution in water and other aqueous suspension media usually employed in dyeing with vat dyes. They furthermore have no tendency to cause the pastes to foam or lather. In addition they act as assistants in the absorption or adsorption of the reduced compounds of the vat dyes by the fiber, and in the penetration of woven fabric by the reduced compounds of the vat dyes during the developing, steaming or aging operations.

While most of the known vat dye printing assistants exert a very definite action, for example catalytic, dissolving, or enolyzing, on the vat dye, the alkyl ester salts of the present invention apparently act on both the vat dye and the fiber itself, causing more effective absorption of the leuco-compound of the dyestuff and greatly increasing the printing strength of printing pastes.

Although I do not wish to be limited to any theory of reaction involved in using the assistants of the present invention, it is possible that the alkyl sulfates referred to are partially saponified by the alkaline reagents present in the printing paste so that during the aging operation these materials are slowly acted upon to liberate the corresponding alcohol, and that therefore the alkyl sulfates behave not only as sulfates but as alcohols, serving to more effectively dissolve or disperse the leuco form of the vat dyestuff. This is further borne out by the fact that other materials which are capable of saponification to produce free alcohols such as the acid alkyl phosphates, phosphites, boro-sulfates, boro-phosphates, borates and silicates, also yield improved results in pad-jig dyeing and printing with vat dyes.

The acid alkyl esters, the soluble salts of which may be employed in accordance with the present invention, include the partial esters of polybasic inorganic acids (as for example, of sulfuric, phosphoric, boro-sulfuric, boro-phosphoric, boric, silicic, etc., acids) and especially those of sulfuric and phosphoric acids containing at least one aliphatic hydrocarbon radical (straight-chain, branched-chain, saturated or unsaturated) which contains not more than 5 carbon atoms, as the organic (ester) radical or radicals. These partial esters (which are herein designated as "acid alkyl esters") may be represented by the formula $(RO)_x—A—(OH)_{n-x}$ in which

R represents an aliphatic hydrocarbon radical which contains not more than 5 carbon atoms,

A represents the residue of the inorganic acid (as for example, the radical SO_2, the radical PO, the radical SiO, the radical B, etc.),

n represents the number of hydrogen atoms, in the uncombined polybasic acid from which the ester is derivable, which are replaceable by a metal (herein designated as "replaceable hydrogen atoms"), and

x is 1 or more but not greater than n-1. As is well known a partial ester, or acid alkyl ester, of a polybasic inorganic acid is an ester in which at least one of the replaceable hydrogen atoms of the parent polybasic inorganic acid has not been replaced.

It is to be noted, in the case of acid alkyl esters which are derivatives of polybasic acids containing 3 or more replaceable hydrogen atoms in which more than one of said hydrogen atoms have been replaced by organic radicals, the said organic radicals (represented by R in the above formula) may be the same or different.

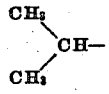
The alkyl ester salts employed in accordance with the present invention comprise especially the soluble salts of the herein described acid alkyl esters, e. g. those resulting from the combination of any suitable metal or base, including the organic bases, with the said acid alkyl esters. It is particularly advantageous, however, to use the alkali metal salts of the acid alkyl sulfates, phosphates, boro-sulfates and boro-phosphates or the salts formed by the interaction of the acid alkyl sulfates, phosphates, boro-sulfates and boro-phosphates with aliphatic or aromatic amines, for example, the alkylol amines. Thus the potassium and sodium salts of the said acid alkyl esters, or the salts of the acid alkyl esters with diethanolamine, triethanolamine, pyridine, or other salt-forming ammonium bases, may be used. The sodium salts, in view of their extremely high solubility in water and alkaline printing pastes (which permits their incorporation into such printing pastes in almost any desired amount), are of especial value.

The said salts of alkyl esters employed in accordance with the present invention may be prepared in any manner well known to the art; as for example, by the treatment of the corresponding alcohol, in the presence or absence of a solvent of diluent, with a suitable inorganic reagent (such as phosphoric acid, phosphorus chloride or oxychloride, concentrated sulfuric acid,

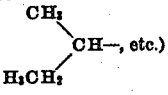
and/or chlorsulfonic acid, and/or one or more of these in the presence of boric acid, etc.), and neutralization of the resulting acid alkyl ester with an inorganic or organic base which forms a readily soluble salt with said acid alkyl ester. It may be noted that the alkyl sulfuric acids and the alkyl boro-sulfuric acids resulting from the use of sulfuric acid or chlorsulfonic acid in the absence or presence of boric acid, may contain varying amounts of sulfonic acids which are sometimes produced due to secondary reactions; the presence of such sulfonic acids, however, does not impair the usefulness of the alkyl sulfuric acids and alkyl boro-sulfuric acids in accordance with the present invention.

