

1

3,139,321

VAT DYE-QUATERNARY AMMONIUM POLYACRYLATE ESTER COMPOSITION AND CONTINUOUS PAD DYEING THEREWITH

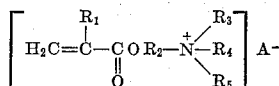
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This invention relates to cationically dispersed vat dyes and an improved continuous dyeing process utilizing these dye compositions.

Heretofore in a pigment padding process of dyeing with a vat dye dispersed with an anionic agent the padded mercerized goods have been dried before being passed into the chemical pad bath to pick up the reducing agents needed to solubilize the dye and to cause the dye to be absorbed on the fabric. By control of the drying conditions, the migration of the dye which occurs in drying can be controlled and an approach to level dyeing is attained. A pigment-pad wet process, i.e. a process in which the pigment-padded fabric is immersed in the chemical pad bath in a wet condition without having been dried, has been inoperable because of the excessive bleeding of the padded dye into the chemical pad bath. Mercerized cotton poplin, for example, is extremely difficult to dye continuously by pigment-pad processing without an intermediate drying step owing to the excessive bleeding or migration of the pigment into the chemical reduction bath. But by employing a cationically dispersed vat dye of the present invention the bleeding is eliminated or reduced to tolerable limits, and a state of fine subdivision of the dye attained by milling provides an attractive, level dyeing of the goods, including open-width mercerized cotton fabrics. In this manner high quality level dyeings are obtained by a more economic process in which a drying step is eliminated and the production of dye goods is materially increased.

It is an object of this invention to provide new cationically dispersed vat dye compositions. A further object is to provide an improved process for dyeing utilizing these new vat dye compositions. Another object is to improve the dyeing of mercerized open width cotton goods by a continuous pigment-pad process. A still further object is to obtain high quality, uniformly level dyeings on mercerized cotton piece goods by a pigment-pad wet process. Other objects will appear hereinafter.

These and other objects of this invention are accomplished by providing a vat dye composition comprising a vat dye dispersed in an aqueous medium and having a particle size of five microns or less obtained by comminuting one part by weight of dye in the presence of from about three parts to about ten parts by weight of water containing from about 0.1 to about 0.5 part by weight of a monomer-polymer mixture of a compound having the structure



wherein R_1 is hydrogen or methyl, R_2 is a straight or branched chain alkylene of 2 to 4 carbon atoms, R_3 and R_4 are hydrogen, straight or branched chain alkyl of 1 to 4 carbon atoms which may be the same or different and taken together may form a heterocyclic ring of 5 to 6 atoms with the nitrogen atom, R_5 is hydrogen, a straight or branched chain alkyl of 1 to 4 carbon atoms, or benzyl, and A^- is the anion of a water-soluble inorganic or organic acid, said monomeric-polymeric mixture having a viscosity from about 400 centipoises to about

2

100,000 centipoises in a 30% aqueous solution at 30° C. as measured by a Brookfield viscometer rotating at 20 r.p.m.

The vat dye compositions as described above are well adapted for dyeing cotton goods such as cotton poplin by pigment padding in a continuous process where the pigment-pad bath consists of from about 0.01 part to about 5.0 parts by weight on a dry basis of the vat dye composition per 100 parts of the aqueous medium comprising the bath. The cationically dispersed vat dye compositions of this invention eliminate the necessity of drying the pigment padded piece goods before passing the piece goods through a reduction bath.

Vat dye compositions containing a vat dye comminuted in the presence of the monomer-polymer mixture of 2-(diethylmethylammonio) ethyl methacrylate methosulfate having a Brookfield viscosity of 6000 centipoises in a 30% water solution at 30° C. are typical dye compositions included by this invention and are well adapted for a continuous dyeing process.

The vat dyes encompassed by the invention are the colored organic compounds containing two or more keto groups



which are capable of undergoing a reversible reduction-oxidation cycle without serious color loss or change of shade. On reduction with sodium hydrosulfite and alkali is created the solubilizing leuco structure



which has affinity for cellulosic fiber. Chemical classes of the applicable vat dyes include the indigoid, anthraquinone, anthanthrone, benzanthrone and indanthrone dyes. Specific dyes which may be advantageously employed in accordance with this invention include such anthraquinone dyes as C.I. Vat Brown 3, C.I. Vat Green 1, C.I. Vat Blue 6, and such an indigoid dye as C.I. Vat Red 1.

