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VAT DYE COMPOSITION AND MANUFACTURE THEREOF

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This invention relates to vat dye compositions and processes for their manufacture.

The dyeing of textile fibers with vat dyes involves absorption or adsorption by the fiber of the dye in a soluble form followed by a fixing treatment, to render insoluble the dye taken up by the fiber, and other finishing operations for removing undesired residual material. It is well known that vat dyes are solid substances which are insoluble in water. In order to render them useful in the dyeing of textile fibers, they are ordinarily converted to a water soluble form, as for example, by treatment with a reducing agent, such as sodium hydrosulfite and alkali.

Two general methods are ordinarily employed in practice for dyeing fibers with vat dyes. In accordance with one method, a solution or dye bath containing the vat dye in the reduced form (a so-called vat) is first prepared, the material to be dyed is worked in this solution or bath whereby the fiber takes up the reduced compound of the dye, and 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 another 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 taken up by the fiber, and it is then subjected 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 the latter method, one of two procedures is usually followed, it depending upon whether the 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 and jig" process is ordinarily employed. If the material is to be dyed in accordance with a pattern or design, the so-called "printing" process is generally utilized.

The pigment padding 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, 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 ("jigging") 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, 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 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. In some cases, as in printing with difficultly reducible vat dyes, the vat dye in the printing paste is subjected to a preliminary 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 "ageing"), whereby the vat dye is reduced (for example, by the action of the sodium-formaldehyde-sulfoxylate and potassium carbonate), or if prereduced its reduction is rendered more complete, and the reduced dye is taken up by the fiber; and then subjecting the printed fabric to oxidizing, washing and other finishing treatments.

The vat dyes in the ordinary unreduced, solid form are not only insoluble in water but they are not readily wetted by water, and even when ground with water for a considerable length of time do not disperse uniformly in the extremely finely divided form desired for use in dyeing by the pigment padding and printing processes. They therefore usually come upon the market in the form of aqueous suspensions or so-called "pastes" which generally contain 10 to 20 per cent. of the vat dye, a small amount of a dispersing agent such as "Leukanol" (a condensation product of formaldehyde and a naphthalene sulfonic acid) and the remainder mainly water, a part of which is sometimes replaced by other liquids, such as amino alcohols, polyhydroxy alkylethers or other polyhydroxy alkyl compounds, and cyclic ethers; as for example, glycol, glycerin, glycol ethers, polyglycerines, polyglycols, etc. These suspensions are ordinarily produced by stirring the dispersing and other agent with a filter cake of the dye resulting from filtration

of a precipitate of the dye, as obtained for example in its manufacture or by precipitation in the finely divided form from a vat or from a sulfuric acid or other solution.

Vat dye pastes as ordinarily prepared, however, have a number of disadvantages from the standpoint of economy. For example they contain a preponderating quantity of material which has no dyeing action (mainly water), which adds considerably to the cost of transportation and handling of the active dye material; care must be exercised in the transportation of the pastes in order to avoid loss of the material by leakage of the container; precautions must be taken in winter to prevent freezing; care must be exercised in the storage of the paste to avoid drying out and formation of an insoluble crust which does not redisperse and which frequently appears as specks in the paste causing imperfections in the resulting dyeings and prints; and upon standing the pastes frequently settle and require thorough agitation to produce uiform dispersion, which is time- and labor-consuming.

Various attempts heretofore have been made to provide vat dyes in the dry or powder form which will wet and disperse to a sufficient extent to be useful for the dyeings of textile fibers by all processes. Thus, vat dye powders have been produced by drying pastes of vat dyes. In some cases dispersing agents have been incorporated into the vat dye pastes prior to the drying. While the resulting powders frequently have improved wetting and dispersing qualities as compared with powders produced by grinding dry vat dyestuffs, when converted into a paste by slurrying with water and/or when incorporated in a printing paste, they do not produce a dispersion of the vat dye which possesses the suitability for dyeing comparable with that of the ordinary commercial vat dye pastes. The principal difficulty with such powders appears to be the failure of the vat dye, upon being added to water or a printing paste, to revert to its original degree of fineness and uniformity of dispersion, which failure is apparently brought about, in part at least, by changes in the physical condition of the vat dye during the drying.

