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VAT DYE COMPOSITION

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This invention relates to dye compositions and particularly to vat dye compositions in the form of dye pastes or powders, which are especially adapted for use in the preparation of aqueous solutions or dispersions for coloring textile materials and the like. The vat dye pastes or powders are particularly valuable for use in the preparation of printing pastes and padding baths. The invention also includes processes for making the vat dye compositions.

In the art of dyeing with vat dyes, two general methods are ordinarily employed. In accordance with one method, a vat comprising an alkaline solution of a reduced vat dye is prepared and the fibrous material to be dyed is worked in this solution whereby the fiber takes up the reduced compound of the dye. The material is then subjected to oxidation and other finishing treatments to convert the vat dye from the reduced to the unreduced form and further complete the fixing of the dye and finishing of the material. In accordance with the other method the dye is applied to the material to be dyed while in the unreduced form; it is then subjected to a reducing treatment whereby the dye is converted to the soluble form in the presence of the fiber and is then taken up by the fiber. It is then subjected to oxidation and/or other finishing treatments to fix the dye on the fiber, remove undesired residual material, and complete the finishing of the material.

In dyeing with vat dyes by the latter method, one of two procedures is usually followed, depending upon whether the material is to be dyed a solid color or with a pattern in one or more colors. If the material is to be dyed a solid color, the pigment padding (pad and jig) process is ordinarily employed, and if the material is to be dyed with a pattern, the printing process is generally utilized.

In the pigment padding process, the unreduced vat dye in finely-divided form is suspended in a suitable suspension medium, usually water containing added materials such as thickeners and alkaline substances. The material to be dyed is passed through this suspension, the fiber mechanically picks up the particles of insoluble dye, and the material is subsequently worked in a reducing bath whereby the dye is reduced to the soluble form and is absorbed and/or adsorbed by the fiber. The material is finally subjected to oxidation and finishing treatments to reconvert the dye to the insoluble form, fix it on the fiber, and further complete the finishing of the material.

The printing process of dyeing a textile fabric generally involves applying a so-called printing paste to the fabric in the form of a design (e. g., 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, in addition to the unreduced vat dye, contain substances which in themselves do not reduce the vat dye under the conditions of the printing operation but which in subsequent operations react with the dye to convert 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. The fixing treatment usually comprises subjecting the printed fabric to a so-called "steaming" or "ageing" treatment to induce reduction of the vat dye by the action of the reducing agent present on the fabric, and cause the reduced dye to be taken up by the fiber. The fabric is then subjected to oxidizing, washing, and other finishing treatments.

In dyeing with the vat dyes, particularly by the pigment padding or printing processes, the success of the operation is in a large measure dependent upon the uniformity with which the vat dye (e. g., the unreduced vat dye) is applied to the fabric. The vat dyes in unreduced form, as is well known, are insoluble in water and are not readily wetted by water. In preparing a padding bath or printing paste it is important that the vat dye be in finely-divided form, that it be uniformly distributed throughout the bath or paste, and in condition such that it may be taken up by the fiber. Further, it is important that the vat dye be capable of rapid and substantially complete reduction to the reduced form. The vat dyes, especially those which are intended for use in the pigment padding and printing processes, are generally marketed in the form of so-called dye pastes or color pastes, and dye powders. A dye paste of this kind is usually an aqueous mixture or suspension of finely divided vat dye, which generally makes up 10 to 20 per cent of the paste. The paste usually contains a small amount of a dispersing agent such as "Leukanol" (a condensation product of formaldehyde and a naphthalene sulfonic acid) and the remainder is mainly water, a part of which is sometimes replaced by other liquids such as amino alcohols, polyhydroxy alkyl ethers or other polyhydroxy alkyl compounds, and cyclic ethers; as, for example, glycol ethers, glycol, glycerine, poly-glycerines, poly-glycols, etc.

These vat dye pastes are ordinarily produced by stirring the dispersing and other agents with the filter cake of the dye resulting from filtration of a precipitate of the dye obtained in its manufacture, or by precipitation in the finely-divided form from a vat of sulfuric acid or other solution.

As noted above, vat dyes for use in the preparation of padding baths and printing pastes may be supplied in the form of vat dye powders. In the case of the powders, it is important that the vat dyes contained therein not only have the properties pointed out above in connection with the vat dye pastes, but also that the powders be rapidly converted to uniform suspensions of the vat dye. Especially successful vat dye powders are described in my United States Patents Nos. 2,067,926 and 2,145,193. These vat dye powders are prepared by incorporating with the usual vat dye paste (e. g., one containing a small amount of a dispersing agent) a soluble salt of an acid alkyl ester of an oxygen-containing polybasic inorganic acid (e. g., a soluble salt of a sulfuric acid ester of a lower aliphatic alcohol) and preferably also an added substance such as, for example, dextrine, sugar, gum arabic, and the like, and then drying and grinding the resulting composition.

