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Morrill et al.

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[54] **DYE COMPOSITION AND METHOD OF DYEING**

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[52] **U.S. Cl.**..... **260/17.4 ST;** 106/214; 427/380; 427/390; 427/392

[51] **Int. Cl.²**..... **C08L 3/02**

[58] **Field of Search**..... 260/17.4 ST; 117/62.5; 427/389, 390, 392; 106/213, 214

[56] **References Cited**

UNITED STATES PATENTS

2,515,170	7/1950	Cassel et al.	260/15
2,533,635	12/1950	Seymour	260/17.4
2,565,358	8/1951	Douglas et al.	260/29.2
2,933,416	4/1960	Haakh et al.	260/17.4

FOREIGN PATENTS OR APPLICATIONS

1,211,149	11/1970	United Kingdom

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[57] **ABSTRACT**

A dye composition comprising a water-insoluble pigment, a cationic flocculating agent and a dispersant. A binder resin may also be present to assure good crockfastness.

17 Claims, No Drawings

DYE COMPOSITION AND METHOD OF DYEING

This invention relates to a method for dyeing and, in particular, to a method which is uniformly applicable to the dyeing of all natural and synthetic fibers. Still more particularly, it relates to such a method which uses pigments, rather than dyes, to impart a desired color to a fabric, i.e., pigment dyeing.

BACKGROUND OF THE INVENTION

The successful application of permanent color to a textile fabric is subject to many strict requirements.

In any method of dyeing, for example, it is essential that the dye color the fabric uniformly, and that it be fixed in position. The dyed fabric should also be light-fast, i.e., it should not fade upon prolonged exposure to light; it should be crock-fast, i.e., it should not rub off on abrasion either wet or dry; and it should be wash-fast, i.e., it should not lose its color upon repeated laundering. This latter may be accomplished by the use of a mordanting substance, such as tannic acid, with which the dye and the fiber are firmly bound; or the dye may itself be chemically reactive with the fabric; or the dye may simply be substantive to the fabric and be bound thereto by means of physical forces.

Various methods of dyeing are known. The padding process is perhaps the best known; typically, the fabric material is first saturated with the concentrated dye liquor, then passed between heavy squeeze rolls so as to squeeze out the excess liquor. This process may be repeated at least once; then the fabric, saturated with the dye liquor, is heated so as to dry it and, in the case of certain fibers, to fix the dye on the fabric. Various additional steps, e.g., reducing, oxidizing, rinsing, soaping, etc, may be employed depending upon the fabric being dyed, as well as the dye itself.

Quite apart from the above method, which in many cases is continuous and therefore only of industrial interest, the home-dyeing of fabrics generally involves merely stirring the article to be dyed in a hot bath containing the dye, rinsing the article, and drying it. This process is quite simple, and necessarily so, but it is also fraught with many difficulties because of its simplicity. For practical reasons, the dye must be applicable to all fabrics, and this is a very difficult requirement. To satisfy it, it has in the past been necessary to market a package which contains several types of dyes, each of which may be applicable to one or two types of fabrics. Thus, in this situation all but one of these types of dyes is superfluous and it is that one which in fact imparts the desired color to the article. Furthermore, some fabrics such as polyester or acrylics must be dyed under specific conditions which are not amenable to a home-dyeing operation; otherwise, the results are not entirely satisfactory. Obviously, this is not an efficient process.

The present invention relates to a method for dyeing fabrics which is particularly useful in the home-dyeing of garments or the like.

It is an object of the present invention to provide a dye composition which is uniformly applicable to all types of fabrics.

It is another object of the present invention to provide an improved pigment dyeing process.

SUMMARY OF THE INVENTION

These and other objects are accomplished by an aqueous dye composition having a pH of from about 1.0 to about 9.0 comprising in combination in (a) water-insoluble pigment, (b) a cationic flocculating agent and (c) an anionic, nonionic or zwitterionic dispersant. Such composition is effective to impart color to virtually any known fabric and, accordingly, represents a significant advance in the art. As a concentrate it is stable on storage for long periods of time. Further, it is especially adaptable to a home-dyeing operation.

The above dye composition comprises an aqueous dispersion of the named ingredients. It may be employed in any of the several well-known dye application processes, including particularly the simple dyeing process employed by the housewife in dyeing or re-dyeing fabric materials.