As illustrating acid alkyl esters, the soluble salts of which may be employed in accordance with the present invention, the following may be mentioned: the mono-ethyl, propyl, butyl and amyl sulfuric acids; the ethyl, propyl, butyl and amyl boro-sulfuric acids, the mono- and di-ethyl, propyl, butyl and amyl phosphoric acids; the ethyl, propyl, butyl and amyl boro-phosphoric acids; etc.

Of special interest in connection with the present invention are the various soluble salts, and particularly the alkali metal and organic amine salts, of the sulfuric acid monoesters of the various monohydric alcohols which contain not more than 5 carbon atoms, including those which contain single or multiple bonds, straight chains and branched chains; as for example, the sodium or potassium salts of the following: ethyl sulfuric acid; normal and isopropyl sulfuric acids; the mono sulfuric acid ester of methyl ethyl carbinol; normal-, iso-, and tertiarybutyl sulfuric acids; the mono sulfuric acid esters of pentasol, of secondary butyl carbinol, and of methyl-n-propyl carbinol; pentene-2-sulfuric acid; normal amyl sulfuric acid; tertiary amyl sulfuric acid; amylene sulfuric acid; etc. The salts of the monoalkyl sulfuric acids which contain from 3 to 5 carbon atoms in the alkyl group are of especial value in the pad-jig dyeing and printing with vat dyes in accordance with the present invention. Those in which the alkyl group comprises an iso-alkyl radical (as for example, an isopropyl radical:



an isobutyl radical:



are somewhat superior in their action to these in which the alkyl group is a normal or straight-chain radical.

The said sulfuric acid mono esters may be prepared for example, by the treatment of the corresponding alcohol, in the presence or absence of a solvent or diluent, with a suitable sulfonating agent (such as concentrated sulfuric acid and/or chlorsulfonic acid or the like), or by the interaction of sulfuric acid or the like with the corresponding unsaturated hydrocarbon. Thus, a suitable alcohol dissolved in an inert organic solvent may be reacted with the necessary amount of sulfonic acid to form the sulfuric acid mono ester of the alcohol, the mixture then may be blown with air to remove hydrogen chloride formed, and subsequently stirred with water.

Mixtures of salts of the said acid alkyl esters may also be employed in accordance with the present invention. For example the salts of suitable inorganic or organic bases with the commercially available and cheap mixtures of alkyl sulfuric acids resulting from the sulfuric acid treatment of mixed gaseous and lighter liquid unsaturated hydrocarbons, such as the mixtures produced in the recovery and removal of unsaturated hydrocarbons in the production and purification of gasoline in the so-called "cracking" process of petroleum distillation.

The percentage of assistant of the present invention that may be employed is not critical and improved results are obtained with even as little as 1 per cent or 2 per cent (based on the total weight of the printing paste or padding liquor).

The advantageous action of the said salts of the acid alkyl esters may be secured in a number of ways. Thus the said alkyl ester salts may be incorporated into the usual printing pastes or padding liquors. The said alkyl ester salts are in general crystalline products and hence may be added directly to the printing paste or padding liquor to cause the desired effect. Further, the advantageous action may be secured by subjecting the cloth to be dyed or printed to a preliminary treatment with the solution of the said alkyl ester salt, as for example, impregnation. In copending application Serial No. 673,030, filed May 26, 1933, vat dye compositions in the form of powders are described containing vat dyestuffs and alkyl ester salts of the type herein disclosed. Such compositions, in view of their content of said alkyl ester salts, may be employed in accordance with the present invention merely by mixing them with the usual thickener, alkali (potassium carbonate), reducing agent (sodium formaldehyde sulfoxylate), water and/or other usual ingredients of printing pastes, and employed for printing in the ordinary manner. The acid alkyl esters may also be employed as such in preparing printing pastes and padding liquors containing alkali inasmuch as the salts of said acid alkyl esters will be formed in the resulting compositions and there exert their advantageous action.

In dyeing by the printing process the printing paste may contain printing catalysts or "boosters", reduction accelerators, hydrotropic and/or enolyzing substances, and the like.