It is the principal object of the present invention to provide vat dye compositions which are productive of excellent dyeings and printings when employed in the usual ways. Another object of the invention is to provide vat dye pastes and powders which are adapted for use in the efficient preparation of padding baths and printing pastes containing uniformly distributed therethrough the finely-divided particles of the vat dyes. Another object of the invention is to provide vat dye pastes and powders which when used in the preparation of padding baths and printing pastes are productive of compositions characterized by the marked efficiency with which the dye is initially taken up by the fiber and the increased brilliancy and strength of the resulting dyeings and printings as compared with the dyeings and printings obtained by the use of padding baths and printing pastes prepared from ordinary vat dye pastes. A further object of the invention is to provide vat dye pastes which remain fluid on standing and which may be easily and quickly mixed with the ingredients making up the conventional padding baths and printing pastes to form homogeneous compositions containing the vat dyes in well-dispersed condition.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

In accordance with the present invention it has been found that valuable vat dye compositions can be prepared by incorporating with a vat dye in the unreduced or other form a soluble organic ester of an aliphatic polycarboxylic acid containing not more than 8 aliphatic carbon atoms joined carbon to carbon. The esters that have been found to be adapted for use in the compositions of the invention contain at least one solubilizing radical which is a sulfonate, sulfate, or phosphate radical and their ester radicals are free from aliphatic radicals containing a total of more than 12 aliphatic carbon atoms per aliphatic radical and from aliphatic radicals containing more than 8 aliphatic carbon atoms in a straight carbon chain. The esters may be monoesters or poly-esters and may contain the solubilizing residue anywhere in their molecules, although preferred esters contain one of such residues, which is preferably a sulfonate group,

in the acyl radical. In speaking of soluble esters it is meant esters that are soluble in water and/or in alkaline solutions. It has been found that esters of this class possess a combination of properties which make them valuable for use in compositions containing vat dyes, and especially in vat dye compositions in paste or powder form intended for use in the preparation of padding baths or printing pastes.

In preparing a vat dye paste in accordance with the present invention, a vat dye, usually in the form of a press cake (a mixture of a vat dye in finely-divided form with water as obtained in the course of manufacture of the dye) is mixed with an ester of the above class and also preferably with a dispersing agent (for example, "Leukanol" or sulfite waste liquor). The resulting mixture is then diluted with water to the desired dye-strength; or if the paste is to be a so-called non-drying paste, that is to say, one in which water is replaced in whole or part by a water miscible, high-boiling alcohol such as iso-butyl alcohol, glycerine, glycol, poly-glycerines, polyglycols and alkyl ethers of these compounds, the requisite amount of such alcohol is added to the mixture and water is removed therefrom by evaporation until the paste has the desired dye strength. The compositions prepared in this way comprise fluid pastes consisting of dispersions of the finely-divided vat dye. The compositions are relatively stable and do not settle on standing over a relatively long period of time. Furthermore, as compared with many available vat dye pastes, they are in a fluid or free-running state. Thus they are adapted to be efficiently and quickly incorporated with the other ingredients of padding baths and printing pastes to prepare such baths and pastes in a form such that the resulting compositions may be efficiently employed in dyeing and printing. When preparing the vat dye compositions of the present invention in the form of vat dye powders, the pastes prepared as described above, but usually with little or no high-boiling water miscible alcohol therein, may be concentrated and/or dried, as by means of a vacuum or atmospheric rotary drum drier, by spray drying, or by means of the addition to the paste of an anhydrous hydrate-forming inorganic salt. It is preferable, however, when preparing the powders to add to the paste before drying a substance such as sugar, dextrine, gum or starch, or derivations of alginic acids and/or other suitable additions. In preparing the dry products employing a mechanical drier, the dry product scraped from the drier is in the form of flakes, scales, or grains, and may be used as such but may also be ground to produce a finely-divided powder.

The esters employed in the vat dye compositions of the present invention are such as are derivable from any aliphatic polycarboxylic acid containing less than 9 carbon atoms (such as, for example, maleic acid, succinic acid, propylsuccinic acid, tartaric acid, pyrotartaric acid, glutaric acid, adipic acid, suberic acid, citric acid, fumaric acid, chlor-succinic acid, dimethylsuccinic acid, methylglutaric acid, pimelic acid, propylglutaric acid, allylmalonic acid, etc.) and an organic hydroxy compound, especially an alcohol containing not more than 8 aliphatic carbon atoms in a straight carbon chain and a total of not more than 12 aliphatic carbon atoms. The acids from which the esters are derivable may be substituted or unsubstituted; e. g., they may

contain substituents; such as halogens, and amino, hydroxyl, and aromatic radicals.

The said esters may be mono-esters or poly-esters, and if poly-esters may be mixed esters. They may be derivatives of aliphatic mono-hydric or poly-hydric alcohols, or of mono- or poly-hydric hydro-aromatic alcohols, cycloaliphatic alcohols, heterocyclic alcohols, aralkyl alcohols, mixed aliphatic-hydro-aromatic alcohols, or of mono- and polyhydric alcohol ethers. As examples of such alcohols there may be mentioned ethyl, propyl, allyl, butyl, amyl, hexyl, heptyl, octyl, and the like alcohols; cyclohexanol, methyl cyclohexanol, cyclopentanol, tetrahydrofurfuryl alcohol, benzyl alcohol, phenyl ethyl alcohol, phenyl methyl carbinol, the various terpene alcohols, ethylene, propylene, di-ethylene and tri-ethylene glycols, and the like; and the methyl and ethyl ethers of ethylene, di-ethylene or other glycols. As typical alcohols there may be also mentioned the following alcohols which are obtainable as by-products in the production of methanol by the catalytic hydrogenation of mixtures of carbon monoxide and carbon dioxide: 4-methyl-1-pentanol; 2 methyl-1-pentanol; 2,4-dimethyl-1-pentanol; 3-methyl-2-pentanol; 2,4-dimethyl-3-pentanol (di-isopropyl carbinol); 2-methyl-3-pentanol; 4-methyl-1-hexanol; 2,4-dimethyl-1-hexanol; 2,5-dimethyl-3-hexanol; 2-ethyl-1-butanol; and others of like character.