The above vat dyes are rendered suitable to provide improved continuous dyeings of cotton goods in accordance with the invention by reducing their particle size to five microns or less by wet milling or grinding in the presence of from about 10% to about 50% by weight of the dry dye of a monomer-polymer mixture of a salt or of a quaternary derivative of a dialkylaminoalkyl acrylate described below. The resultant dye is dispersed in finely divided form in an aqueous medium and stabilized with the selected cationic agent. A lower limit of about 10% of cationic agent is specified because much less than 10% is not enough to stabilize the dispersion of most of vat dyes. A preferred amount of cationic agent is 20%. As much as 50% may be used. More than this is usually uneconomic and the higher concentrations of some of the monomer-polymer cationic agents may yield solutions which are too viscous for effective milling of the dye.

An effective procedure for milling or grinding the dye is that described in U.S. Patent 2,816,115. By such a procedure the vat dye, a selected monomeric-polymeric cationic agent, water, and a powdered water-insoluble grinding agent, usually sand of a size between 100-mesh and 250-mesh, form a viscous, workable mass in a disc mill described in U.S. Patent 2,581,414. By subjecting the mixture to milling under conditions producing internal shear the vat dye is ground to the desired size and the pigment is recovered as a dispersion free of the grinding agent. Milling is continued, for example, until samples of the mass after dilution and centrifuging out the sand show by microscopic examination pigment particles which

are 5 microns or less in diameter. Dyes having larger particles cause specking when padded on fabric and are to be avoided to produce high quality, uniformly level dyeings.

The milling of the dye may also be done in a heavy duty internal mixer fitted, for example, with sigmoid blades. A dough-like aqueous paste of the vat dye containing the cationic agent is milled with internal shearing to reduce the particle size of the dye. A grinding agent such as fine sand may also be present to facilitate the grinding in the mixer. Other suitable ways of milling or grinding the vat dye in the presence of the required cationic agent will be apparent to those skilled in the art; the invention is not restricted to any particular method by which the dye with at most a 5-micron particle size dispersed with the specified cationic agent is obtained.

The cationic dispersing agent of the invention comprises a monomer-polymer mixture of a water-soluble inorganic or organic acid salt or quaternary derivative of an (alkylamino)alkyl acrylate. The (alkylamino)alkyl acrylates which may be used for salt formation and partial polymerization include the esters of acrylic and methacrylic acids and such amino alcohols as 2-(methylamino)ethanol, 2-(dimethylamino)ethanol, 2-(diethylamino)ethanol, 2-(ethylamino)ethanol, 2-(propylamino)ethanol, 2-(dipropylamino)ethanol, 2-(diisopropylamino)ethanol, 2-(tert-butylamino)ethanol, 2-(diisobutylamino)ethanol, 2-(N-methyl-N-butylamino)ethanol, 2-piperidinoethanol, 3-(diethylamino)-1-propanol, 2-(diethylamino)-1-propanol, 4-(diethylamino)-1-butanol, 4-(diisobutylamino)-1-butanol, 1-(dimethylamino)-2-butanol, 4-(diethylamino)-2-butanol, 1-(ethylamino)-2-methyl-2-propanyl, and the like. These esters are prepared as described in U.S. Patent 2,138,763.

Quaternary derivatives of the above (alkylamino)alkyl acrylates are prepared by reacting the monomeric ester with alkyl, aryl, aralkyl or alicyclic sulfates or halides including dimethyl sulfate, diethyl sulfate, methyl bromide, ethyl iodide, benzyl chloride. The preferred acids for forming acid salts are acetic and propionic acid. The resultant quaternary derivative or acid salt is polymerized in aqueous medium to provide a monomer-polymer mixture having a viscosity from about 400 centipoises to 100,000 centipoises in a 30% solution of the material at 30° C. as measured by a Brookfield viscometer rotating at 20 r.p.m. The preferred viscosity range is from about 2,000 to about 20,000 centipoises in a 30% solution of material at 30° C. Polymerization is carried out until the desired viscosity is reached. At this point, the solution is stabilized against further polymerization by using a "short stopping" agent such as sodium dimethyldithiocarbamate or 2-mercaptoethanol. There is always a certain amount of unpolymerized monomer present after the partially polymerized solution has been "short stopped." The polymeric component, however, is the part of the monomer-polymer mixtures which is effective in dispersing the vat dye during milling and in fixing the dye on the fabric in the dyeing process. The monomeric form of the selected cationic agents is not effective in the milling operation and does not produce a dye paste which is operable in the dyeing process. The preferred product is the monomer-polymer mixture of 2-(diethylmethylammonio)ethyl methacrylate methosulfate having a viscosity of 6000 centipoises in 30% water solution at 30° C.