PIGMENT

The pigment is, as indicated, water insoluble. It may be organic or inorganic, the former being preferable because of a wider availability of desired shades. Toners, lakes, and extended pigments are contemplated for use in the process. The average particle size of the pigment is an important factor in the utility of the pigment.

The average particle size should be in the range of from about 0.01 to about 40 microns, preferably between 0.05 and 15 microns. This preferred particle size permits a more uniform color and good exhaustion of pigment from the dye bath. Also, "splotchiness" or uneven color on the fabric is avoided.

The pigment may be used in any of several available forms. It may be used as such, i.e., a 100% pigment powder. Alternatively, it may be used as a powdered mixture of pigment and a dispersant, so as to permit ready dispersion in the aqueous dye bath. Such mixtures may be prepared in a ball mill or the like, so as to insure intimate mixing of the pigment and dispersant. Still another form in which the pigment is useful is as an aqueous paste containing both the pigment and dispersant. This is the most usually available form and is preferred because it allows more convenient incorporation into the aqueous dye bath. Such pigment pastes normally contain 20–40% pigment and 15–30% dispersant.

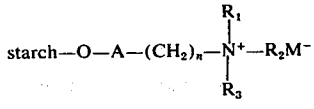
The availability of pigments is almost limitless. They include chiefly the oxides, sulfides, and sulfates of cobalt, chromium, aluminum, iron, zinc, cadmiun, manganese, and selenium; also, a carbon black; organic pigments include principally the phthalocyanine, anthraquinone, thioindigoid and indanthrene vat dyes; disperse dye pigments; stilbene and coumarin fluorescent pigments; and Hansa yellow. An indication of the pigments which are available for use in the invention herein is set out in Kirk-Othmer's "Encyclopedia of Chemical Technology," 2nd Ed., Interscience (1968), Vol. 15, pp. 495–604. See also the Colour Index, 3rd Ed., Society of Dyers and Colourists, Bradford, England and American Association of Textile Chemists and Colorists, Research Triangle Park, North Carolina (1971), Vol. 3, pp. 3267–90, wherein various pigments are identified in terms of a "Colour Index" (C.I.) number.

The concentration of pigment in these concentrates may be as low as 0.01 and range upward to about 10%. Generally, the pigment will be present in a range of

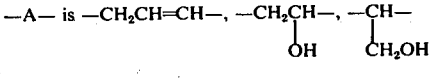
concentration of from about 0.1 to about 5.0%. In certain instances, it is desirable to incorporate two or more pigments into a particular concentrate so as to produce a desired color and, in those instances, the total amount of pigment present in the concentrate is within the above limits.

CATIONIC FLOCCULATING AGENT

The cationic flocculating agent is a positively charged material, generally polymeric, having an average molecular weight up to about 3 million. On the other hand, the molecular weight may be as low as about 200 although, preferably, its molecular weight is above about 2,000. Its degree of substitution (D.S.) preferably is 0.005 to about 0.5 and having the formula:



wherein

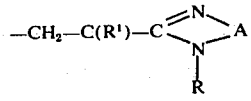


or $-CH_2-$; n is zero or 1; R_1 and R_2 are each alkyl having 1–22 carbon atoms, phenyl, lower alkyl phenyl, halophenyl or together form a morpholinyl, pyrrolidyl or piperidinyl ring, which ring may contain one or more methyl or ethyl groups; R_3 is hydrogen or lower alkyl; M is halogen, sulfate, phosphate or RCOO—, and R is hydrogen or lower alkyl. The term lower alkyl, as used herein, designates an alkyl group having less than 6 carbon atoms.

A preferred cationic flocculant is one conforming to the above structure, prepared by the reaction of a starch with a cationic reagent which in turn is prepared by the reaction of epichlorohydrin and trimethylamine; such a cationic starch product preferably has a D.S. of from about 0.02 to about 0.5. The term "starch" is used herein to denote modified, oxidyzed and dextrinized starches as well as thick boiling starch.