The above parent alcohols may be primary or secondary but all of them are characterized by containing no straight carbon chains of more than 8 aliphatic carbon atoms. The esters derived from alcohols wherein the direct chain between the esterified alcohol function and the nearest branching point in the ester group (alcohol residue) is not longer than 4, or at most 6 carbon atoms, are particularly valuable for use in the vat dye compositions.

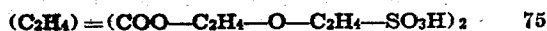
Where in the appended claims an ester of an alcohol and an aliphatic polycarboxylic acid is referred to it will be understood that a mono- or poly-ester (symmetrical or mixed) of one or more alcohols of the above described classes is intended, unless otherwise indicated.

It will be understood that the alcohols from which the esters are derivable may contain substituents which do not alter the essential physical or chemical characteristics of the esters. As indicated above, polyhydric alcohols may be employed and in this case either one or both of the hydroxyl groups may be esterified with the carboxylic acid group of the acid employed. When only one of the hydroxy groups is esterified, one or more free hydroxyl groups remain, which are not objectionable, and in some cases appear to have an advantageous effect upon the properties of the esters. The amino group may also be mentioned as an example of a substituent which may be present in the alcohol residue of the esters, valuable esters adapted for use in the vat dye compositions being derivable from amino alcohols. Also, the alcohols may contain alkylamino substituents and the solubilizing radical may be attached to the N-alkyl radical.

Although any of the above-described esters may be used with advantage in the vat dye compositions of the present invention, it will be understood that these esters will vary in degree in their possession of the valuable properties characteristic of the class. It has been found that the best results are obtained with esters of the above class which contain sulfonate and/or sulfate groups and which display high solu-

bility in aqueous solutions and/or alkaline printing pastes. Accordingly, the preferred esters are those which are derived from lower aliphatic alcohols (i. e., containing 2 to 6 carbon atoms), cycloalkyl alcohols, and aromatic alcohols. It has been found that esters which are derivatives of isobutyl alcohol are of markedly high value. For similar reasons, the esters derived from the shorter chain-length aliphatic poly-carboxylic acids (i. e., containing 3 to 6 carbon atoms) are of particular value. Succinic acid is preferred as the aliphatic poly-carboxylic acid. While, as before indicated, the esters may contain one or more solubilizing groups, it has been found that those esters which contain at least one sulfonic acid group are ordinarily to be preferred. Further, although the solubilizing group or groups present in the esters may be in the alcohol radical or radicals, the acyl radical, or in all of said radicals, it is preferred to employ esters in which a solubilizing group, preferably a sulfonate group, is in the acyl radical and the ester radical is free from solubilizing groups.

In view of the foregoing disclosure, it will be readily apparent that a large number of esters are available for use in the compositions of the invention. The following esters (described in the form of the free acids of the inorganic acid residues contained therein) are given as examples of typical esters of the class hereinabove disclosed; di-ethyl sulfosuccinate; methyl isopropyl sulfosuccinate; mono-isobutyl sulfosuccinate; di-isobutyl sulfosuccinate; di-isobutyl phosphatosuccinate; di-n-butyl sulfosuccinate; di-amyl sulfoadipate; di-isobutyl sulfonypyrotartrate; di-isopropyl sulfoglutarate; isopropyl n-amyl sulfopropylsuccinate; di-benzyl sulfosuccinate; di-benzyl sulfatosuccinate; sucrose sulfosuccinate; di-(mono-phosphatoglyceryl) sulfosuccinate; di-(ethylene glycol) sulfosuccinate; di-(ethylene glycol) sulfatosuccinate; mono-(methoxybutyl) sulfatosuccinate; di-cyclohexyl sulfatosuccinate; the mono- and di-esters of alpha-sulfonypyrotartaric acid and the ethyl ether of ethylene glycol; the symmetrical di-esters prepared from the mono-butyl ether of di-ethylene glycol and sulfatosuccinic acid, sulfosuccinic acid, or phosphatosuccinic acid; di-(ethoxyethyl) phosphato- or sulfatopyrotartrate; di-cyclohexyl sulfatoglutarate; di-cyclohexyl sulfoglutarate; di-phenyl sulfatopyrotartrate; di-phenyl sulfonypyrotartrate; di-phenyl phosphatopyrotartrate; di-tetrahydrofurfuryl sulfatosuccinate; di-tetrahydrofurfuryl sulfosuccinate; di-tetrahydrofurfuryl phosphatosuccinate; the mono- and di-esters of sulfatosuberlic acid, sulfosuberlic acid, or phosphatosuberlic acid and methyl isobutyl carbinol; the mono- and di-glyceryl esters of sulfatosuccinic acid, sulfosuccinic acid, or phosphatosuccinic acid; the monocarboxylic acid ester of maleic acid and the monosulfuric acid ester of ethylene glycol; the di-ester of sulfosuccinic acid and the monosulfuric acid ester of di-ethylene glycol; the mixed ester obtainable from hydroxy-ethyl-benzene para-sulfo acid, isobutyl alcohol, and sulfosuccinic acid; di-sulfo-benzyl sulfosuccinate; the di-ester of maleic acid and the omega-sulfo-acid ester of amino butylol; tri-isobutyl sulfatocitrate; tri-isobutyl phosphatocitrate; the di-sulfo ester obtainable from the chlorhydrin of di-ethylene glycol and succinic acid followed by a bisulfite treatment, and having the formula



mono-(sulfoethyl) succinate; p-sulfobenzyl-
amyl-sulfosuccinate; and bis-(p-sulfobenzyl)-
sulfosuccinate.