While the foregoing objections to the vat dye powders heretofore known to the art are of consequence in connection with their use in dyeing with a reduced bath or vat, owing to the greater period of time required for complete solution of the vat dye in the course of preparation of the bath and its resulting increased cost of dyeing, they do not prevent the use of such powders in certain connections such as dyeing by the reduced bath or vat process. In connection with the dyeing of textile material by the pigment padding and printing processes, however, the said objections are ordinarily of so great importance as to render such powders of little value for use in the latter processes. This is due to the fact that, in both the pigment padding and printing processes, the insoluble vat dye is ordinarily converted to the soluble form in contact with the fiber to be dyed, and consequently uniformity of dispersion of the dye in the padding liquor or printing paste is required to avoid unevenness of shade and/or streaking, extremely fine subdivision of the insoluble dye is necessary for level dyeing and sharpness of outline as well as rapidity of reduction in the steaming or ageing step of the printing process, and specks or large particles of insoluble dye must be absent to prevent the formation of specked or spotted prints.

The present invention is based upon the discovery that the readily soluble salts of the hereindescribed acid alkyl esters of polybasic inorganic acids possess a combination of properties which render them of particular value for the production and manufacture of vat dye preparations in the form of suspensions, pastes and powders, and especially for the manufacture of vat dye powders which can be used as initial material for the preparation of dye baths and pastes for dyeing textile fibers, in particular by printing and pad and jig processes. Thus, the soluble salts of the said 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 hereindescribed 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 for vat dyes. They furthermore have little or no tendency to foam and lather, which is in contradistinction to the foaming and lathering action of the sulfuric acid esters of alcohols of high molecular weight (e. g., lauryl sulfate). In addition they act as dyeing assistants, e. g., 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 ageing operations.

The invention accordingly comprises the compositions having the properties, ingredients and proportions of ingredients, exemplified in the compositions hereinafter disclosed, and the processes comprising steps and their relation exemplified in the processes hereinafter disclosed. The scope of the invention will be indicated in the appended patent claims.

In the preparation of a vat dye composition of the present invention, a vat dye is mixed with one or more of the soluble salts of the acid alkyl esters of polybasic inorganic acids more fully identified hereinafter. The said preparation of the compositions of the present invention may be carried out in a number of ways, for example, by intimately grinding the salt of the acid alkyl ester in the solid form with a solid form of the vat dye. The compositions of the present invention are preferably prepared by dissolving the said salt of the acid alkyl ester in an aqueous dispersion or suspension of the vat dye, which preferably contains a dispersing agent, with or without addition of fillers and/or other substances desired in the final product, and drying the resulting mixture, preferably with agitation and preferably by evaporation to substantial dryness. I have found, by removing water, as by evaporation to substantial dryness, from an aqueous disperson or suspension of a vat dye containing one or more of the soluble salts of the said acid alkyl esters, that the final product has the appearance of a solid dispersed suspension. In those cases where a very large amount of the salt of the acid alkyl ester is employed, a part of said salt may crystallize during the evaporation, but the crystals are so finely divided and evenly distributed throughout the whole composition, that the product appears to be substantially homogeneous.

The soluble salts of acid alkyl esters which may be employed in accordance with the present invention include those of the organic, acidic re-

action products resulting from the interaction of an aliphatic monohydric alcohol containing 5 or less carbon atoms with a polybasic inorganic acid or suitable derivative thereof and which are considered to be partial esters of polybasic inorganic acids consisting, on the one hand, of a radical of an inorganic polybasic acid in which at least one of the replaceable hydrogen atoms is present and, on the other hand, of one or more lower alkyl hydrocarbon radicals (straight-chain, branched-chain, saturated or unsaturated) directly linked to the inorganic radical. As employed herein the expression "lower alkyl hydrocarbon radical" denotes an aliphatic hydrocarbon radical containing a maximum of 5 carbon atoms. The salts of the said acid alkyl esters which contain a radical of sulfuric, boric, phosphoric or thiophosphoric acid, and especially of sulfuric or phosphoric acid, are of particular interest in connection with the present invention. 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 less than 6 carbon atoms,

A represents the residue of the inorganic acid (as for example the radical SO_2, the radical PO, 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 one or more but not greater than n—1. As is well known, a partial ester (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.

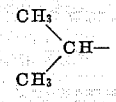
It is to be noted in the case of acid alkyl esters which are derivatives of polybasic acids containing 3 or more replaceable hydrogen atoms in which more than one of said hydrogen atoms have been replaced by organic radicals, the said organic radicals (represented by R in the above formula) may be the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

The alkyl ester salts employed in accordance with the present invention comprise the soluble salts of the herein-described acid alkyl esters; e. g., those resulting from the combination of the said acid alkyl esters with any suitable metal or base, including the organic bases, producing salts having good solubility and also preferably a finely crystalline or amorphous form in the solid state. For example, alkali metal, alkali earth metal, ammonium, etc. salts may be employed or the salts formed by the interaction of the said acid alkyl esters with such organic bases as alkyl amines (particularly the hydroxy alkayl amines), pyridine, guanidine, urea or other salt-forming organic ammonium bases.