The continuous dyeing process for which the invention cationically dispersed vat dye is particularly well adapted is described in U.S. Patent 2,487,197. In this process the fabric is padded with a dilute aqueous suspension of the invention vat dye and then immediately padded without drying with an alkaline solution of sodium hydro-sulfite at a temperature below that at which any material reduction of the dye takes place. The fabric so padded is then subjected to the action of steam in the absence of oxygen to effect reduction and fixation of the dye in the fabric. The pigment-pad bath will contain from about

0.01 part to about 5.0 parts by weight on a dry basis of the vat dye per 100 parts of the aqueous medium comprising the bath, depending upon the depth of shade desired. In addition, the pad bath may contain 0.1% to 0.5% glacial acetic acid and from about 0.02% to 0.1% of the monomer-polymer mixture of the cationic agent with which the dye has been milled. These additions ensure a pad bath having a pH range of 3 to 5, improve the stability of the suspended pigment, and provide a still more level dyeing. The vat dye will be padded on the fabric at from about 65° F. to 180° F. In general, to obtain the best quality dyeing the pigment pad liquor pickup should be kept as low as possible. The concentration of the sodium hydroxide and of the sodium hydro-sulfite in the chemical pad bath will vary from about 1.5% to about 8%, depending upon the amount of dye on the fiber. In addition, the chemical pad bath may contain from 0.5% to 15% common salt or Glauber's salt to suppress any tendency of the dye to bleed from the padded fabric to the bath. The chemical pad bath is preferably maintained at a temperature between 40° F. and 140° F.; the cooler the bath the better because bleeding is increased in the higher temperature baths. With cotton poplin a chemical pad bath temperature of between 75° and 80° F. will give good results. The pigment-impregnated and chemical-impregnated fabric is then steamed at 212° F. for from about 10 seconds to about 60 seconds. Further processing consists of an oxidation of the reduced dye to insolubilize it, a rinsing, soaping, re-rinsing, and final finishing of the fabric in accord with established practice.

In place of the chemical padding as described above the pigment-padded fabric may receive an immersion in a chemical bath, and the excess liquor from the reducing solution may be removed by running the fabric over revolving tension bars. The fabric is then steamed and processed in the usual way.

The invention dispersed vat dyes are primarily adapted for application to open-width mercerized cotton goods such as poplins, sateens, and twills.

Example 1

A. *Milling and dispersion of dye.*—A double disc mill of the type described in U.S. Patent 2,581,414 was charged with dye paste, dispersing agent, water, and sand and operated to grind the dye as described in U.S. Patent 2,816,115. The mill was first charged with 400 parts of a 25% water paste of C.I. Vat Green 1 (prepared by mixing with water the press cake of the dye containing no added agent), 66 parts of a 30% water solution of a monomer-polymer mixture of 2-(diethylmethylammonio)ethyl methacrylate methosulfate having a viscosity at 30° C. of 6000 centipoises as measured with a Brookfield viscometer rotating at 20 r.p.m., and 85 parts of water. The mixture was agitated until smooth. Then 490 parts of 250-mesh sand was added to the mixture and remained viscous enough to provide internal shear for the milling continued for about three hours when microscopic examination showed the dye particles to be five microns or less in diameter. During the milling small increments of water were added from time to time to keep the mixture sufficiently fluid for proper working while it remained viscous enough to provide internal shear for grinding. The mill charge was then filtered under vacuum to remove the sand. The sand was washed free of dye, and the washings were added to the filtered paste to provide a composition comprising 10 parts of 100% dye, 2 parts of the monomer-polymer mixture of the quaternary dispersing agent, and 88 parts of water.

B. *Dyeing of fabric.*—For a continuous pigment padding dye operation a pad bath was prepared to contain 100 g./l. of the 10% dispersion of the C.I. Vat Green 1 described in (A) above. In this bath mercerized cotton poplin was padded to a pickup of 50%, i.e. a pickup of 0.5% of pure dye on the basis of the dry fabric. Without drying, the padded wet fabric was immediately im-

5

mersed in a bath at room temperature containing 20 g./l. each of sodium hydroxide and sodium hydrosulfite and 150 g./l. of sodium chloride. A mild squeeze applied to the fabric as it came from the chemical bath left a total weight pickup of about 130% on the fabric. The fabric was then steamed for 15 seconds at 212 F., and then it was passed into a dilute acidified hydrogen peroxide bath. The dyed fabric was rinsed, soaped, rerinsed, dried and pressed. An excellent, bright green level dyeing was obtained. The chemical reduction bath was colored by only a trace of dye which bled from the fabric.