The esters employed in the present invention
5 may be prepared in any well known or suitable
manner. For example, the sulfated esters may
be prepared by reacting the ester of the corre-
sponding unsaturated aliphatic acid with concen-
10 trated sulfuric acid or the ester of the corre-
sponding hydroxy-aliphatic acid with chlorosul-
fonic acid, and neutralizing the resulting product
with the desired inorganic or organic base. The
sulfonated esters may be prepared by reacting
15 the ester of the corresponding halogenated ali-
phatic acid with sodium sulfite.

The esters are preferably employed in the form
of their neutral soluble salts. The alkali-metal
salts, and the salts obtained by neutralizing the
acid esters with organic derivatives of ammonia
20 are especially important. As examples of suitable
organic derivatives of ammonia, the following are
mentioned: the alkylolamines (e. g., mono-, di-,
or triethanolamine); the alkylol diamines (e. g.,
1,2-di-(2'-ethanolamino) ethane and 1,3-di-(2'-
25 ethanolamino)-2-propanol); the quaternary al-
kylolamines, the diquaternary alkylolamines
(e. g., tetra-hydroxy-ethylamine ammonium hy-
droxide, hexa-hydroxy-ethyl-ethylene diammo-
nium hydroxide); and the quaternary aralkyl-al-
30 kyl ammonium hydroxides or the aralkyl-hydrox-
yalkyl-ammonium hydroxides (e. g., tri-methyl-
benzyl ammonium hydroxide, tri-(hydroxyethyl)-
benzyl ammonium hydroxide, etc.).

The valuable effects resulting from the inclu-
35 sion of the above described esters in vat dye com-
positions in accordance with the present inven-
tion are noticed both in vat dye pastes and pow-
ders from which dyeing compositions (baths and
printing pastes) are prepared and also in the
40 dyeings and printings obtained with the ultimate
compositions.

The value of vat dye compositions is primarily
dependent upon the excellence of the dyeings and
printings obtained therefrom. The physical form
45 of vat dye pastes and powders prior to their use
in dyeing, and also prior to their incorporation
in the ultimate dyeing compositions, has an im-
portant effect on the coloring properties of these
compositions. In the vat dye pastes, the esters
50 described above act to increase the fluidity of
the pastes and also apparently to prevent floccu-
lation of the dye particles. In the vat dye
powders, the esters make possible the rapid dis-
integration of the dye particles in dye baths
55 and aqueous printing compositions, a result which
is believed to be due to the fact that the esters
are so combined or commingled with the vat dye
particles as to form therewith a composition re-
sembling a solid dispersed suspension. The par-
60 ticles of the vat dyes, therefore, are prevented
from combining to form larger particles which
would be difficult to disperse in a padding bath
or printing paste.

When the vat dye pastes and powders are in-
65 corporated with the other usual ingredients of
vats, padding baths, or printing pastes, several
advantageous results are obtained. First, as pre-
viously noted, the compositions may be mixed
readily with such ingredients to form homogene-
70 ous dyeing compositions. Further, it appears that
the esters act to increase the solubility of leuco
vat dyes and increase the strength and brilliancy
of the dyeings and printings obtained. This is
because, while leuco vat dyes are regarded as be-
75 ing soluble in alkaline solutions, and because of

this solubility may be taken up by the fiber to
be dyed, they are not freely soluble and their in-
creased solubility caused by the esters accelerates
the rate of their absorption or adsorption by the
fiber.

The vat dye compositions of the present in-
vention are particularly valuable as compared
with ordinary vat dye compositions when they
are applied to synthetic fibers composed of re-
generated cellulose, or to unbleached natural
10 fibers, such as cotton and raw silk. It is known
that these latter fibers do not, as a rule, readily
absorb the reduced vat dyes because of their
coating of natural waxes which act as resist
agents.

As before stated, the soluble esters of this in-
vention may be used per se or in admixture with
other substances ordinarily used in the art of
dyeing or printing textiles. These substances
may be in the nature of the alkyl partial in-
20 organic esters specifically disclosed in my pat-
ents above referred to, other substances used in
dyeing and printing, such as the alkylolamines,
polyhydric alcohols, and ethers, e. g., the ethers
of diethylene glycol, glucosic compounds, dex-
25 trines, gums, starches, etc., or compounds in the
nature of printing catalysts, such as heavy metal
compounds or the heavy metal salts of alkyl par-
tial esters, such as isobutyl-nickel-sulfate, or the
heavy metal salts of the soluble carboxylic esters
30 of the present invention, themselves.