It is to be noted that under the term "hydrotropic substances" are to be understood not only the substances specifically enumerated by Neuberg and Tamba (compare Carl Neuberg, Biochemische Zeitschrift, vol. 76, 1916, page 107 ff., and Tamba, Biochemische Zeitschrift, vol. 145, 1924, page 415; Carl Neuberg, Sitzungsberichte der Koengl. Preussischen Akademie der Wissenschafter, 1916, page 1034), but all of those substances, which comply with the definition of the word "hydrotropic" as given by Neuberg. As examples of such substances the following may be mentioned: urea, substituted ureas, thiourea, hexamethylene tetramine, the potassium salt of ethyl sufonic acid, potassium or sodium isovalerate, the alkali metal salts of the following acids: isobutyric acid, phenylacetic acid, benzoic acid, o-toluene-carboxylic acid, salicylic acid, the benzene sulfonic acids, p-toluene-sulfonic acid, the benzene sulphinic acids, 1.4-toluene sulphinic acid, naphthalene sulfonic acids, aniline sulfonic acids and substitution products thereof, naphthylamine sulfonic acids (as for example, 1-aminonaphthalene - 3.6.8 - trisulfonic acid), pico-

linic acid, hydroaromatic carboxylic or sulfonic acids, and the like. It will be further noted that substances which are not, strictly speaking, hydrotropic substances but which possess enolyzing properties are included, as for example, 1-naphthalene sulfonic acid (sodium salt).

The presence of enolyzing substances in vat dye printing pastes prepared in accordance with the present invention is of particular advantage in connection with vat dyes of the indigoid and thioindigoid series, inasmuch as they tend to minimize or prevent isomerization of the reduced vat dye to the keto form.

If desired, foam breaking or foam-preventing agents may also be included in the compositions of the present invention in connection with vat dyes which have a tendency to produce foaming.

The invention may be employed in connection with vat dyes of all types including those derived from anthraquinone, indophenols, various indigoid, thioindigoid and indirubin compounds, etc.; as for example, indanthrones, pyranthrones, flavanthrones, dibenzanthrones, isodibenzanthrones, perylene quinones, anthanthrones, dibenzpyrene quinones, anthrimidocarbazols, naphthacridones, indigo, thioindigo, indirubin, etc., including derivatives thereof, such as their halogen, nitro, sulfur, and/or alkoxy derivatives. The term "vat dye compound" is intended to cover specifically the vat dye in the insoluble form and in the form of the free leuco compound or a soluble metal (or organic ammonium base) salt thereof (in the presence of alkaline compounds.) Ordinarily a vat dye printing paste contains the vat dye in the insoluble form. It may also contain the vat dye in the leuco form either alone or in addition to the vat dye, as when the vat dye is prereduced.

Examples of vat dyestuffs with which the present invention may be employed are such indigoid and thioindigoid dyestuffs as the following:

National Vat Orange R	Color Index No. 1217
National Vat Red Violet RH	Color Index No. 1212
5,5'-Dichlor-7,7' Dibrom Indigo	Color Index No. 1188
National Brilliant Indigo 4G	Color Index No. 1189
National Brilliant Indigo B	Color Index No. 1190
National Brilliant Indigo 4B	Color Index No. 1184
National Vat Scarlet G	Color Index No. 1228

National Vat Brown G (dinaphthylthioindigo)

National Vat Violet R	Color Index No. 1222
National Vat Green G	Color Index No. 1199

National Vat Pink (6,6'-dichlor-4,4' dimethyl-2,2'-bis-thio-naphthenindigo)

National Vat Pink BG	Color Index No. 1210
National Vat Yellow G	Color Index No. 1196
National Vat Yellow R	Color Index No. 1170

and such anthraquinone vat dyes as the following:

National Carbanthrene Blue RS	Color Index No. 1106
National Carbanthrene Blue 3G	Color Index No. 1109
National Carbanthrene Blue GCD	Color Index No. 1113
National Carbanthrene Yellow G	Color Index No. 1118
National Carbanthrene Golden Orange 2RT	Color Index No. 1097
National Carbanthrene Golden Orange G	Color Index No. 1096
National Carbanthrene Blue Green FFB	Color Index No. 1173
National Carbanthrene Violet 2R	Color Index No. 1104
National Carbanthrene Dark Blue DR	Color Index No. 1099
National Carbanthrene Flavine GC	Color Index No. 1095
National Carbanthrene Red Violet 2RNX	Color Index No. 1161
National Carbanthrene Brilliant Green supra	Color Index No. 1101
National Carbanthrene Green B	Color Index No. 1102
National Carbanthrene Brown AR	Color Index No. 1151
National Carbanthrene Olive R	Color Index No. 1150
National Carbanthrene Red BN	Color Index No. 1162
National Carbanthrene Red AFF	Color Index No. 1133
National Carbanthrene Black J	

Furthermore, mixtures of two or more vat dyes may be employed, for example when it is desired to produce compound shades such as scarlets, navy blues, blacks and browns.

Other assistants may be used together with the assistants of the present invention, as their effectiveness is not impaired by the use of any of the usual assistants; for example, suitable mono- or polyhydric alcohols (f. i., glycerine), hydroxyalkyl ethers, alkylol amines, etc.