C. The milling of the dye was repeated as in Part A and the milling discontinued when most of the dye particles measured 6 to 10 microns in diameter. When the dye of this degree of subdivision was padded onto cotton poplin and the pigment-padded fabric processed as described above the resultant dyeing was speckled and unacceptable. When in place of the C.I. Vat Green 1, such a dye as C.I. Vat Blue 6, C.I. Vat Brown 3, C.I. Vat Red 1 was ground in the disc mill as previously described to provide a particle size of 5 microns or less and the resultant dispersion employed in the pad bath as outlined above similar excellent quality level dyeings were obtained in the absence of a fabric drying step between the pigment padding and the chemical treatment.

When mercerized cotton twill, mercerized sateen, and unmercerized muslin fabrics were subjected to the same dyeing operation as the cotton poplin employing the same cationically dispersed fine particle size vat dyes, similar high quality level dyeings were obtained.

D. The C.I. Vat Green 1 was also milled for five hours in a 2 liter capacity internal mixer of the Werner-Pfleiderer type. The mixer charge comprised 600 parts of a 28.7% aqueous paste of the dye (prepared from press cake with no surface active agent added), 159 parts of a 30% solution of a monomer-polymer mixture of 2-(diethylmethylammonio)ethyl methacrylate methosulfate having a viscosity of 6000 centipoises at 30° C. (as employed for the double disc mill above), and 400 parts of 250-mesh sand. At the end of the milling the dye was observed to have a particle size of 5 microns or less. The viscous mass from the mixer was diluted with water and filtered to remove the sand. The resultant dye paste had a solids content of 11.75%. When 50 g./l. of this dispersion was employed in the pigment pad bath for the continuous wet dyeing of cotton poplin as described above, an acceptable, level dyeing was obtained with only a trace of bleeding of the dye into the alkaline hydrosulfite bath.

E. *Polymerization of quaternary derivative.*—To a reaction vessel was charged an equal weight of 2-(diethylamino)ethyl methacrylate and water, and the mixture was cooled to about 25° C. Dimethylsulfate in a molar proportion equal to the amine was then added and the mixture agitated for about 45 min. keeping the temperature below 35° C. The resultant solution of 2-(diethylmethylammonio)ethyl methacrylate methosulfate was diluted to provide a 30% solution and its pH adjusted to 7.5.

Portions of the 30% quaternary derivative solution were treated with 0.2% of ammonium persulfate and 0.003% of p-tert-butylpyrocatechol based on the weight of the quaternary derivative present and polymerized under nitrogen at 50° to 55° C. The viscosity of the polymerizing solution was measured from time to time with a Brookfield viscometer rotating at 20 r.p.m. When a desired degree of polymerization, as indicated by the viscosity of the solution, was reached the polymerization was stopped by adding 0.1% sodium dimethyldithiocarbamate based on the weight of the quaternary derivative. Over a period of about four hours were obtained 30% solutions of the partially polymerized quaternary derivative in which the viscosity at 30° C. was 450; 2000; 6000; 7500; 24,500; 44,000 and over 100,000 centipoises, respectively.

6

Each of these solutions, except that having a viscosity in excess of 100,000 centipoises, was employed satisfactorily in the milling of C.I. Vat Blue 6 to provide dispersions of the dye that gave high quality level dyeings with little or no bleeding into the chemical pad bath in the continuous pigment pad wet process of dyeing. Similarly, polymeric 2-(trimethylammonio)ethyl methacrylate methosulfate having a viscosity in 30% solution at 27° C. of 4200 centipoises was prepared and successfully employed in the pigment pad wet dyeing process as a dispersant for milled C.I. Vat Blue 6. A dispersion of the blue dye was also made employing polymerized 2-(dimethylbenzylammonio)ethyl methacrylate chloride having a viscosity of 22,000 centipoises in 40% solution at 27° C. as the dispersing agent. When this dispersion was used in the pad bath for the pigment padding of the fabric in the continuous pigment pad wet process of dyeing cotton poplin high quality level dyeings were obtained.

EXAMPLE 2

C.I. Vat Blue 6 having a particle size of less than 5 microns was obtained as a 9% aqueous dispersed paste by sand milling the dye as described in Example 1A except that a monomer-polymer mixture of 2-(diethylamino)ethyl methacrylate acetic acid salt having a viscosity of 3250 centipoises in 30% solution at 30° C. was employed as the dispersing agent. A dyeing of mercerized cotton poplin fabric was made by the continuous pigment-pad wet process employed in Example 1B with 100 g./l. of the 9.1% dispersion of the dye in the pad bath. An excellent quality level dyeing was obtained. Only a trace of bleeding occurred in the chemical pad bath.