Inasmuch as the quality and dispersibility of
the resulting dye composition are dependent to
a considerable extent upon the original degree
of dispersion of the dye in the suspension or in
35 the dry form, the vat dye is preferably treated
in the highly dispersed form. A suitable dispers-
ing agent is preferably incorporated into the dis-
persion or suspension so as to aid in preventing
precipitation and agglutination of the dye par-
40 ticles during storage or during the drying and to
increase the fluidity and render easier the in-
corporation of the soluble salts of the carboxylic
acid esters.

Among the dispersing agents which may be
45 employed for this purpose there may be men-
tioned, for example, the sulfonic acids of benzene,
hydroxybenzenes, naphthalene, hydroxynaphtha-
lenes, their nuclear alkyl, nuclear aralkyl, and
hydrogenated derivatives, as well as aldehyde
50 condensation products thereof (as for example,
2,6-naphthalene-disulfonic acid, 1,7-naphtha-
lene-disulfonic acid, 2,8-naphthalene-disulfonic
acid, isopropyl-naphthalene sulfonic acids, dibu-
tyl-naphthalene sulfonic acids, amyl-naphtha-
55 lene sulfonic acids, butyl-benzyl-naphthalene sul-
fonic acids, cyclohexyl-naphthalene sulfonic acids,
methylene-di(beta-naphthalene sulfonic acid),
methylene-di(di-isopropyl-naphthalene sulfonic
acid), in the form of the free acids or salts (e. g.,
60 alkali metal salts), etc.; sulfite cellulose waste
liquors and their mildly oxidized products and
evaporated residues; sulfonated resins; abietene,
abietine and abietane sulfonic acids; soaps; sul-
65 fonated higher fatty acids, fats and oils; and the
like, as well as mixtures of two or more of such
substances.

Further, additional substances having diluent,
antifoaming, assisting, wetting, catalytic, eno-
70 lyzing, or other suitable action in the subsequent
use of the compositions may also be incorporated
into the compositions of the present invention,
preferably while the latter are in the form of
aqueous suspensions or in the form of non- 75

drying pastes containing high boiling alcohols or alcohol ethers.

In preparing the vat dye pastes and powders in accordance with a preferred manner of proceeding, the mixture of vat dye in aqueous or high boiling solvent dispersion is agitated with the appropriate amount of the poly-carboxylic acid ester salt together with the other substances, if added, until a homogeneous paste is formed, or the mixture of the aqueous suspension of the dispersed vat dye and a poly-carboxylic acid ester salt together with the other substances, if added, is evaporated with agitation until a thick paste is formed with or without the aid of vacuum and preferably at a temperature not exceeding 100° C. The resulting paste constitutes a valuable vat dye paste. If desired, it may be brought to substantial dryness to form a dry vat dye composition. Thus, the paste may be evaporated to dryness on an atmospheric or vacuum rotary drum drier, and the dry product scraped off in the form of flakes, scales, or grains which may be used as such, or the paste, with or without preliminary evaporation, may be admixed with a suitable hydrate-forming soluble salt in an anhydrous condition, such as anhydrous trisodium phosphate, and the admixture stirred to produce a dry product. If desired, the dry product may be disintegrated in any suitable manner into a powder.

Mixtures of the carboxylic acid ester salts or mixtures of them with alkyl inorganic ester salts, disclosed in my patents referred to above may also be employed in accordance with the present invention. Further, the esters used in the compositions of the invention may be used together with or in place of the esters disclosed in my applications Serial Nos. 253,345 and 253,347, filed of even date herewith.

The amount of the soluble carboxylic acid esters employed in the preparation of the compositions of the present invention may be varied over a considerable range, depending in part upon the concentration of vat dye in the composition, the use to which the composition is to be put, and whether or not other diluents and other materials having a catalytic, assisting, wetting, enolyzing, dispersing, or other action, are included in the composition.

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, anthranthrones, dibenzpyrene quinones, anthrimido-carbazoles, naphthacridones, indigo, thioindigo, indirubin, etc., including derivatives thereof, such as their halogen, nitro, sulfur and/or alkoxy derivatives.

It should be noted that while the vat dyes in the compositions of the invention are preferably in the unreduced form, they may also be in the reduced or leuco form. For example, leuco ester salts of vat dyes and leuco compounds of vat dyes prepared by careful acidification of an alkaline vat, or by other methods, may be used, if desired.

Although it is generally preferable and desirable, in order to take full advantage of their properties, to employ the esters in vat dye pastes or powders which are used in the preparation of padding baths or printing pastes, esters may also be mixed with the other ingredients used in padding baths or printing pastes at the time

these compositions are prepared. In proceeding in this way, the dye may be introduced into the mixture in the form of a press cake or an ordinary dye or other form of paste, the ester or esters being added at any desired or suitable point in the preparation of the compositions.

In the foregoing description, the use of the vat dye compositions in the dyeing and/or printing of textile materials has been stressed since this is the most important application of the compositions. The compositions, however, especially when in the form of powders, may be used in the preparation of dispersions of vat dyes for use in the pigment form in the dyeing of paper, the tinting of fibers and other materials, and the like. The ready dispersibility of the compositions makes them especially valuable for such purposes.

The invention will be further described in connection with the following specific examples (in which the parts are by weight), which are given to illustrate the invention. It will be realized, however, that the invention is not limited thereto but that changes may be made in the materials treated and their proportions, manipulative steps, and other conditions without departing from the scope of the appended patent claims.