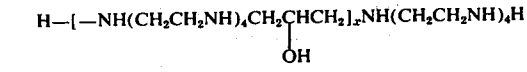
Other suitable cationic starch materials include those prepared by the reaction of starch with cationic reagents prepared in turn by the reaction of epichlorohydrin with trimethylamine; N,N-dimethyl-N-ethylamine; N-methyl-N,N-diethyl amine; dimethyl amine; trimethyl-n-butyl amine; N,N-dimethyl-N-butyl amine; N,N-dimethyl-N-phenyl amine; N,N-dimethyl-N-(4-chlorophenyl)-amine; N,N-dimethyl-N-(3-methyl phenyl) amine; piperidine; 4-methyl piperidine; and the like. Also, N,N-(2-hydroxy-3-chloropropyl) trimethyl ammonium chloride; N-(2-chloro-3-hydroxy propyl) triethyl ammonium bromide; N-(2-chloro-3-hydroxy propyl) trimethyl ammonium chloride; N-(2-chloro-3-hydroxy hexyl) tributyl ammonium iodide; N-(2-chloroethyl) dioctadecyl amine hydrochloride; N-(3-chloro propyl) didodecyl methyl ammonium chloride and the like. The prior art is replete with references to cationic reagents of the sort contemplated herein and illustrative examples of such cationic reagents and their methods of preparation are described in U.S. Pat. Nos. 2,813,093; 2,876,217; 2,917,506; 2,970,140; 2,995,513; 3,135,739; 3,320,118; 3,346,563 and 3,448,101. The disclosures of these patents are incorporated herein by reference.

Other suitable cationic flocculants include water-soluble linear polyamines such as "Primafloc-C-3," available from the Rohm & Haas Company. This polymer has a molecular weight within the range of from about 30,000 to about 80,000 and contains at least 15 mole percent of units of the formula:

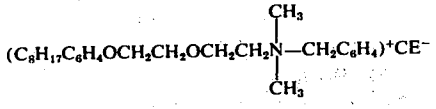


wherein A is a (C_2–C_3)-alkylene group having at least two carbon atoms extending in a chain between the adjoined N atoms and R and R^1 are each hydrogen or methyl. This and related polymers operable herein, as well as a method for their preparation are fully described in U.S. Pat. No. 3,288,707.

Also suitable are water-soluble polymers of tetraethylene pentamine and epichlorohydrin, commercially available from the Nalco Chemical Company under the trade names Nalco 600 and Nalcolite 605. These polymers have the formula:



where x is an integer consistent with the above molecular weight limitation, i.e., between about 2,000 and 3 million. Hyamine 1622 and Hyamine 10-X are suitable cationic flocculants. They are relatively low molecular weight quaternary chlorides conforming to the formula:



and the corresponding cresoxy compound. Another eminently suitable cationic flocculant is di-(hydrogenated tallow) dimethyl amine sulfate.

Other suitable cationic flocculants include copolymers of acrylamide and 2-methacryloxyethyl trimethyl ammonium methosulfate and other copolymers of this type disclosed in U.S. Pat. Nos. 3,336,269 and 3,336,270. Reten 210, marketed by Hercules Incorporated is such a copolymer.

The cationic flocculating agent should be present in the concentrate to the extent of from about 0.01 to about 10%. Preferably, this range is from about 0.1 to about 8%.

DISPERSANT

The concentrate must also contain a dispersant, since it is to be used in the preparation of a dye bath in which at least certain of the ingredients are insoluble and must therefore be maintained in uniform dispersion so as to be effective. Ordinarily, the pigment itself is supplied as a paste which contains not only the pigment but also a dispersing agent. In some instances, the dispersant supplied in pigment paste may be sufficient to serve the purposes of the dye bath and no additional dispersant need be added. In most instances, however,

it is desirable to add a dispersant so as to supplement the amounts of those which may be present with the pigment. Such dispersant preferably is a nonionic dispersant, although anionic and zwitterionic dispersants are also very useful for the purposes of this invention. Nonionic dispersants may be described as compounds produced by the condensation of alkylene (such as ethylene and propylene) oxide groups (hydrophilic in nature) with organic hydrophobic compounds, which may be aliphatic or alkylaromatic in nature. As those skilled in the art are well aware, the length of the hydrophilic or polyoxyalkylene radical required for condensation with any particular hydrophobic group can be readily adjusted to yield the water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

A well-known class of nonionic dispersants is available on the market under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule, of course, exhibits water insolubility. The molecular weight of this portion is of the order of 950 to 4,000. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole. Liquid products are obtained up to the point where polyoxyethylene content is about 50% of the weight of the condensation product.