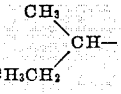
The said alkyl ester salts employed in accordance with the present invention may be prepared in any manner well known to the art; as for example by the treatment of the corresponding alcohol, in the presence or absence of a solvent or diluent, with a suitable inorganic reagent (such as phosphorus chloride or oxychloride, concentrated sulfuric acid and/or chlorsulfonic 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 monoalkyl sulfuric acids resulting from the use of sulfuric acid or chlorsulfonic 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 monoalkyl sulfuric acids in accordance with the present invention.

As illustrating various types of acid alkyl esters, the soluble salts of which may be employed in accordance with the present invention, there may be mentioned the acid alkyl esters which are derivatives of open-chain monohydric aliphatic alcohols which contain not more than 5 carbon atoms; as for example, the monoethyl, propyl, butyl and amyl sulfuric acids; the mono- and di-ethyl, propyl, butyl and amyl phosphoric and boric acids; diamyl dithiophosphoric acids; etc.

Of special interest in connection with the present invention are the alkali metal salts of the sulfuric acid mono esters of the various alcohols which contain not more than 5 carbon atoms, including those which contain single or multiple bonds, straight chains and branched chains. Thus, there may be particularly mentioned, by way of illustration, the sodium or potassium salts of the following: ethyl sulfuric acid; normal and isopropyl sulfuric acids; the monosulfuric acid ester of methyl ethyl carbinol; normal-, iso-, and tertiary-butyl 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 production of vat dye composition 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:



etc.) are somewhat superior in their action to those in which the alkyl group is a normal or straight-chain radical, although they are somewhat more hygroscopic than those in which the alkyl group is a normal or straight-chain radical.

The said sulfuric acid mono alkyl esters 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 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 chlorsulfonic 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 said salts of acid alkyl esters may also be employed in accordance with the present invention; as for example the salts of alkali metals or organic bases with the commercially available and cheap mixtures of alkyl sulfuric acids resulting from the sulfuric acid treatment of

gaseous and lighter liquid unsaturated hydrocarbons, such as 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.

Inasmuch as the quality and dispersibility of the resulting dye composition is dependent to a considerable extent upon the original degree of dispersion of the dye in the dispersion or suspension before drying, the vat dye is preferably treated in the highly dispersed form. A suitable dispersing agent is preferably included in the dispersion or suspension so as to aid in preventing precipitation and agglutination of the dye particles during the drying and to increase the fluidity and render easier the incorporation of the monoalkyl sulfuric acid salt. Among the dispersing agents which may be employed for this purpose there may be mentioned for example, the sulfonic acids of benzene, hydroxybenzenes, naphthalene, hydroxynaphthalenes, their nuclear alkyl, nuclear aralkyl and hydrogenated derivatives, as well as aldehyde condensation products thereof (as for example 2,6-naphthalenedisulfonic acid, 1.7-naphthalenedisulfonic acid, 2.8-naphthalenedisulfonic acid, isopropylnaphthalenesulfonic acids, dibutylnaphthalenesulfonic acids, amylnaphthalenesulfonic acids, butylbenzylnaphthalenesulfonic acids, cyclohexylnaphthalenesulfonic acids, methylene-di (beta-napthalenesulfonic acid), acetal-di (beta-naphthalenesulfonic acid), benzal-di (beta-naphthalenesulfonic acid), methylene - di (diisopropylnaphthalenesulfonic acid), etc.); sulfite cellulose waste liquors and their mildly oxidized products and evaporated residues; sulfonated resins; abietene, abietine and abietane sulfonic acids; and the like, as well as mixtures of two or more of such substances.

If desired, additional substances having diluent, anti-foaming, assisting, wetting, catalytic, enolyzing, or other suitable action in the subsequent use of the compostions may also be incorporated into the compositions of the present invention, preferably while the latter are in the form of aqueous suspensions.

In order that the compositions may be in a more satisfactory form for subsequent use, the mixture of vat dye in aqueous dispersion and salt of acid alkyl ester, together with the other substances, if added, are preferably 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 may be employed as such, but it is preferably brought to substantial dryness. Thus, the paste may be evaporated to dryness on an atmospheric or vacuum rotary drum drier, preferably at a temperature not exceeding 100° C., and the dry products 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 and the admixture stirred to produce a dry product. If desired, the dry products may be disintegrated into a powder in any suitable manner, as for example by grinding in a ball mill, and subsequently screened.