The invention is not restricted to any particular method of applying the vat dyes but includes the dyeing of piece goods (cotton, rayon, etc.) by the pad-jig process and the printing of piece goods by the various printing processes (including discharge printing and color discharge printing as well as ordinary types of vat dye printing), in which various methods of applying the padding liquor or printing paste are employed.

The alkyl ester salts of the present invention yield especially beneficial results. Because of their non-volatility, there is no danger of their evaporation prior to the ageing process; hence the uniformity of the vat dye printing pastes is retained and a proper drying of the printed material is secured. While formerly known assistants produce little or no improvement in prints of light shades, the compounds of the present invention are especially distinguished by the noticeable increase in printing strength obtainable by their use, even with very light shades. The alkyl ester salts of the present invention are particularly valuable in pad-jig dyeing and printing of so-called "gray-goods" (unbleached cotton fabrics, raw regenerated cellulose fabrics and the like) with vat dyes, inasmuch as the dyeings and prints obtained with the aid of such alkyl ester salts have exceedingly high tinctorial value and excellent penetration as compared with dyeings and prints made in the absence of said alkyl ester salts.

The salts of the acid alkyl esters of the present invention are further of particular benefit in dyeing and printing with vat dye compositions which contain heavy metal compounds as printing catalysts or "boosters" or reduction accelerators. It has heretofore been suggested to employ compounds of heavy metals (and metalloids) which are capable of exhibiting more than one valency, as for example, the salts (halides, sulfates, acetates, etc.), oxides or hydroxides of iron, copper, tin, zinc, titanium, chromium, nickel, mercury, arsenic, etc., for this purpose. Many compounds of this type do not exhibit, however, the desired catalytic or "boosting" action when employed in the usual printnig pastes. In accordance with the present invention, such heavy metal compounds are employed in conjunction with the acid alkyl esters herein described, whereby an effective catalytic reducing action on the vat dyes is secured. Thus, when the alkyl ester salts herein described are employed in connection with heavy metal salts of said type exhibiting catalytic or "boosting" action when present, for example, in proportion to about 0.05 to about 3 per cent by weight of the vat dye printing pastes, an increase in the catalytic or "boosting" action of said heavy metal salts is obtained. Further, when the hereindescribed acid alkyl esters are employed in conjunction with heavy metal compounds of the said type not exhibiting catalytic or "boosting" action in the usual vat dyestuff printing pastes, catalytic or "boosting" action is secured. This combined advantageous effect may be secured by employing the said heavy metal compound in the presence of a soluble salt of an acid alkyl ester,

for example, one of those hereindescribed, or by employing the heavy metal compound and acid alkyl ester in combination, as for example, in the form of a salt of the heavy metal with the acid alkyl ester (as for example, the iron, nickel, cobalt, manganese or chromium salts of the acid alkyl sulfates, phosphates, boro-sulfates and boro-phosphates hereinbefore mentioned). Of particular value in this connection are the salts and other compounds containing nickel, cobalt or manganese.

The following examples, in which the parts are by weight, will serve to illustrate the invention.

Textile printing

A standard starch-tragacanth thickener is prepared by mixing together and boiling the following ingredients, any loss of water being replaced after boiling:

1 part cornstarch
3 parts British gum
1 part 5% tragacanth solution
5 parts water.

Example 1

Part 1.—A stock printing thickener is made up by mixing

52 parts of the above standard starch-tragacanth thickener,
15 parts of potassium carbonate (K_2CO_3), and
10 parts of water.

and heating until the potassium carbonate is completely dissolved, bringing the resulting paste to a temperature of 160° F. and adding

12 parts of sodium formaldehyde sulfoxylate, and
11 parts of water (or 5 parts of glycerine and 6 parts of water).

Part 2

20 parts of National Vat Orange R paste (containing about 13% of dye solids).

70 parts of the stock printing thickener of Part 1, and

10 parts of dry isobutyl sodium sulfate are thoroughly mixed to insure a paste of uniform composition. The resulting vat dye printing paste is printed, for example by means of an engraved roll, upon a cotton fabric, the printed fabric is dried, and then subjected to the aging action of air-free, saturated steam at 102° C. for 3 to 5 minutes. After this aging treatment the fabric is rinsed in a stream of cold water and is then soaped at boiling temperature in the presence of air until the dye is fully developed. The resulting printed fabric exhibits full penetration and a strength of print 20% to 30% greater than is obtained by the same printing method and printing paste but with the isobutyl sodium sulfate omitted.