Example 1

400 parts of indigo paste (containing 20 per cent of pure indigo as shown by indigotine titration and resulting from the precipitation of indigo from an alkaline solution of indoxyl by aeration) are stirred with two parts of "Leukanol" until a thin fluid paste is obtained. 13 parts of cane sugar and 5 parts of di-normal-butyl sodium sulfosuccinate are then added, the mixture is stirred until solution of the sulfosuccinate is complete, and the resulting mixture is evaporated with stirring until a thick paste is formed. The thick paste is then placed in drying pans and evaporated to dryness. The dry product is ground screened.

There is thus obtained an indigo powder containing 80 per cent of indigo which, when added to water, disperses readily. When employed for the preparation of an indigo vat with the aid of the usual reducing agents (for example, alkaline sodium hydrosulfite), the powder reduces very rapidly and produces a clear vat which dyes cotton even, blue shades of high tinctorial value. Instead of the di-normal-butyl sodium sulfosuccinate, an equal amount of di-isopropyl sodium sulfosuccinate or diamyl sodium sulfopyrutarate, or others of the above-described esters may be used.

Example 2

To 100 parts of the chlorinated indanthrone vat dye known as National Carbanthrene Blue BCS (Color Index No. 1114), in the form of an aqueous suspension or commercial paste containing 18 per cent of total dye solids, there are added, with stirring, 2 parts of "Leukanol" (or 6 parts of a 30% solution of "Leukanol"), 50 parts of cane sugar, and 25 parts of dextrine. The suspension is stirred until homogeneous, and then 5 parts of di-isobutyl sodium sulfosuccinate are added and the mixture is stirred until solution of the sulfosuccinate is complete. The resulting mass, either as such or after evaporation, may be used as a paste; or it may be evaporated to dryness, ground and screened, as in Example 1, to produce a powder that is readily dispersed when added to water. The product, either in the form of paste or powder, gives uniform dyeings of high tinctorial value when

employed to dye fabrics in accordance with standard practice, and especially by the pad and jig method. Instead of the di-isobutyl sodium sulfosuccinate, any one of the soluble dicarboxylic acid esters herein disclosed may be used.

Example 3

To 200 parts of National Carbanthrene Violet 2R Standard Paste (Color Index No. 1104) containing 11 per cent of dye solids in the form of an aqueous suspension, there are added 2 parts of "Leukanol," 5 parts of di-(ethylene-glycol) sodium sulfosuccinate and 71 parts of cane sugar or cerelose.

The mixture is stirred until all the soluble material is dissolved, and is then evaporated to dryness, ground to a powder, and screened through a 60-mesh screen. The resulting product is a violet colored powder which is readily dispersed upon adding to water and is especially suitable for dyeing fibers by the pad and jig process. When the powder is made into a printing paste containing the usual additional ingredients, and the resulting paste is employed to print a textile fabric which is then dried, aged, developed, and soaped in accordance with the standard procedure, a bright violet, fully penetrated, and level print is produced. Instead of the di-(ethylene-glycol) sodium sulfosuccinate, equivalent parts of the di-cyclohexyl sodium sulfosuccinate may be used.

Example 4

100 parts of Nation Carbanthrene Violet 2R Paste (cf. Example 3) are mixed with 25 parts of cane sugar and 68 parts of di-cyclohexyl sodium sulfatosuccinate, and the mixture is stirred until the latter are dissolved. The resulting suspension is then evaporated to dryness, ground and screened. 100 parts of a violet powder is obtained which is suitable for dyeing by all known methods. It is especially useful for making pastes to be used in dyeing by the printing process.

Example 5

100 parts of the thioindigoid vat dye known as National Vat Orange R (Color Index No. 1217) in the form of an aqueous paste containing about 11 per cent of dye solids, are mixed with 2 parts of "Leukanol" and 87 parts of isopropyl n-amyl sodium sulfopropylsuccinate until solution of the latter is complete. The resulting suspension is evaporated to dryness, ground and screen. 100 parts of a Vat Orange R powder are thus obtained which, when employed in the preparation of a printing paste (for example, by mixing 150 parts of the powder with 200 parts of British gum, 140 parts of potassium carbanate, 80 parts of sodium formaldehyde sulfoxylate, 50 parts of glycerine, and 380 parts of water) and utilized in the printing of rayon materials in accordance with the usual procedure, produces prints on these materials which in heavy shades are about 25 to 30 per cent greater in strength than corresponding prints made without the isopropyl n-amyl sodium sulfopropylsuccinate. In addition, the presence of the neutral soluble carboxylic acid ester salt results in a much greater brilliancy of shade and more complete penetration of the material, so that in many instances there are no back sides and the fastness to crocking is much enhanced. Instead of the isopropyl n-amyl sodium sulfopropylsuccinate, equivalent amounts of isopropyl n-amyl sodium sulfoglutarate may be employed.

In connection with the above example it is

pointed out that the soluble salts of isopropyl and isobutyl dicarboxylic acid esters are of especial value for use with vat dyes of the thioindigoid series when the latter are to be employed for the preparation of printing pastes. Such esters are preferably di-esters in which the other alcohol residue is also a short chain.

