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2,902,453

DYE STRIPPING SOLUTION

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This invention relates to the stripping of dyes from textile goods by the use of reducing agents. It is particularly concerned with an improvement in stripping baths and in processes of stripping in accordance with which novel scavengers are employed in the stripping bath or process for the purpose of assisting the removal of the dye or preventing re-deposition of the dye during the stripping operation.

In stripping dyes from dyed textile materials, the reducing agent may either convert the dye to a colorless form as in the case of vat dyes which are converted to a leuco form, or the dye is decomposed into components which may have a residual color but of a different hue or tint than that of the original dye. In either event, it is difficult to prevent re-deposition of the leuco form of vat dye or of the somewhat colored residual components of dyes that are decomposed by the reducing agent. In many cases, the stripping operation which utilizes merely a reducing agent serves only to reduce the depth of color or to change the hue to a rather dark yellow. Quaternary ammonium compounds have been used heretofore for the purpose of adsorbing some of the dye or other colored matter that is dissolved in the stripping bath to prevent re-deposition of such dye or coloring matter on the textile goods. However, generally the quaternary ammonium compounds have a very limited capacity to prevent re-deposition of the dye or other coloring matter.

In accordance with the present invention, applicant has discovered that dye-stripping operations are greatly improved by the introduction of a novel scavenger system, which comprises a water-soluble polymeric acid and a quaternary ammonium compound containing at least one hydrophobic substituent having at least 8 carbon atoms. These two components of applicant's novel scavenger system are employed in quite low proportions in the stripping baths, and they are believed to form a complex colloid salt type of coacervate. Such a coacervate consists of clusters or micelles formed by the interaction of two oppositely charged materials, at least one of which is of relatively high molecular weight.

The scavenger system of the present invention is useful in any aqueous stripping bath containing a reducing agent. The pH of the bath may be from about 3 to about 13. Examples of reducing agents that may be used include sodium or zinc hydrosulfite at pH's greater than 9; sodium or zinc formaldehyde sulfoxylates at low pH's around 3 to 4; basic zinc formaldehyde sulfoxylate, generally in a pH range of 3 to 7; and thiourea dioxide (formamidine-sulfinic acid) which may be used in any pH within the range of 3 to 13. The amount of reducing agent may be from 2% to 5% on the weight of the goods to be stripped of dye. In practice, the concentration of the reducing agent in the aqueous stripping bath may be from 0.01 to 1% on the total weight of the bath and is preferably in the range of 0.02 to 0.25%.

The amount of the scavenger system (that is the total of the quaternary ammonium compound and the polymeric acid) may be from about 0.5 to 4% on the weight

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of the fabric and is preferably about 2% on the weight of the fabric. The concentration of the scavenger system used in the stripping bath may range from 0.01 to 0.10%, that is preferably about 0.05% based on the total weight of the bath liquor. The bath to fabric ratio may be from 20:1 to 100:1 and is preferably on the order of about 40:1.

The quaternary ammonium compound of the scavenger system may comprise one or more compounds of formula I:

(I)



where at least one of R, R⁰, R' and R'' is an aliphatic, arylaliphatic, or alicyclicaliphatic group having at least 8 carbon atoms, such as octyl, dodecyl, hexadecyl, octadecyl, butylbenzyl, methyl-hexahydrobenzyl, and so on, and any other of R, R⁰, R' and R'' may be selected individually from such groups as lower alkyl having 1 to 7 carbons, including methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, also allyl, methallyl, benzyl, methylbenzyl, β-hydroxyethyl, γ-hydroxypropyl, β-hydroxypropyl, phenoxyethyl, ethoxyethyl, phenoxyethoxyethyl, tetrahydrobenzyl, hexahydrobenzyl, and so on, and A is an anion.

Examples of quaternary ammonium compounds that may be used include cetyldimethylethylammonium ethosulfate; cetyldimethylbenzylammonium chloride; laurylpyridinium chloride; trimethyloctadecylammonium bromide; (p-t-octylphenoxyethoxyethyl)dimethylbenzylammonium chloride; (p-tolyl-dodecyl)trimethylammonium methosulfate; oleylbenzyltrimethylammonium chloride; octadecylpyridinium bromide; cetylpyridinium bromide; octadecyltrimethylammonium iodide; cetyltrimethylammonium bromide; cetyltriethylammonium bromide; β-hydroxyethyl-N-octadecyl morpholinium bromide; dodecyltrimethylammonium tartrate (of Serial No. 531,277, filed August 29, 1955); didodecyltrimethylammonium chloride (of 2,706,195). Besides the anions mentioned, any of these compounds may be added as the hydroxides or as salts having other anions, such as bromide, chloride, sulfate, acetate, lactate, tartrate, citrate, phosphate, and glycinate. All of these anions are of non-oxidizing character.