Similar improved results may be obtained by mixing 20 parts of the vat dye powder described in Example 7 of copending application Serial No. 673,030, filed May 26, 1933 (which contains isobutyl sodium sulfate as a part thereof) with 80 parts of the stock thickener of Part 1 of the present example and employing the resulting paste in the printing process of this example.

Prints of lighter shade may be obtained by cutting the printing paste as given in Part 2 of the present example with a thickener for reduction containing a considerably lower percentage of potassium carbonate and sodium formaldehyde sulfoxylate, for example a thickener obtained by reducing the amounts of potassium carbonate and sodium formaldehyde sulfoxylate in the stock printing thickener of this example to, for example, about 7% potassium carbonate and 5% sodium formaldehyde sulfoxylate.

The isobutyl sodium sulfate may be prepared, for example, by reacting 516 parts of isobutyl alcohol with 813 parts of chlorsulfonic acid at a temperature of about 14° to 16° C.; adding the resulting reaction mixture slowly to 8100 parts of water to which 418 parts of hydrated lime, $Ca(OH)_2$, have been added, while cooling the resulting mass to a temperature of about 20° C.; filtering off calcium sulfate; converting the calcium isobutyl sulfate, contained in the filtrate, to sodium isobutyl sulfate, for example, by treating with sodium carbonate and removing calcium carbonate, and recovering the sodium isobutyl sulfate in the form of a dry solid.

Example 2

20 parts of National Vata Red Violet RH paste (containing about 18% of dye solids)
68 parts of the stock printing thickener of Example 1, Part 1, and
12 parts of isopropyl sodium sulfate are intimately mixed to produce a uniform printing paste, and the paste is printed and developed as in Example 1. A strength of print is obtained which is 25% greater than that obtained without isopropyl sodium sulfate.

Example 3

20 parts of National Vat Pink Paste (containing 15% of dye solids),
68 parts of the stock printing thickener of Example 1, Part 1, and
12 parts of sodium ethyl sulfate are intimately mixed to form a uniform printing paste. When printed and developed as in Example 1, the resulting prints are brighter and 15 to 20% stronger than those obtained without the addition of sodium ethyl sulfate.

Example 4

20 parts of 5,5'-dichlor-7,7'-dibrom indigo (20% paste),
70 parts of the stock printing thickener of Example 1, Part 1, and
10 parts of n-amyl sodium sulfate are mixed, printed and developed as in the preceding examples. A print of improved strength and brightness is obtained.

Example 5

20 parts of 5.5'-dichlor-7.7'-dibrom-indigo paste (containing 20% of dye solids)
0.5 part nickel sulfate ($NiSO_4 7H_2O$)
70 parts of the stock printing thickener of Example 1, Part 1, and
9.5 parts of sodium isobutyl sulfate are mixed, printed and developed as in the preceding examples. A print of appreciably improved strength and brightness is obtained. In the above example the 5.5'-dichlor-7.7'-dibrom-indigo may be replaced by 20 parts of National Vat pink FF paste (containing 15% of dye solids).

Example 6

20 parts of National Vat Pink FF paste (containing 15% of dye solids)
68 parts of the stock printing thickener of Example 1, Part 1, and
12 parts of sodium isobutyl boro-sulfate are intimately mixed to form a uniform printing

paste. When printed and developed as in Example 1, the resulting prints are brighter and from 20 to 25% stronger than those obtained without the addition of the sodium isobutyl boro-sulfate. (The sodium isobutyl boro-sulfate may be prepared, for example, by stirring 918 parts of 100% sulfuric acid with 200 parts of boric acid at a temperature of 75° C. until a uniform solution results; then adding 320 parts of isobutyl alcohol in a slow stream with agitation, while keeping the temperature at 30 to 35° C.; after stirring this solution two hours, running it into a mixture of 2000 parts of 40% caustic soda and 1000 parts of isobutyl alcohol while stirring and cooling; permitting the resulting mixture to stratify; drawing off the aqueous layer; neutralizing the remaining isobutyl alcohol layer with sodium carbonate or caustic soda, heating it to boiling and filtering hot; and drying the filtrate on a rotary drum drier.)

Example 7

Part 1.—A printing thickener is prepared by mixing

52 parts of the above standard starch tragacanth thickener,
17 parts of potassium carbonate,
14 parts of sodium formaldehyde sulfoxylate,
5 parts of glycerine, and
12 parts of water.

A printing paste is formed by mixing

68 parts of the printing thickener of Part 1 with
20 parts of National Carbanthrene Blue GCD dye paste (containing 17% of dye solids) and
12 parts of an alkyl sulfate salt (for example, sodium ethyl sulfate or sodium isobutyl, butyl, boro-sulfate or a mixture of several of the alkyl sulfates or alkyl boro-sulfates previously enumerated).