The amount of salt of acid alkyl ester employed in the preparation of the compositions of the present invention may be varied over a considerable range, depending in part upon the nature and concentration of the 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. For example, an ideal vat dye composition in dry form is obtained by replacing all of the water in a vat dye paste with an equal amount of said alkyl ester salt, in which case the composition of the powder may be for example:

	Per cent
Vat dye (actual dye solids)	10–20
Dispersing agent (e. g. "Leukanol")	1– 2
Salt of the acid alkyl ester	89–78

While a powder composition having such a large content of the alkyl ester salt is an extremely advantageous product, in that it is applicable for the preparation of vat dyes of all classes in the powdered form which, when slurried with water, yield pastes which in many cases are even superior to the corresponding vat dye pastes which do not contain said alkyl ester salt, it is frequently unnecessary to employ such large amounts of said alkyl ester salts.

For example, when the vat dye powder is to be employed for the preparation of a dye bath (a vat) or when the powder is to be employed for the preparation of a paste useful as a pigment (as for example for the coloring of paper and the like), only a sufficient amount of alkyl ester salt need be employed which will produce the desired disintegration of the powder when added to water. Furthermore, by including diluents and fillers in the composition, a much smaller amount of the ester salt may be used, inasmuch as the presence of a relatively small quantity of it is effective in overcoming the disadvantageous properties of the diluents and fillers previously known and used. As a result, a part of the alkyl ester salt may be replaced in the composition by less expensive diluents and fillers.

As diluents and fillers many known products may be used. For example, the carbohydrates are quite suitable, such as sucrose (ordinary cane or beet sugar), cerelose (or corn sugar), etc. Dextrines, glue, gelatin, gum arabic, or other substances included in the general class of so-called "protective colloids" also may be used; as well as other products which do not cause precipitation of suspended vat dye particles or otherwise produce specky printing pastes (as for example, urea, various other highly soluble amides, etc.).

When the vat dye powder compositions of the present invention are to be employed in the preparation of vat dye printing pastes and it is desired to take advantage of the solubilizing action of the said alkyl ester salts, and especially the monoalkyl sulfuric acid salts, in the preparation of the printing pastes and their assisting action in the printing operation, a larger amount of said salts will ordinarily be employed than would be necessary merely for the preparation of a readily dispersible vat dye powder. As has been pointed out hereinbefore, the specific amount of alkyl ester salt to be employed in any particular composition will vary with the particular dyestuff and with the nature and amounts of other materials present in the composition.

It will be further observed, in the preparation of printing pastes with the aid of vat dye powders of the present invention, that the printing pastes frequently show signs of prereduction, even in the absence of printing catalysts or reduction accelerators employed in the art, such as

the sodium salt of anthraquinone-2-sulfonic acid, ferrous salts, and the like. As above noted, vat dye powders intended for use in dyeing by the printing process may also include, however, printing catalysts or "boosters", reduction accelerators, hydrotropic and/or enolyzing substances, in addition to or in replacement of part of other diluents.

It is to be noted that under the term "hydrotropic substances" are to be understood not only the substances specially enumerated by Neuberg and Tamba (compare Carl Neuberg, Biochemische Zeitchrift, vol. 76, 1916, page 107 ff., and Tamba, Biochemische Zeitchrift, vol. 145, 1924, page 415; Carl Neuberg, Sitzungsberichte der Koengl. Preussischen Akademie der Wissenschaften, 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 sulphonic 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 sulphonic acids, p-toluene-sulphonic acid, the benzene sulphinic acids, 1.4-toluene sulphinic acid, naphthalene sulphonic acids, aniline sulphonic acids and substitution products thereof, naphthylamine sulfonic acids (as for example, 1-amino-naphthalene-3.6.8-trisulfonic acid), picolinic acid, hydro aromatic carboxylic or sulphonic 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 sulphonic acid (sodium salt).

The presence of enolyzing substances in vat dye powders 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.

It may be noted, in connection with the use of the vat dye pastes and powders of the present invention in dyeing and printing, that the vat dye pastes and powders of the present invention may be substituted in ordinary dye baths, padding liquors and printing pastes in place of the usual vat dye pastes (on the basis of the weight of the dye in the paste or powder) without otherwise changing the proportions and ingredients of said compositions.