Suitable nonionic dispersants include also the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having from about 6 to about 12 carbon atoms, either straight chain or branched chain, in the alkyl group, with ethylene oxide in amounts equal to 6–100 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane or nonane, for example.

Other suitable nonionic dispersants may be derived by the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. Here again, a series of compounds may be produced, depending upon the desired relative proportions of hydrophobic and hydrophilic elements. Satisfactory compounds, for example, are those having a molecular weight of from about 5,000 to about 11,000 and comprising from about 40% to about 80% of polyoxyethylene, resulting from the reaction of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000.

Further satisfactory nonionic dispersants include the condensation product of aliphatic alcohols having 8–18 carbon atoms, either straight chain or branched chain, with ethylene oxide, an example being a coconut alcohol/ethylene oxide condensate having 10–30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol having 10–14 carbon atoms.

Suitable anionic dispersants include water-soluble salts having in their molecular structure an alkyl group containing from about 8 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester radical. Such dispersants include the sodium, potassium, and triethanolamine alkyl sulfates, especially those derived by sulfation of higher alcohols produced by reduction of tallow or coconut oil glycerides; sodium or potassium alkyl benzene sulfonates, especially those of the types described in U.S. Pat. No. 2,477,383, in which the alkyl group contains from about 9 to about 15 carbon atoms, sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols obtained from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium salts of sulfuric acid esters of the reaction product of one mole of a higher alcohol (i.e., tallow or coconut oil alcohols) and about 3 moles of ethylene oxide; and the watersoluble salts of condensation products of fatty acids with sarcosine, e.g., triethanolamine N-acyl sarcosinate, the acyl radicals being derived from coconut oil fatty acids.

Conventional soaps are also operable anionic surfactants for the purposes of this invention. Suitable soaps include the water-soluble salts, e.g., sodium, potassium, and lower alkanolamine salts of fatty acids derived from coconut oil, soybean oil, caster oil or tallow or synthetically produced fatty acids. These are operable, of course, only in relatively soft water, i.e., water which contains small proportions of calcium and magnesium.

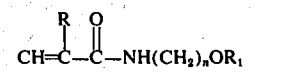
The zwitterionic dispersants contemplated herein include the substituted betaines, specifically those N-alkyl N,N-dimethyl ammonio acetates wherein the alkyl group contain 12-20 carbon atoms. Also included are those amphoteric dispersants available in the trade as "Deriphats," prepared by the reaction of long chain primary amines with an acrylic monomer, followed in certain instances by neutralization with sodium hydroxide or sodium carbonate.

The amount of dispersant in the dye concentrate ranges from about 0.01 to about 5%, preferably from about 0.1 to about 2%.

For purposes of crock-fastness it is highly desirable to incorporate a binder resin in the dye compositions of this invention. Suitable binder resins for this purpose are those polymers which contain N-alkylolamide groups or N-alkoxyalkyl amide groups in certain proportions. These groups provide cross-linking sites in the resin which are sufficiently reactive as to react at relatively low temperatures, i.e., between about 60°F and 250°F.

The dye compositions containing such binder compositions provide a dyed fabric which is notably resistant to crocking, i.e., loss of dye by rubbing or abrasion. Apparently the cross-linked polymer is effective to bind the dye tightly to the fabric so that it resists abrasive wear. The amount of such binder resin to be used in the concentrates of this invention ranges from about 0.1 to about 10%. The effectiveness of the resin is believed to reside in its ability to bind the pigment to the fabric; this is borne out by the observation that the crock-fastness of a dyed fabric is improved by the use of increasingly large amounts of resin, with respect to the amount of pigment, up to a point, after which no significant improvement is apparent. For the purposes of crock-fastness, the amount of binder resin should be at least about the same as the amount of pigment and, preferably, the ratio of binder resin to pigment should be at least about 2.5.

The N-alkylolamide and N-alkoxy-alkyl amide groups are provided by acrylic monomers having the structure



where R is hydrogen or an alkyl group having 1–4 carbon atoms, R_1 is hydrogen or an alkyl group having 1–8 carbon atoms, and *n* is an integer from 1 to 4. Preferred monomers of this type are those wherein R_1 is hydrogen and *n* is 1. N-methylol acrylamide and N-methylol methacrylamide are especially preferred. More than one such monomer may be used in preparing the binder resin.