When this printing paste is printed upon a textile fabric as in Example 1 and the print is dried, aged, oxidized, rinsed, soaped and finished in a similar manner, prints of increased strength are produced.

Prints of lighter shades may be obtained by diluting the printing paste as illustrated by this example, with a thickener for reductions, for example a thickener analogous in composition to the printing thickener given in Part 1 of this example, but in which the percentages of potassium carbonate and of sodium formaldehyde sulfoxylate have been reduced to 8% and to 6% of the total printing thickener, respectively. The increased strength over prints obtained without the addition of the alkyl sulfate is especially noticeable with such lighter shades.

PAD-JIG DYEING

Example 8

A padding liquor is prepared containing the following ingredients in the following approximate amounts:

National Carbanthrene Blue GCD in the form of the double paste (Color Index No. 1113)	grams	30
n-Amyl sodium sulfate	do	5
Gum Tragacanth	do	3.6
Gum Arabic	do	6.8
Water sufficient to make up volume to approximately	cc.	1700

for example, by mixing the dyestuff paste with the n-amyl sodium sulfate, which is preferably employed in the form of an aqueous solution, adding the gum arabic and gum tragacanth in the form of water solution, bringing the total volume up to the said volume with additional water, and straining the mixture through a cloth of fine mesh. Cotton piece goods are padded or printed with the liquor in any suitable manner (for example, by passing the cloth between rolls through a vessel containing the padding liquor which is preferably at a temperature of about 120° F.). The padded or printed cloth is then treated on the jig in the well known manner, for example, in an alkaline hydrosulfite bath preferably maintained at a temperature of about 140° to 160° F., wherein the color rapidly develops, and is then finished in any convenient known way.

The dyeings thus obtained are of an increased brightness and fullness of shade and are better penetrated as compared with those obtained by the same process but with the employment of a padding liquor containing no n-amyl sodium sulfate.

In this example any one of the acid alkyl ester salts hereinbefore referred to, and especially the sodium and potassium salts of the acid alkyl sulfates may be used instead of n-amyl sodium sulfate. Similar improved dyeings may be obtained by replacing the vat dye paste and n-amyl sodium sulfate of the present example by 30 grams of the powder produced in Example 10 of copending application Serial No. 673,030, filed May 26, 1933, and containing isobutyl sodium sulfate as a part thereof.

The action of the acid alkyl ester salts as penetrating agents and surface tension lowering agents may be enhanced by adding to the padding liquor a small amount of caustic alkali, alkali metal carbonate, trisodium phosphate, sodium silicate, etc. For example, 1 to 3 parts of said substances may be added to the padding liquor of this example.

As above indicated, the advantageous action of the salts of the acid alkyl esters as assistants in pad-jig dyeing and printing also may be secured by pretreating the fiber with the salt of the acid alkyl ester. The following example illustrates such pretreatment.

Example 9

Bleached or unbleached cotton cloth is padded with a solution containing, for example, about 5 to about 30 parts of sodium isobutyl sulfate or any of the other salts of acid alkyl esters herein described, per 1000 parts of water, for example by passing the cloth through the solution contained in a padding box equipped with squeeze rolls. Preferably, the padding liquor also contains about 2 to about 5 parts of gum tragacanth or other suitable thickener per 1000 parts of liquor. The pressure of the squeeze rolls is preferably so regulated that the cloth retains its own weight of the padding liquor. The padded cloth is then passed through a hot air drier or over hot cans, is rolled up and is then ready for printing or dyeing. The penetration obtained this way is superior, especially for lighter shades. This process is particularly suitable for artificial fibers of the regenerated cellulose type. If desired, alkalies, such as caustic alkalies, alkali metal carbonates, trisodium phosphate, etc. may also be added to the padding liquor.

This application is a continuation-in-part of applications Serial Nos. 673,030 and 673,031, filed May 26, 1933.

I claim:

1. In the dyeing of textile fibers by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye compound, the improvement which comprises carrying out the dyeing with the aid of a soluble salt of an acid alkyl ester containing not more than 5 carbon atoms in the alkyl group and derivable from a polybasic inorganic acid and an aliphatic alcohol containing not more than 5 carbon atoms.

2. In the dyeing of textile fibers of the vegetable type by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye, the improvement which comprises carrying out the absorption of the leuco-compound by the fiber in the presence of a soluble salt of an acid alkyl ester containing not more than 5 carbon atoms in the alkyl group and derivable from a polybasic inorganic acid and an aliphatic alcohol containing not more than 5 carbon atoms.