Polymerization of Acetic Acid Salt

A reaction vessel was charged with 1888 g. of water and 198 g. of glacial acetic acid, swept with nitrogen, and heated to 80° C. To the acid solution was added 6.3 g. of potassium persulfate and 614 g. of 2-(diethylamino)ethyl methacrylate. The temperature was maintained at 80±5° C. for one hour when the viscosity of a portion of the polymerized solution cooled to 30° C. measured 2800 centipoises employing a Brookfield viscometer rotating at 20 r.p.m. To the reaction vessel was then added 6.3 g. of 2-mercaptoethanol to stop the polymerization. The resultant solution had a viscosity at 30° C. of 3250 centipoises. Solutions of lower viscosity (500 centipoises) and of higher viscosity (8600 centipoises, greater than 100,000 centipoises) were similarly prepared by shortstopping the polymerization in shorter and longer times. Each of the solutions except that having a viscosity in excess of 100,000 centipoises could be employed satisfactorily in milling the vat dye to provide dispersions of the fine particle size dye that gave high quality level dyeings with little or no bleeding into the chemical-pad bath in the continuous pigment-pad wet process of dyeing.

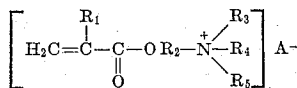
The preceding examples were given to better illustrate the nature of the present invention; however, the invention is not intended to be limited to these examples. Parts are by weight unless otherwise indicated.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. A dye composition comprising an aqueous dispersion of one part by weight of a vat dye having a particle size of no greater than 5 microns and from about 3 parts to about 10 parts by weight of water containing from about 0.1 to about 0.5 part by weight of a monomer-poly-

mer mixture consisting essentially of a monomer having the structure



and polymers thereof, wherein R_1 is selected from the group consisting of hydrogen and methyl; R_2 is an alkylene radical of 2 to 4 carbon atoms; R_3 and R_4 are selected from the group consisting of hydrogen, alkyl radicals of 1 to 4 carbon atoms and, when taken together, form a ring of 5 to 6 carbon atoms with the nitrogen to which they are attached; R_5 is selected from the group consisting of hydrogen, benzyl, and alkyl radicals of 1 to 4 carbon atoms; and A^- is an anion selected from the group consisting of water-soluble inorganic and water-soluble organic acids, said monomeric-polymeric mixture having a Brookfield viscosity from about 400 centipoises to about 100,000 centipoises in a 30% aqueous solution at 30° C. as measured by a Brookfield viscometer rotating at 20 r.p.m.

2. A dye composition according to claim 1 wherein the monomeric-polymeric mixture has a Brookfield viscosity of from about 2,000 to about 20,000 centipoises in a 30% aqueous solution at 30° C. as measured by a Brookfield viscometer rotating at 20 r.p.m.

3. A dye composition comprising an aqueous dispersion of one part of a vat dye having a particle size of no greater than 5 microns and from about 3 parts to about 10 parts of water containing from about 0.1 to about 0.5 part of a monomer-polymer mixture consisting essentially of the monomer 2-(diethylmethylammonio)ethyl methacrylate methosulfate and polymers thereof, said monomeric-polymeric mixture having a Brookfield viscosity from about 400 centipoises to about 100,000 centipoises in a 30% aqueous solution at 30° C. as measured by a Brookfield viscometer rotating at 20 r.p.m.

4. A dye composition comprising an aqueous dispersion of one part of a vat dye having a particle size of no

greater than 5 microns and from about 3 parts to about 10 parts of water containing from about 0.1 to about 0.5 part of a monomer-polymer mixture consisting essentially of the monomer 2-(diethylmethylammonio)ethyl methacrylate methosulfate and polymer thereof, said monomeric-polymeric mixture having a Brookfield viscosity of 6,000 centipoises in a 30% aqueous solution at 30° C. as measured by a Brookfield viscometer rotating at 20 r.p.m.

5. In a continuous process for dyeing goods by pigment padding, the improvement which comprises employing in the pigment pad bath a vat dye composition as set forth in claim 1 in an amount from about 0.01 part to about 5.0 parts by weight on a dry basis of the vat dye contained in said vat dye composition per 100 parts by weight of the aqueous medium comprising bath.

6. In a continuous process for dyeing goods by pigment padding, the improvement which comprises employing in the pigment pad bath a vat dye composition as set forth in claim 3 in an amount from about 0.01 part to about 5.0 parts by weight on a dry basis of the vat dye contained in said vat dye composition per 100 parts by weight of the aqueous medium comprising the bath.

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