The amount of N-alkylolamide or N-alkoxyalkyl monomer used in preparing the polymers herein is 0.1 to 5% by weight based on the weight of total monomer mixture.

Other monomers with which the above cross-linking monomer may be reacted to form the polymers of this invention included, in a preferred instance, other amide containing monomers, which are reactive with the N-alkolamide or N-alkoxyalkyl amide groups. These co-reactive monomers contain reactive hydrogen atoms in the amide groups and include, particularly, acrylamide and methacrylamide. When used to prepare the copolymers herein they should be used in an amount of from 0.5 to 25% by weight, based on the weight of total monomer mixture.

The remaining monomer content of these polymerization mixtures may include one or more of the following: acrylonitrile, styrene, vinyl toluene, vinyl acetate, lower alkyl esters of acrylic and methacrylic acids, vinyl chloride, vinylidene chloride; carboxylic monomers such as acrylic acid, methacrylic acid, and maleic anhydride, conjugated dienes such as butadiene, isoprene and piperylene; alpha olexins such as ethylene, propylene, isobutylene, butene-1, and 4-methyl pentene-1; alkyl vinyl ethers such as methyl vinyl ether, isobutyl vinyl ether and n-butyl vinyl ether; acrylonitrile and methacrylonitrile, etc. These other polymerizable comonomers may be present in the polymerization mixture in an amount up to 99% by weight; generally they are used in an amount between about 70% and about 98% by weight. More than one of these additional copolymerizable comonomers may be used in preparing a particular binder resin.

A preferred copolymer is one which contains acrylate ester groups, e.g., methyl acrylate, ethyl acrylate and 2-ethylhexyl acrylate and methyl methacrylate.

Another preferred copolymer is one which contains carboxylic groups, in which case one of the monomers employed is a carboxylic vinyl monomer which contains 3–6 carbon atoms. Illustrative examples of such carboxylic monomers include acrylic acid, methacrylic acid, ethacrylic acid, alpha-chloracrylic acid, alpha-cyanoacrylic acid, crotonic acid, beta-acryloxy propylonic acid, hydrosorbic acid, sorbic acid, alpha-chlorosorbic acid, hydromuconic acid, muconic acid, aconitic acid and the like.

The amount of carboxylic monomer which may be used to prepare suitable copolymers ranges up to about 25% by weight based on the weight of total monomers. Preferably, it is less than about 5%. Mixtures of two or more of the above-mentioned carboxylic acid monomers may be employed to prepare the desired carboxylic polymer.

Typical polymers which are useful in the invention herein are disclosed in U.S. Pat. Nos. 3,157,562; 3,682,871; and 3,702,785. There are many commercially available self-cross-linking polymers including several marketed under the trade name Rhoplex. These include Rhoplex HA8, Rhoplex HA4 and others. Also available are such self-cross-linking carboxylic polymers as Geon 460×1, Geon 460×2 and Hycar 2600×189.

The dye bath herein, as applied to home use, may be marketed in the form of concentrates. The pH of such concentrates may range from as low as about 1.0 up to about 7.0 Concentrates having a pH outside this range are not suitably stable. Preferably, the pH is within the range from about 3.5 to about 5.5 The dye baths prepared from such concentrates are more effective if they are slightly acid, although a range of from about 1.0 to about 9.0 is suitable. Glass fiber fabrics can be dyed effectively at the very low pH's but other fabrics are quite vulnerable to decomposition under these conditions. Preferably the pH of the dye bath is within the range of from about 4.0 to about 7.0. The dye bath itself is quite stable, i.e., it continues to be operative even after standing for long periods of time.

The concentrations of ingredients in the dye baths herein are as follows:

	Broad	Preferred
Pigment	0.00006–0.1%	0.0006–0.05%
Cationic Flocculant	0.00006–0.1%	0.0006–0.05%
Dispersant	0.00006–0.03%	0.0006–0.024%
Binder Resin	0.0006–0.25%	

Other ingredients may also be used in the bath; these include soluble, polyvalent metal salts which are effective to increase the efficiency of operation of the dye baths, i.e., a deeper, more intense color is developed in the dyed fabric. These polyvalent metal salts include principally the calcium, magnesium and aluminum chlorides, bromides, sulfates and nitrates. They may be used in concentrations ranging from about 0.01 to about 1.0%, based on the dye bath concentrate.