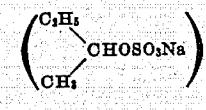
The vat dye compositions of the present invention are particularly valuable for dyeing and printing so-called "gray goods" (unbleached cellulose fabrics, raw artificial silk fabrics and the like) inasmuch as the dyeings and prints obtained with the aid of such compositions have exceedingly high tinctorial value and excellent penetration, particularly when compared with dyeings and prints made in the absence of the acid alkyl esters, and their salts, employed in accordance with the present invention.

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

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 2 parts of "Leukanol" until a thin fluid paste is obtained. 13 parts of cane sugar and 5 parts of normal butyl sodium sulfate ($C_4H_9OSO_3Na$) are then added, the mixture is stirred until solution of the alkyl sulfate 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 and 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 normal butyl sodium sulfate, an equal amount of normal amyl sodium sulfate ($C_5H_{11}OSO_3Na$) or of any of the other salts of acid alkyl esters hereinbefore mentioned, and especially lower monoalkyl sulfuric acid soluble salts, 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 per cent solution of Leukanol), 50 parts of cane sugar, and 25 parts of dextrine. The suspension is stirred until homogeneous, and then 5 parts of secondary butyl sodium sulfate

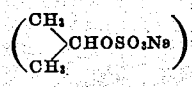


are added and the mixture is stirred until solution of the alkyl sulfate is complete. The resulting mass, either as such or after evaporation, may be used as a paste; or it may be evaporated to dryness, ground and screened, as in Example 1, to produce a powder that is readily dispersed when added to 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 secondary butyl sodium sulfate, the potassium salt of the monosulfuric acid ester of dimethyl ethyl carbinol may be used.

Example 3.—To 200 parts of National Carbanthrene Violet 2R Standard Paste (Color Index 1104) containing 11 per cent of dye solids in the form of an aqueous suspension, there are added 1 part of Leukanol, 5 parts of normal butyl sodium sulfate, and 72 parts of cane sugar or cerelose. The mixture is stirred until all the soluble mate-

rial 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 normal butyl sodium sulfate, the potassium salt of the acid sulfuric ester of dimethyl ethyl carbinol or readily soluble salts of any of the other acid esters above disclosed may be used.

Example 4.—100 parts of National Carbanthrene Violet 2R Paste (cf. Example 3) are mixed with 25 parts of cane sugar and 68 parts of isopropyl sodium sulfate



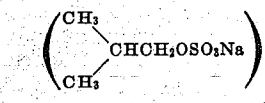
and the mixture is stirred until the latter are dissolved. The resulting suspension is then evaporated to dryness, ground and screened. 100 parts of a violet powder is obtained which is suitable for dyeing by all known methods. It is especially useful for making pastes to be used in dyeing by the printing process.

Example 5.—100 parts of the thioindigoid vat dye known as National Vat Orange R (Color Index 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 ethyl sodium sulfate ($C_2H_5OSO_3Na$) until solution of the latter is complete. The resulting suspension is evaporated to dryness, ground and screened. instead of the ethyl sodium sulfate other salts of the lower alkyl sulfates may be employed. 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 carbonate, 80 parts of sodium formaldehyde sulfoxylate, 50 parts of glycerin, and 380 parts of water) and utilized in the printing of cotton in accordance with the usual procedure, produces prints which in heavy shades are about 20 to 25 per cent greater in strength than corresponding prints made without the alkyl sodium sulfate. In addition, the presence of the monoalkyl sulfuric acid 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.

It may be noted that the soluble salts of acid alkyl esters which contain an iso-radical (as for example, the isopropyl radical, the isobutyl radical, etc.) are preferably employed in connection with vat dyes of the thioindigoid series when the latter are to be employed for the preparation of printing pastes, in view of their superior action in the printing process.

Example 6.—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, 50 parts isobutyl sodium sulfate, 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 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. The potatssium 2-carboxy-benzophenone-4'-sulfonate acts as an assistant or adjuvant, as more fully disclosed and claimed in my application Serial No. 723,332, filed May 1, 1934.

Example 7.—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, 64 parts of isobutyl sodium sulfate

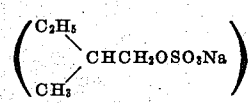


and 18 parts of cane sugar. The mixture is stirred until the soluble material is all dissolved, and is then evaporated to dryness, ground and screened. A highly colored pink pigment is obtained which is readily dispersed in water or in printing pastes. If desired 1 part of ferrous sulfate and a sufficient amount (a few drops) of sodium hydroxide solution to render the mixture slightly alkaline to brilliant yellow paper may be added to the mixture before evaporation in order to enhance the printing action of the composition.