3. In the dyeing of textile fibers of the vegetable type by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye, the improvement which comprises carrying out said reduction in the presence of an alkali metal salt of an acid alkyl ester having the formula

$$(RO)_x—A—(OH)_{n-x}$$

in which R represents an aliphatic hydrocarbon radical which contains not more than 5 carbon atoms, A represents the radical SO_2 or the radical PO, n represents the number of replaceable hydrogen atoms in the uncombined acid from which the ester is derivable, and x represents a whole number not greater than n—1.

4. In the dyeing of textile fibers of the vegetable type by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye, the improvement which comprises carrying out said reduction in the presence of an organic amine salt of an acid alkyl ester having the formula

$$(RO)_x—A—(OH)_{n-x}$$

in which R represents an aliphatic hydrocarbon radical which contains not more than 5 carbon atoms, A represents the radical SO_2 or the radical PO, n represents the number of replaceable hydrogen atoms in the uncombined polybasic acid from which the ester is derivable, and x represents a whole number not greater than n—1.

5. In the dyeing of textile fibers of the vegetable type by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye, the improvement which comprises applying to the fiber a vat dye composition containing a vat dye in the unreduced form and a soluble salt of an acid alkyl ester having the formula

$$(RO)_x—A—(OH)_{n-x}$$

in which R represents an aliphatic hydrocarbon radical which contains not more than 5 carbon atoms, A represents the radical SO_2 or the radical PO, n represents the number of replaceable hydrogen atoms in the uncombined polybasic acid from which the ester is derivable, and x represents a whole number not greater than n—1.

6. In the dyeing of textile fibers of the vegetable type by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye, the improvement which comprises applying to the fiber a vat dye composition containing a vat dye in the unreduced form and a soluble salt of an acid alkyl sulfate containing not more than 5 carbon atoms in the alkyl group.

7. In the dyeing of textile fabrics of the vegetable type by a printing process, the improvement which comprises applying to the textile fabric a printing paste containing a vat dye compound, an alkali, a reducing agent, a thickener and an alkali metal salt of an acid alkyl ester having the formula

$$(RO)_x—A—(OH)_{n-x}$$

in which R represents an aliphatic hydrocarbon radical which contains not more than 5 carbon atoms, A represents the radical SO_2 or the radical PO, n represents the number of replaceable hydrogen atoms in the uncombined polybasic acid from which the ester is derivable, and x represents a whole number not greater than n—1.

8. In the dyeing of textile fabrics of the vegetable type by a printing process, the improvement which comprises applying to the textile fabric a printing paste containing a vat dye compound, a reducing agent, an alkali and an alkali metal salt of an acid alkyl sulfate containing 2 to 5 carbon atoms.

9. In the dyeing of textile fabrics of the vegetable type by a printing process, the improvement which comprises applying to the textile fabric a printing paste containing a vat dye in the unreduced form, a reducing agent, an alkali and isobutyl sodium sulfate.

10. In the dyeing of textile fibers of the vegetable type by the pad-jig process, the improvement which comprises padding the textile fiber with a padding liquor containing a vat dye in the unreduced form and a soluble salt of an acid alkyl ester having the formula

$$(RO)_x—A—(OH)_{n-x}$$

in which R represents an aliphatic hydrocarbon radical which contains not more than 5 carbon atoms, A represents the radical SO_2 or the radical PO, n represents the number of replaceable hydrogen atoms in the uncombined polybasic acid from which the ester is derivable, and x represents a whole number not greater than n—1.

11. In the dyeing of textile fabrics of the vegetable type by the pad-jig process, the improvement which comprises padding the textile fabric with a padding liquor containing a vat dye in the unreduced form and an alkali metal salt of an acid alkyl sulfate containing 3 to 5 carbon atoms.

12. In the dyeing of textile fibers of the vegetable type by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye compound, the improvement which comprises treating the fiber to be dyed with a solution of a salt of an acid alkyl ester containing not more than 5 carbon atoms in the alkyl group and derivable from a polybasic inorganic acid and an aliphatic alcohol containing not more than 5 carbon atoms, and subjecting the treated fiber to the dyeing process.

13. In the dyeing of textile fibers of the vegetable type by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye compound, the improvement which comprises treating the fiber to be dyed with a solution of a salt of an acid alkyl ester having the formula

$$(RO)_x—A—(OH)_{n-x}$$

in which R represents an aliphatic hydrocarbon radical which contains not more than 5 carbon atoms, A represents the radical SO_2 or the radical PO, n represents the number of replaceable hydrogen atoms in the uncombined polybasic acid from which the ester is derivable, and x represents a whole number not greater than $n-1$, and subjecting the treated fiber to the dyeing process.