The polymeric acid of the scavenger system may be a simple polymer of acrylic acid, methacrylic acid, itaconic acid, aconitic acid, citraconic acid, maleic acid, fumaric acid, the dimer of methacrylic acid, or the trimer of methacrylic acid. The polymeric acid may also be a copolymer containing at least 10% by weight of at least one of the monomeric acids just mentioned. It is essential that the polymeric acid be soluble in water to the extent of at least 0.1%. By water-soluble it is meant to include polymers which produce colloidal dispersions as well as true solutions. The molecular weight of the polymeric acid should be at least 1500 and is preferably at least 7500. However, the molecular weight may be much higher, such as from 10,000 to 200,000 or more.

The copolymers of the acids mentioned hereinbefore may contain as comonomers one or more compounds selected from the group consisting of alkyl acrylates, alkyl methacrylates, styrene, acrylonitrile, methacrylonitrile, vinyl chloride, vinylidene chloride, vinyl acetate, and the like. Preferred comonomers are the alkyl acrylates or methacrylates in which the alkyl group has from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, and butyl acrylates and methacrylates.

Stripping baths of the present invention which contain a reducing agent and the novel scavenger system described hereinabove are useful for removing many types of dyes from a wide variety of textiles. Thus, these baths serve

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to remove anthraquinone dyes, azo dyes, and indigoid dyes, being especially useful for vat dyes which are generally the most difficult to remove. They may be used for stripping these dyes from textile goods of natural or artificial fibers including cotton, wool, silk, linen, viscose rayon, cuprammonium cellulose rayon; cellulose esters including cellulose acetate, cellulose acetate butyrate; vinyl resins such as polymers of vinyl chloride and acrylonitrile, especially those containing 75% to 95% of vinyl chloride or acrylonitrile, copolymerized with other monomers such as vinyl acetate, vinylpyridine, methacrylonitrile or mixtures thereof; polyethylene; polymers of vinylidene chloride including copolymers thereof with vinyl chloride and acrylonitrile; polyamides, especially nylon 66 and caprolactam types; polyester including especially polyethylene terephthalate; casein, α -protein, and so on.

In carrying out the stripping operation, the stripping bath may be made by dissolving the reducing agent to be used in proper concentration in water. Then the polymeric acid and the quaternary ammonium compound are added separately in either order. If desired, the reducing agent may be added to the stripping bath after the introduction of one or both of the polymeric acid and quaternary ammonium compound. The amounts of polymeric acid and quaternary ammonium compound are generally used in stoichiometrically equivalent proportions. However, an excess of the quaternary ammonium compound may be provided for the purpose of modifying the hand of the stripped goods, that is, for imparting a softer feel thereto. The stripping bath is employed at any temperature from room temperature to the boil at atmospheric pressure or, if desired, up to about 120° C. with a suitable pressure vessel. The temperature employed must, of course, be selected in dependence upon the nature of the goods. Preferably, a temperature of 80° C. to 100° C. is employed for most purposes. For cellulose acetate, it is generally desirable to stay close to 80° C.; 80° to 95° C. is quite useful for wool; about 95° C. is entirely satisfactory for cotton and regenerated cellulose rayon; and temperatures from 95° to 120° C. may be employed with nylon, polymers containing at least 75% acrylonitrile, such as Orlon and Acrilan, and polyethylene terephthalate (Dacron). The goods may be kept within the bath until such time as the stripping operation is completed, during which time it is desirable to provide suitable agitation of the liquor and fabric or other goods. If desired, the fabric may be run repeatedly through the bath until the stripping has been completed.

If desired, the goods after removal from the stripping bath may be subjected to a final supplemental oxidative treatment to remove any residual yellowish color in the textile goods. This may involve treatment with a hypochlorite or a peroxide or perborate, such as those of sodium or potassium.

The employment of the novel scavenger system of the present invention provides a much cleaner or white ground. It appears that the coacervate serves to adsorb the color that is removed from the fabric or other goods and thereby prevents the color from re-depositing. It appears that this action occurs not only when a leuco form of a vat dye is formed but also in the case of non-vats when colored decomposition products are produced from the dye by the reducing agent.