Example 8.—100 parts of 5.5'-dichlor-7.7'-dibrom indigo paste (cf. Color Index 1188), containing 20 per cent of dye solids, are mixed with 2 parts of Leukanol or other suitable dispersing agent to produce a thin fluid suspension. Then 20 parts of cane sugar and 57 parts of isopropyl sodium sulfate 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 especial 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 any of the substances above referred to as hydrotropic or enolyzing substances.

Example 9.—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 isobutyl sodium sulfate 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 10.—To 100 parts of National Carbanthrene Flavine GC (cf. U. S. P. 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 24 parts of sucrose, 55 parts of the sodium salt of the monosulfuric acid ester of secondary butyl carbinol



and 1 part of the disodium salt of 2.6-dihydroxy-anthraquinone. 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.

In the preparation of the compositions of the present invention, it is not necessary to employ a previously prepared dyestuff paste but the filter cakes and other separated forms of the dye may be employed; as for example, the press cakes resulting from the filtration of aqueous suspensions of the dye, such as are obtained in the course of manufacture or produced in the purification of a crude vat dye by the vatting, acid pasting or other known processes. In the latter case it is preferable to modify somewhat the method of procedure of the above examples, so as to obtain superior dispersion of the vat dye, as illustrated by the following example:

Example 11.—2 parts of the sodium salt of anthraquinone-2-sulfonic acid are dissolved in 200 parts of water, with the aid of heat if necessary, 100 parts of dextrine are added, and the mixture is stirred until a smooth paste is obtained. 110 parts of National Vat Orange R (in the form of a press cake containing 21 per cent of dye solids) and 15 parts of Leukanol solution (30 per cent) are then added. The mixture is stirred until a well-dispersed thin fluid suspension is obtained. Then 74 parts of isobutyl sodium sulfate are added, and stirring is continued until the latter is dissolved. The resulting mass is evaporated with stirring until a thick paste is obtained and is then dried, ground and screened as in the foregoing examples. 200 parts of a brilliant orange powder is thus obtained having similar properties to those of the product of Example 6.

In the above examples other readily soluble salts of the hereindescribed acid alkyl esters, and especially other salts of alkyl sulfuric acids which are included within the formula $ROSO_3H$ (in which R is a hydrocarbon radical containing a maximum of 5 carbon atoms), may be employed instead of all or a part of the monalkyl sulfuric acid salts therein disclosed. The vat dyes disclosed may be replaced by any other vat dye; as for example:

National Carbanthrene Yellow G	Color Index No. 1118
National Carbanthrene Golden Orange G	Color Index No. 1096
National Carbanthrene Golden Orange 2RT	Color Index No. 1097
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 Red Violet 2RNX	Color Index No. 1161
National Carbanthrene Brilliant Green supra	Color Index No. 1101
National Vat Red Violet RH	(Cf. U. S. P. 916,029)
National Vat Scarlet G	Color Index No. 1228
National Vat Brown G (dinaphthylthioindigo)	
National Vat Violet R	Color Index No. 1222
National Brilliant Indigo B	Color Index No. 1190
National Brilliant Indigo 4B	Color Index No. 1184
National Brilliant Indigo 4G	Color Index No. 1189
National Carbanthrene Red BN	Color Index No. 1162
National Carbanthrene Brown AR	Color Index No. 1151
National Carbanthrene Green B	Color Index No. 1102
National Carbanthrene Olive B	Color Index No. 1150
National Vat Yellow G	Color Index No. 1196
National Carbanthrene Red AFF	Color Index No. 1133
National Carbanthrene Blue RS	Color Index No. 1106
National Vat Pink BG	Color Index No. 1210
National Vat Yellow R	Color Index No. 1170
National Carbanthrene Blue 3G	Color Index No. 1109

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

In the above examples the production of dry products by evaporating the pastes to dryness has been described. As hereinbefore noted, however, dry products may also be obtained in accordance with the present invention by admixing a suitable hydrate forming soluble salt in an anhydrous condition with the paste, whereby a dry product is formed by formation of a hydrate of said salt. Thus, as will be further illustrated by the following specific examples, trisodium phosphate, sodium sulfate, sodium acetate or other suitable hydrate-forming soluble salts (having regard for the nature and intended use of the product) may be admixed in an anhydrous condition (in the anhydrous form or a partially dehydrated form) by stirring with a vat dye composition of the present invention in the form of a paste, preferably in the form of a partially evaporated mixture. The resulting dry mixture may be ground and screened to form a powder. This latter procedure has the advantage of saving time and labor as compared with the evaporation procedure of drying. Furthermore, the danger of decomposition of the products by lengthy exposure to heat is considerably reduced. In most cases the resulting product is considerably denser (less bulky) and dusts less, and consequently is cheaped to ship on a volume basis and more convenient to use.