Usually, it is necessary to add a small proportion of an acid or base so as to adjust the pH of the dye concentrate. As noted earlier herein, the pH should be within the range of from about 1.0 to about 7.0. For most concentrates, it is desirable to add a small amount of acid to maintain the pH well within this range. Suitable acids for this purpose include formic acid, acetic acid, glycolic acid, citric acid, malic acid, hydrochloric acid, sulfuric acid, phosphoric acid, or the like.

Additional optional ingredients include collodial stabilizers such as acid modified and oxidized starches; preservatives such as phenol, formaldehyde or methyl paraben, to prevent bacterial degradation of the product during shelf storage; perfumes to impart a pleasing odor to the concentrate; and anti-foam additives.

The dye bath composition of this invention may be used both in commercial processes and in home dyeing with equal facility. Its principal advantages however are associated with the latter because a single concentrate affords efficient dyeing of all types of fabric materials.

In a typical home dyeing process, the fabric should be clean and without stains; this may be accomplished either by laundering or dry cleaning. Although the dry fabric may be placed directly in the dye bath, preferably, it should first be wetted. The volume of the dye bath should be sufficient to cover the fabric completely; the concentration of dye should be such, for example, as is afforded by dilution of 2–16 fluid ounces of concentrates, as represented by the examples which follow, to about 15 gallons of water. The temperature of the dye bath may range from about 60°F to about 212°F.

The fabric is agitated in the dye bath for a period of time ranging from about 5 minutes to about 60 minutes, then rinsed and dried. It may be dried simply by air drying, or in an automatic dryer, or it may be ironed dry.

For test purposes it is desirable to dye a so-called "multifiber" fabric, i.e., a 3 × 6 cm. sample comprising swatches of wool, Orlon (polyacrylonitrite), Dacron (polyester), nylon, cotton and acetate rayon sewn together. The use of such a fabric permits one to ascertain the uniform application of a particular dye bath to those different types of fabrics with but one dyeing operation.

EXAMPLE 1 (BLUE)

	Per Cent
C.I. Pigment Blue 15 (Paste, 38% solids)	1.260
Polyoxyethylene (30) nonyl phenol	0.294
Geon 460×2 (50% solids)	5.700
Cationic Starch (D.S. 0.020)*	1.100
Acetic acid, glacial	0.650
Water	90.996

EXAMPLE 2 (CORAL)

	Per Cent
C.I. Pigment Red 5 (Paste, 37% solids)	2.950
C.I. Pigment Yellow 74 (Paste, 41% total solids)	0.840
Polyoxyethylene (30) nonyl phenol	0.588
Geon 460×2 (50% solids)	11.410
Cationic Starch (D.S. 0.038)*	1.160
C.I. Disperse Red 17 (no dispersant)	0.020
C.I. Disperse Red 1 (no dispersant)	0.020
Acetic acid, glacial	0.150
Antifoam	0.010
Methylparaben	0.100
Water	82.752

EXAMPLE 3 (BLUE)

	Per Cent
C.I. Pigment Blue 15 (Paste, 38% solids)	3.800
Polyoxyethylene (30) nonyl phenol	0.588
Hycar 2600×189 (51% solids)	11.410
Cationic Starch (D.S. 0.034)*	2.890
Acetic acid, glacial	1.800
Water	79.512

EXAMPLE 4 (BLUE)

	Per Cent
C.I. Pigment Blue 15 (Paste, 38% solids)	3.800
Polyoxyethylene (30) nonyl phenol	0.588
Hycar 2600×189 (51% solids)	11.410
Reten 210	0.570
Acetic acid, glacial	1.800
Water	81.832

EXAMPLE 5 (RED)

	Per Cent
C.I. Pigment Red 5 (Paste, 37% solids)	2.432
Sodium lauryl sulfate	0.110
Copolymer of 40% vinyl chloride, 30% ethyl acrylate, 3% acrylonitrile, 24% vinyl acetate, 1.2% acrylic acid, and 1.8% N-methylol acrylamide (44% solids)	4.800
Cationic Starch (D.S. 0.02)*	1.920
Citric acid	0.150
Water	90.588

EXAMPLE 6 (BLUE)