In the following examples, which are illustrative of the present invention, the parts are by weight unless otherwise designated:

Example 1

Cotton, vat dyed blue with 4% Indanthrene Blue GCD (an anthraquinone type—Color Index No. 1112), was stripped under conditions of 50:1 bath, 85° C., pH 12–13, 30 minutes, with:

5% o.w.g. (0.10% w./v.) sodium hydrosulfite
10% o.w.g. (.20% w./v.) NaOH

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2% o.w.g. (.04% w./v.) polyacrylic acid (PAA), M.W. 10,000–20,000

3% o.w.g. (.06% w./v.) (methyldodecylbenzyl)trimethylammonium chloride

NOTE.—Percent in first column based on weight of goods; percent in second column=g./100 cc. of bath.

The stripping was also run with the quaternary alone as additive, and with polyvinylpyrrolidone (PVP) as sole additive to the reducing bath. Results are:

Additive	Color of Goods After Stripping
PVP	light blue.
quaternary	dirty blue-gray.
quaternary/PAA	very faint yellow.

Example 2

Viscose, vat dyed gray with 2% Indanthrene Black BB (an anthraquinone type—Color Index No. 1102), was stripped at 100:1 bath, 30 minutes, 80° C., pH 12–13, with:

5% o.w.g. (0.05% w./v.) sodium hydrosulfite

10% o.w.g. (.10% w./v.) NaOH

1% o.w.g. (.01% w./v.) polyacrylic acid (PAA) of M.W. 10,000–20,000

2% o.w.g. (.02% w./v.) (di-iso-butylphenoxyethoxyethyl)dimethylbenzylammonium chloride

As above, two other strippings were run, one with PVP as additive, the other with the quaternary as sole additive:

Additive	Color of Stripped Goods
PVP	light gray.
quaternary	somewhat darker gray.
quaternary/PAA	very faint yellow.

Example 3

Cellulose acetate, disperse-dyed a royal blue with 3% Setacyl Blue RF (a modified Primuline type—Color Index prototype No. 228), was stripped at 85° C., 40:1 bath, 30 minutes, with:

5% o.w.g. (0.125% w./v.) zinc formaldehyde sulfoxylate

1% o.w.g. (.025% w./v.) polyacrylic acid (PAA) M.W. of 10,000–20,000

1% o.w.g. (.025% w./v.) didodecenyldimethylammonium chloride (U.S. Patent 2,706,195)

with enough formic acid added to give a pH of 3–4. A stripping was also run with the quaternary as sole additive to the reducing bath.

Additive	Color of Stripped Goods
quaternary	pale greenish blue.
quaternary/PAA	pale yellow.

Example 4

Wool, acid-dyed bright reddish blue with 3% Xylene Milling Blue BL (an azo type color, Color Index No. 833), was scoured in a solution of ammonia and di-iso-butylphenoxyethoxyethanol and after rinsing was entered wet into the stripping bath:

5% o.w.g. (0.125% w./v.) sodium formaldehyde sulfoxylate

1% o.w.g. (.025% w./v.) 40/60 EA/AA (copolymer—40% by weight of ethyl acrylate and 60% by weight of acrylic acid, molecular weight about 100,000)

1% o.w.g. (.025% w./v.) (di-iso-butylcresoxyethyl)dimethylbenzylammonium chloride

The stripping was run at 100° C., with enough formic acid to give a pH of 3-4, at 40:1 ratio for 30 minutes. A similar stripping was run with the quaternary as sole additive in the reducing bath.

Additive	Color of Stripped Goods
quaternary	dull, dirty blue.
quaternary/acrylic acid copolymer	lighter blue.

Example 5

Cotton, direct-dyed blue with 5% Pontamine Sky Blue FF, was stripped at 50:1, 100° C., 30 minutes, in:

5% o.w.g. (0.10% w./v.) sodium hydrosulfite
1.5% o.w.g. (.03% w./v.) 40/60 EA/AA, M.W. ca. 100,000
2% o.w.g. (.04% w./v.) (methyldodecenybenzyl)trimethylammonium chloride

with enough soda ash (Na₂CO₃) to give a pH of ca. 10-11. Strippings were also run with PVP and with the quaternary as sole additives to the reducing bath:

Additive	Color of Stripped Goods
PVP	light blue.
quaternary	somewhat darker blue.
quaternary/acrylic acid copolymer	dull white.