14. In the dyeing of textile fibers of the vegetable type by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye compound, the improvement which comprises treating the fiber to be dyed with a solution of an alkali metal salt of an acid alkyl sulfate containing 3 to 5 carbon atoms.

15. A vat dye paste for direct application to textile fibers, comprising a vat dye in the unreduced form, a thickener, water and a soluble salt of an acid alkyl ester containing not more than 5 carbon atoms in the alkyl group and derivable from a polybasic inorganic acid and an aliphatic alcohol containing not more than 5 carbon atoms.

16. A vat dye paste for direct application to textile fibers comprising a vat dye in the unreduced form, a thickener, water and a soluble salt of an acid alkyl ester having the formula

$$(RO)_x—A—(OH)_{n-x}$$

in which R represents an aliphatic hydrocarbon radical which contains not more than 5 carbon atoms, A represents the radical SO_2 or the radical PO, n represents the number of replaceable hydrogen atoms in the uncombined polybasic acid from which the ester is derivable, and x represents a whole number not greater than $n-1$.

17. A vat dye paste for direct application to textile fibers comprising a vat dye in the unreduced form, a thickener, water and an alkali metal salt of an acid alkyl sulfate containing 2 to 5 carbon atoms.

18. A vat dye paste for direct application to textile fibers comprising a vat dye in the unreduced form, a thickener, water and isobutyl sodium sulfate.

19. In the dyeing of textile fibers by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye compound, the improvement which comprises carrying out the dyeing with the aid of a compound of a heavy metal capable of exhibiting more than one valency and a soluble salt of an acid alkyl ester containing not more than 5 carbon atoms in the alkyl group and derivable from a polybasic inorganic acid and an aliphatic alcohol containing not more than 5 carbon atoms.

20. In the dyeing of textile fibers by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye compound, the improvement which comprises carrying out the dyeing with the aid of a salt of one of the metals nickel, cobalt and manganese, and a soluble salt of an acid alkyl ester having the formula

$$(RO)_x—A—(OH)_{n-x}$$

in which R represents an aliphatic hydrocarbon radical which contains not more than 5 carbon atoms, A represents the radical SO_2 or the radical PO, n represents the number of replaceable hydrogen atoms in the uncombined acid from which the ester is derivable, and x represents a whole number not greater than $n-1$.

21. In the dyeing of textile fibers of the vegetable type by a process in which a leuco compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye, the improvement which comprises applying to the fiber a vat dye composition containing a vat dye in the unreduced form, a soluble salt of an acid alkyl ester containing not more than 5 carbon atoms in the alkyl group and derivable from a polybasic inorganic acid and an aliphatic alcohol containing not more than 5 carbon atoms, and a salt of a heavy metal capable of exhibiting more than one valency.

22. In the dyeing of textile fibers by a process in which a leuco-compound of a vat dye is formed in the presence of the fiber by reduction of a vat dye compound, the improvement which comprises carrying out the dyeing with the aid of a compound of a heavy metal capable of exhibiting more than one valency and a soluble salt of an acid alkyl ester having the formula

$$(RO)_x—A—(OH)_{n-x}$$

in which R represents an aliphatic hydrocarbon radical which contains not more than 5 carbon atoms, A represents the radical SO_2 or the radical PO, n represents the number of replaceable hydrogen atoms in the uncombined polybasic acid from which the ester is derivable and x represents a whole number not greater than $n-1$.

23. In the dyeing of textile fabrics by a printing process, the improvement which comprises applying to the textile fabric a printing paste containing a vat dye in the unreduced form, an alkali, a reducing agent, a thickener, an alkali metal salt of an acid alkyl sulfate containing 3 to 5 carbon atoms, and a sulfate of a heavy metal capable of exhibiting more than one valency.

24. In the dyeing of textile fabrics by a printing process, the improvement which comprises applying to the textile fabric a printing paste containing a vat dye in the unreduced form, a salt of one of the metals nickel, cobalt and manganese, and an alkali metal salt of an acid alkyl ester having the formula

$$(RO)_x—A—(OH)_{n-x}$$

in which R represents an aliphatic hydrocarbon radical which contains not more than 5 carbon atoms, A represents the radical SO_2 or the radical PO, n represents the number of replaceable hydrogen atoms in the uncombined polybasic acid from which the ester is derivable and x represents a whole number not greater than $n-1$.

25. In the dyeing of textile fabrics by a printing process, the improvement which comprises applying to the textile fabric a printing paste containing a vat dye in the unreduced form, a salt of one of the metals nickel, cobalt and manganese, and an alkali metal salt of an acid alkyl sulfate containing 2 to 5 carbon atoms.

JEAN G. KERN.