Example 12.—300 parts of indigo paste (containing 20 per cent of pure indigo, as shown by indigotin titration), are stirred with 2 parts of dry "Leukanol" until a thin fluid paste is obtained. 5 parts of normal butyl sodium sulfate are then added, the mixture is stirred until solution of the alkyl sulfate is complete, and the resulting mixture is evaporated with stirring until a thick paste containing about 19 to 20 per cent of water is formed. 15 parts of anhydrous trisodium phosphate are then added and the mass is intimately mixed until a dry product is obtained. There is thus produced 100 parts of the dry composition containing 60 per cent of indigo. Upon grinding the product and screening through a screen of fine mesh, a fine dry powder is obtained which disperses very readily and may be used for all dyeing purposes.

Example 13.—To 100 parts of the pyranthrone vat dyestuff known as National Carbanthrene Golden Orange 2 RT 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 50 parts of isobutyl sodium sulfate. The mixture is evaporated with stirring until a paste containing 18 to 20 per cent of water is obtained. 15 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 14.—To 100 parts of National Vat Orange R paste (employed in Example 5), there are added 2 parts of Leukanol, 50 parts of ethyl sodium sulfate, 1 part of the sodium salt of anthraquinone-2-sulfonic acid, and 10 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 12 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.

While the invention has been described particularly with relation to the preparation of compositions which are especially suitable for the dyeing and printing of textile fabrics, it is to be understood that the invention is not limited thereto but that the readily dispersible powders of the present invention are also of especial utility in the preparation of aqueous suspensions of the dyestuff for use in the pigment form for the dyeing of paper, the tinting of fibers and other material, and the like.

It is further to be noted that the vat dye compositions of the present invention containing soluble salts of acid alkyl esters may also be utilized as components of discharge and resist printing preparations as well as of the dyeing and printing compositions above described.

This application is a division of my application Serial No. 673,031, filed May 26, 1933, for Art of dyeing and coloring, and is in part a continuation of my application Serial No. 673,030, filed May 26, 1933, for Vat dye composition.

I claim:

1. A vat dye composition comprising a vat dye and a soluble salt of an alkyl sulfuric acid corresponding with the formula $ROSO_3H$, in which R represents a hydrocarbon radical containing less than 6 carbon atoms.

2. A vat dye composition comprising a vat dye and a soluble salt of an alkyl sulfuric acid corresponding with the formula $ROSO_3H$, in which R represents a hydrocarbon radical containing less than 6 carbon atoms, said composition being in the form of powder which disperses readily when added to water.

3. A vat dye composition in solid form for use in coloring, dyeing and textile printing which comprises a vat dye, a dispersing agent, and a soluble salt of an alkyl sulfuric acid corresponding with the formula $ROSO_3H$, in which R represents a hydrocarbon radical containing from 3 to 5 carbon atoms.

4. A vat dye composition in the solid form comprising a vat dye and a soluble salt of an alkyl sulfuric acid containing less than 6 carbon atoms in the alkyl group, said salt corresponding with the formula $ROSO_3M$, in which R represents an open chain hydrocarbon radical containing less than 6 carbon atoms, and M represents an alkali metal, an alkaline earth metal or the $-NH_4$ radical.

5. A vat dye composition in the dry solid form comprising a vat dye and an alkali metal salt of an alkyl sulfuric acid containing 3 to 5 carbon atoms in the alkyl group, said salt corresponding with the formula $ROSO_3M$, in which R represents a saturated hydrpcarbon radical containing from 3 to 5 carbon atoms, and M represents an alkali metal.

6. A vat dye composition in solid form adapted for use in textile printing which comprises a vat dye, an alkali metal salt of an alkyl sulfuric acid containing less than 6 carbon atoms, said salt corresponding with the formula $ROSO_3M$, in which R represents an open-chain hydrocarbon radical containing less than 6 carbon atoms and M represents an alkali metal, and a material selected from the class of carbohydrates, printing catalysts, assistants, hydrotropic substances, and enolyzing substances.

7. A vat dye composition in solid form for use in textile printing which comprises a vat dye and the sodium salt of an alkyl sulfuric acid containing less than 6 carbon atoms in the alkyl group, said salt corresponding with the formula $ROSO_3Na$, in which R represents an alkyl radical containing less than 6 carbon atoms, such as is obtainable by drying an aqueous mixture comprising the vat dye and the sodium salt of the alkyl sulfuric acid.