Example 6

Cotton, vat-dyed blue with 8% Indigo (Color Index No. 1177), was stripped at 100:1, 90° C., 30 mins., pH 12-13, in:

5% o.w.g. (0.05% w./v.) sodium hydrosulfite
10% o.w.g. (.10% w./v.) NaOH
2% o.w.g. (.02% w./v.) (di-iso-butylphenoxyethoxyethyl)dimethylbenzylammonium chloride
2% o.w.g. (.02% w./v.) 50/50% weight of copolymer of ethyl acrylate and methacrylic acid, M.W. ca. 50,000-100,000

Strippings were also run with PVP as sole additive, and with the quaternary as sole additive to the reducing bath:

Additive	Color of Stripped Goods
PVP	light blue.
quaternary	Do.
quaternary/methacrylic acid copolymer	faintly yellowish white.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. An aqueous composition comprising a solution in water of 0.01 to 1% of a reducing agent selected from the group consisting of hydrosulfites, aldehyde, sulfoxylates and sulfinic acids, a quaternary ammonium compound containing a hydrophobic substituent having at least 8 carbon atoms and having the Formula I:



where at least one of R, R⁰, R', and R'' is selected from the group consisting of aliphatic, aryl-aliphatic, and alicyclicaliphatic groups having at least 8 carbon atoms, and each of any other of the R, R⁰, R', and R'' radicals is selected individually from the group consisting of lower alkyl groups having 1 to 7 carbon atoms, allyl, methallyl,

benzyl, methylbenzyl, β-hydroxyethyl, γ-hydroxypropyl, phenoxyethyl, ethoxyethyl, phenoxyethoxyethyl, tetrahydrobenzyl, and hexahydrobenzyl, and A is an anion of non-oxidizing character, and a water-soluble polymeric acid having a molecular weight of at least 1,500 to 200,000, the concentration of the polymeric acid being about 0.01 to 0.04% and the concentration of the quaternary ammonium compound being about 0.01 to 0.06%.

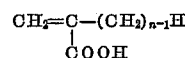
2. An aqueous composition comprising a solution in water of 0.01 to 1% of a reducing agent selected from the group consisting of hydrosulfites, aldehyde sulfoxylates, and sulfinic acids, a quaternary ammonium compound containing a hydrophobic substituent having at least 8 carbon atoms and having the Formula I as defined in claim 1, and a water-soluble polymeric acid having a molecular weight of at least 1,500 to 200,000 selected from the group consisting of polymers of an acid selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, aconitic acid, citraconic acid, maleic acid, and fumaric acid, the concentration of the quaternary ammonium compound being about 0.01 to 0.06% and the concentration of the polymeric acid being about 0.01 to 0.04%.

3. A composition as defined in claim 2 in which the polymer is a copolymer containing at least 10% by weight of at least one of the acids mentioned.

4. An aqueous composition comprising a solution in water of 0.01 to 1% of a reducing agent selected from the group consisting of hydrosulfites, aldehyde sulfoxylates, and sulfinic acids, a quaternary ammonium compound containing a hydrophobic substituent having at least 8 carbon atoms and having the Formula I as defined in claim 1, and a water-soluble polymer of acrylic acid having a molecular weight of at least 1,500 to 200,000, the concentration of the quaternary ammonium compound being about 0.01 to 0.06% and the concentration of the polymeric acid being about 0.01 to 0.04%.

5. An aqueous composition comprising a solution in water of 0.01 to 1% of a reducing agent selected from the group consisting of hydrosulfites, aldehyde sulfoxylates, and sulfinic acids, a quaternary ammonium compound containing a hydrophobic substituent having at least 8 carbon atoms and having the Formula I as defined in claim 1, and polyacrylic acid having a molecular weight of at least 1,500 to 200,000, the concentration of the quaternary ammonium compound being about 0.01 to 0.06% and the concentration of the polymeric acid being about 0.01 to 0.04%.

6. An aqueous composition comprising a solution in water of 0.01 to 1% of a reducing agent selected from the group consisting of hydrosulfites, aldehyde sulfoxylates, and sulfinic acids, 0.01 to 0.06% of a quaternary ammonium compound containing a hydrophobic substituent having at least 8 carbon atoms and having the structure of Formula I as defined in claim 1 and 0.01 to 0.04% of a copolymer of methacrylic acid with an ester of an alcohol having 1 to 4 carbon atoms with an acid of the formula



where n is an integer having a value of 1 to 2, having a molecular weight of at least 1,500 to 200,000.

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