Example 6

To 100 parts of National Vat Orange R Paste (employed in Example 5), there are added 2 parts of "Leukanol," 1 part of the sodium salt of anthraquinone-2-sulfonic acid, 45.5 parts of cane sugar, 40 parts of di-(secondary-hexyl) sodium sulfosuccinate, and 0.5 part of triamylamine. The mixture is stirred to dissolve said soluble material, and the resulting suspension is evaporated to dryness, ground and screened. 100 parts of a bright orange pigment is obtained which disperses readily in vat printing pastes. When printed on textile fabrics of all kinds, it yields a very brilliant orange of increased strength over prints made from the original Vat Orange R Paste in the ordinary method.

Example 7

To 100 parts of National Vat Orange R Paste (employed in Example 5), there are added 2 parts of "Leukanol," 4 parts of the potassium salt of 2-carboxy-benzophenone-4'-sulfonic acid, 25 parts of isobutyl sodium sulfate, 25 parts of di-isobutyl sodium sulfosuccinate, and 33 parts of dextrine.

The resulting mixture is stirred until all soluble matter is dissolved and the resulting suspension is evaporated to dryness, ground and screened. A bright orange pigment is obtained similar to that of Example 6, which exhibits similar superior printing qualities.

Example 8

To 100 parts of the vat dye known as National Vat Pink FF (6,6'-dichlor-4,4'-dimethyl-thioindigo) in the form of an aqueous paste or suspension containing 15 per cent of dye solids, there are added 2 parts of "Leukanol," 40 parts of sodium dibenzyl sulfosuccinate, and 42 parts of cane sugar. The mixture is stirred until the soluble material is all dissolved, and is then evaporated to dryness, ground and screened. A highly colored pink pigment is obtained which is readily dispersed in water or in printing pastes. If desired, 1 part of ferrous sulfate may be added to the mixture before evaporation in order to enhance the printing action of the composition.

Example 9

100 parts of 5,5'-dichlor-7,7'-dibrom indigo paste (cf. Color Index No. 1188), containing 20 per cent of dye solids, are mixed with 2 parts of "Leukanol" or other suitable dispersing agent to produce a thick fluid suspension. Then, 17 parts of cane sugar and 40 parts of di-sucrose sodium sulfosuccinate are added. The mixture is stirred until all the soluble matter is completely dissolved, and is then evaporated to dryness, ground and screened. 100 parts of a blue powder are obtained which is of special value for the preparation of printing pastes. The cane sugar employed in this example may be replaced by dextrine, gum arabic, glue, or other so-called protective colloids, alone or with the addition of enolyzing substances.

Example 10

To 100 parts of National Carbanthrene Blue

GCD Double Paste (Color Index #1113) containing 16.5 per cent of dye solids and 1 per cent of "Leukanol," there are added 50 parts of di-isobutyl phosphatosuccinate and 32.5 parts of urea, and the mixture is stirred until the latter are dissolved. The resulting suspension is evaporated to dryness, ground and screened. A very readily dispersible vat powder is obtained which is suitable for printing as well as dyeing.

Example 11

To 100 parts of National Carbanthrene Flavine GC (cf. U. S. Patent No. 993,992) in the form of a commercial paste containing about 23 per cent of dye solids and about 2 per cent of "Leukanol," there are added 39 parts of sucrose, 40 parts of di- (secondary-butyl-carbinol) sodium sulfoadipate and 1 part of the disodium salt of 2,6-dihydroxyanthraquinone. The mixture is stirred until all soluble matter is dissolved and the resulting suspension is evaporated to dryness, ground and screened. 100 parts of a brilliant yellow powder is obtained which is suitable for dyeing and printing.

Example 12

A standard thickener is prepared as follows:

	Parts
Cornstarch	100
British gum	300
Gum tragacanth 5%	100
Water	500
	1000

These are well mixed together and boiled thoroughly to a smooth paste.

To 520 parts of the above standard thickening paste, 170 parts of potassium carbonate are added and about 60 parts water, and heat applied to boil until the whole forms a homogeneous paste which is then left to cool to about 60° C., after which 140 parts of sodium formaldehyde sulfoxylate, 50 parts glycerine and 60 parts water are added.

A blue vat dye printing color paste is then made up by adding 200 parts of Carbanthrene Blue GCD Double Paste (C. I. No. 1113) to 700 parts of the above thickening, after which 100 parts of di-isobutyl sodium sulfosuccinate are added, and these various ingredients mixed until a smooth printing paste is obtained.

Cotton and rayon cloth are printed therewith by means of a rotary intaglio printing machine; the material is thereafter dried and aged for five minutes in air-free saturated steam at 102° C., after which it is rinsed in cold water, soaped at the boil, rinsed and dried. The resulting print is a very dark shade of blue of exceptional brilliancy and depth as compared to a print obtained under similar conditions with a printing paste where the above assistant has been left out. Weaker shades of the above blue dye may be obtained by reducing the above vat dye printing color paste with a paste for reductions which contains, for example, 600 parts of above standard thickener, and 230 parts of water into which 80 parts potassium carbonate, 60 parts sodium formaldehyde sulfoxylate and 30 parts glycerine have been dissolved.

The above example is exceptionally well adapted for all Indanthrene Vat Dye brands and for dyes of the halogenated violanthrone and benzanthrone series.

In the above example, the di-isobutyl sodium sulfosuccinate may be replaced by any one of the esters disclosed above in equivalent amounts.