8. A vat dye composition in solid form adapted for use in textile printing which comprises a vat dye selected from the group of anthraquinone, indigoid and thioindigoid vat dyes, and the sodium salt of an alkyl sulfuric acid containing 3 to 5 carbon atoms in the alkyl group, said salt corresponding with the formula $ROSO_3Na$, in which R represents a saturated hydrocarbon radical containing 3 to 5 carbon atoms.

9. A vat dye composition in dry solid form, which comprises an intimate mixture of a vat dye, an aldehyde condensation product of an aromatic sulfonic acid, a carbohydrate and a highly soluble salt of a monoalkyl sulfuric acid containing less than 6 carbon atoms.

10. A vat dye composition in dry solid form, which comprises an intimate mixture of a vat dye, a formaldehyde condensation product of a naphthalene sulfonic acid, a carbohydrate, and sodium isobutyl sulfate.

11. A method of making a vat dye composition which comprises incorporating a soluble salt of an alkyl sulfuric acid corresponding with the formula $ROSO_3H$, in which R represents a hydrocarbon radical containing less than 6 carbon atoms, into an aqueous suspension comprising a vat dye and a dispersing agent, and drying the mass.

12. A method of making a vat dye composition which comprises incorporating a soluble salt of an alkyl sulfuric acid having the formula $ROSO_3M$, in which R represents an open-chain hydrocarbon radical containing less than 6 carbon atoms and M represents an alkali metal, into an aqueous suspension comprising a vat dye and an aldehyde condensation product of a naphthalene sulfonic acid as a dispersing agent, and drying the mass.

13. A method of making a vat dye composition, which comprises incorporating an alkali metal salt of a monoalkyl sulfuric acid containing 2 to 5 carbon atoms into an aqueous mixture comprising a vat dye, a formaldehyde condensation product of a naphthalene sulfonic acid, and a carbohydrate, and drying the mass.

14. A vat dye composition in the form of an aqueous paste comprising a vat dye, an aldehyde condensation product of a naphthalene sulfonic acid as a dispersing agent, and a soluble salt of an alkyl sulfuric acid containing less than 6 carbon atoms in the alkyl group, said salt corresponding with the formula $ROSO_3M$, in which R represents an open-chain hydrocarbon radical containing less than 6 carbon atoms, and M represents an alkali metal.

15. A vat dye composition in the form of an aqueous paste comprising a vat dye, a formaldehyde condensation product of a naphthalene sulfonic acid and an alkali metal salt of an alkyl sulfuric acid containing 3 to 5 carbon atoms in the alkyl group, said salt corresponding with the formula $ROSO_3M$, in which R represents a saturated hydrocarbon radical containing from 3 to 5 carbon atoms, and M represents an alkali metal.

16. A vat dye composition in the form of an aqueous paste comprising a vat dye, a dispersing agent, and a soluble salt of an acid alkyl ester consisting on the one hand of a radical of an inorganic polybasic acid in which at least one of the replaceable hydrogen atoms is present and

on the other hand of one or more lower alkyl hydrocarbon radicals directly linked to the inorganic radical.

17. A vat dye composition comprising a vat dye and a soluble salt of an acid alkyl ester consisting on the one hand of a radical of an inorganic polybasic acid in which at least one of the replaceable hydrogen atoms is present and on the other hand of one or more lower alkyl hydrocarbon radicals directly linked to the inorganic radical.

18. A vat dye composition in the dry solid form comprising a vat dye and an alkali metal salt of an acid alkyl ester consisting on the one hand of a radical of an inorganic polybasic acid in which at least one of the replaceable hydrogen atoms is present and on the other hand of one or more lower alkyl hydrocarbon radicals directly linked to the inorganic radical.

19. A vat dye composition in dry solid form, which comprises an intimate mixture of a vat dye, an aldehyde condensation product of an aromatic sulfonic acid and a highly soluble salt of an acid alkyl ester consisting on the one hand of a radical of an inorganic polybasic acid in which at least one of the replaceable hydrogen atoms is present and on the other hand of one or more lower alkyl hydrocarbon radicals directly linked to the inorganic radical.

20. A method of making a vat dye composition which comprises incorporating a soluble salt of an acid alkyl ester into an aqueous suspension comprising a vat dye and a dispersing agent, and drying the mass, said acid alkyl ester consisting on the one hand of a radical of an inorganic polybasic acid in which at least one of the replaceable hydrogen atoms is present and on the other hand of one or more lower alkyl hydrocarbon radicals directly linked to the inorganic radical.

JEAN G. KERN.