Example 13

Example 12 may be modified as follows:

A blue vat dye printing color paste is made up by adding 200 parts of Carbanthrene Blue GCD Double Paste (Color Index #1113) to 650 parts of the thickening given in Example 11, after which 75 parts diethylene glycol or 75 parts triethanolamine or 75 parts mono-methyl ether of ethylene glycol, and 75 parts of di-isobutyl sodium sulfosuccinate are added and the various ingredients mixed until a smooth printing paste is obtained. When applied on gray cotton goods or on rayon materials, the prints obtained show remarkable penetration and intense blue shade of great depth and brilliancy, approximately 30 per cent stronger than prints obtained without the addition of the di-isobutyl sodium sulfosuccinate of this invention.

Example 14

To 100 parts of the pyranthrone vat dyestuff known as National Carbanthrene Golden Orange 2RT Paste (Color Index #1097), containing 10 per cent of dye solids in the form of an aqueous suspension and 1 per cent of "Leukanol," there are added 10 parts of cane sugar and 30 parts of di-isobutyl sodium sulfatotartrate and 10 parts of isobutyl sodium sulfate.

The mixture is evaporated with stirring until a paste containing approximately 14 per cent water is obtained. 25 parts of anhydrous trisodium phosphate are then added and the mixture is stirred until a dry mass is produced. Upon grinding and screening the dry product, a very readily dispersible powder is obtained which produces deep and brilliant shades when employed for the printing of textile fibers in accordance with the standard procedure.

Example 15

To 100 parts of National Vat Orange R Paste (employed in Example 5), there are added 2 parts of "Leukanol" 40 parts of ethyl isobutyl sodium sulfatotartrate, 1 part of the sodium salt of anthraquinone-2-sulfonic acid, and 14 parts of cane sugar.

The mixture is stirred to dissolve the soluble material, and then evaporated with stirring until a paste containing approximately 16 per cent of water is produced. The resulting paste is intimately mixed with 16 parts of anhydrous trisodium phosphate whereby a dry product is obtained, which, when ground and screened, results in a bright orange powder having advantageous properties similar to those of the product of Example 6.

It will be understood that the above examples are merely illustrative of the invention and that the vat dyes, esters, and other materials employed can be replaced by equivalent substances. Thus the esters used can be replaced by others of the class of esters hereinbefore disclosed; for example, by one or a mixture of those specifically mentioned. The following are representative of vat dyes that may be used in the compositions of the invention:

	Color Index No.
Brilliant Indigo 4G	1189
National Vat Scarlet G	1228
National Vat Violet R	1222
National Vat Green G	1199
Carbanthrene Yellow G	1118
Carbanthrene Golden Orange 2RT	1097
Carbanthrene Golden Orange G	1096
Carbanthrene Blue Green FFB	1173

	Color Index No.
Carbanthrene Violet 2R	1104
Carbanthrene Dark Blue DR.....	1099
Carbanthrene Flavine GC.....	1095
Carbanthrene Blue GCD.....	1113
National Vat Orange R.....	1217

I claim:

1. A vat dye composition for use in the preparation of printing pastes and padding baths and dye baths comprising a vat dye compound and a soluble isobutyl ester of an aliphatic polycarboxylic acid containing 3 to 6 carbon atoms, said ester containing at least one solubilizing radical selected from the group consisting of the sulfonate, sulfate, and phosphate radicals.

2. A vat dye composition for use in the preparation of printing pastes and padding baths and dye baths comprising a vat dye compound and a soluble alkali metal salt of an isobutyl ester of an aliphatic poly-carboxylic acid containing 3 to 6 carbon atoms, said ester containing in the acyl radical thereof a solubilizing radical derived from sulfuric acid.

3. A vat dye composition for use in the preparation of printing pastes and padding baths and dye baths comprising a vat dye compound and an alkali metal salt of the di-ester of an aliphatic dicarboxylic acid containing 3 to 6 carbon atoms and isobutyl alcohol, said ester containing a sulfonate radical in the acyl radical thereof.

4. A vat dye composition for use in the preparation of printing pastes and padding baths and dye baths comprising a vat dye compound and

a soluble salt of an isobutyl ester of sulfosuccinic acid.

5. A vat dye composition for use in the preparation of printing pastes and padding baths and dye baths comprising a vat dye compound and sodium di-isobutyl sulfosuccinate.

6. A vat dye paste for use in printing textile fibers comprising an unreduced vat dye, a dispersing agent, and a soluble salt of an isobutyl ester of an aliphatic poly-carboxylic acid containing 3 to 6 carbon atoms, said ester containing in the acyl radical thereof at least one solubilizing radical selected from the group consisting of the sulfonate, sulfate, and phosphate radicals.

7. A vat dye paste for use in printing textile fibers comprising an unreduced vat dye, a dispersing agent, and an alkali metal salt of a di-isobutyl ester of sulfosuccinic acid.

8. A vat dye printing paste comprising an unreduced vat dye, a dispersing agent, and a soluble butyl ester of an aliphatic poly-carboxylic acid containing 3 to 6 carbon atoms, said ester containing in the acyl radical thereof at least one solubilizing radical selected from the group consisting of the sulfonate, sulfate, and phosphate radicals.

9. A vat dye printing paste comprising an unreduced vat dye, a dispersing agent, and a soluble salt of a dibutyl ester of an aliphatic dicarboxylic acid containing 3 to 6 carbon atoms, said ester containing a sulfonate radical in the acyl radical thereof.

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