	Per Cent
C.I. Pigment Blue 15 (Paste, 38% solids)	3.800
Polyoxyethylene (30) nonyl phenol	0.588
Hycar 2600×189 (51% solids)	11.410
Di-isobutyl phenoxyethoxyl ethyl dimethylbenzyl ammonium chloride	5.710
Acetic acid, glacial	1.800
Water	76.692

EXAMPLE 7 (BLUE)

	Per Cent
C.I. Pigment Blue 15 (Paste, 38% solids)	3.800
Polyoxyethylene (30) nonyl phenol	0.588
Cationic Starch (D.S. 0.034)*	1.040
Rhoplex HA-8 (45.5% solids)	11.410
Acetic acid, glacial	0.950
Water	82.212

EXAMPLE 8 (YELLOW)

	Per Cent
C.I. Pigment Yellow 74 (Paste, 41% solids)	2.210
Polyoxyethylene 15 coconut alcohol	0.610
Copolymer of 40% vinyl chloride, 56% n-butyl acrylate, 2% acrylic acid and 2%, N-methylol acrylamide (40% solids)	6.420
Cationic Starch (D.S. 0.22)**	1.000
Acetic acid	0.108
Water	89.047

EXAMPLE 9 (ROYAL BLUE)

	Per Cent
C.I. Pigment Blue 15 (Paste, 38% solids)	7.600
Polyoxyethylene (30) nonyl phenol	0.588
Geon 460×2 (50% solids)	11.410
Cationic Starch (D.S. 0.020)*	2.240
C.I. Disperse Blue 112 (no dispersant)	0.170
Acetic acid, glacial	2.000
Water	75.992

EXAMPLE 10 (ROYAL BLUE)

	Per Cent
C.I. Pigment Blue 15 (Paste, 38% solids)	7.600
Polyoxyethylene (30) nonyl phenol	0.588
Geon 460×2 (50% solids)	11.410
Cationic Starch (D.S. 0.02)*	2.240
Acetic acid, glacial	2.000
Water	76.162

EXAMPLE 11 (YELLOW)

	Per Cent
C.I. Pigment Yellow 74 (Paste, 41% solids)	1.880
C.I. Pigment Red 5 (Paste, 37% total solids)	0.020
Polyoxyethylene (30) nonyl phenol	0.294
Geon 460×2 (50% solids)	5.700
Cationic Starch (D.S. 0.038)*	0.680
C.I. Disperse Yellow 3 (no dispersant)	0.040
Acetic acid, glacial	0.150
Antifoam	0.010
Methylparaben	0.100
Water	91.126

EXAMPLE 12 (ROSE PINK)

	Per Cent
C.I. Pigment Red 5 (Paste, 37% solids)	1.270
Polyoxyethylene (30) nonyl phenol	0.189
Geon 460×2 (50% solids)	3.800
Cationic Starch (D.S. 0.020)*	0.630
C.I. Disperse Red 137 (no dispersant)	0.020
Acetic acid, glacial	0.060
Antifoam	0.010
Methylparaben	0.100
Water	93.921

EXAMPLE 13 (BLUE)

	Per Cent
C.I. Pigment Blue 15 (Paste, 38% solids)	3.800
Polyoxyethylene (30) nonyl phenol	0.588
Stearyl betaine (50% in water)	2.640
Geon 460×2 (50% solids)	11.410
Acetic acid, glacial	6.050
Water	75.512

*Prepared by the reaction of starch with a cationic reagent which is prepared in turn by the reaction of equal moler proportions of epichlorohydrin and trimethyl amine.

**Prepared by the reaction of starch with 2-chloroethyl, dimethyl amine hydrochloride.

The pigment content of the above pigment pastes is as follows:

C.I. Pigment Blue 15	20%
C.I. Pigment Red 5	21%
C.I. Pigment Yellow 74	32%

Illustrative examples of the process of dyeing fabric materials with dye bath prepared from the above concentrates are as follows:

EXAMPLE 14

A dye bath is prepared by adding 3.7 ml. of the concentrate of Example 12 (rose pink) to 1 l. of water at 140°F. A 7 × 12 inch swatch of white polyester fabric, previously washed and rinsed, and a multifiber fabric as above is added. The fabrics are agitated in the bath for 20 minutes, then removed, rinsed in cool water, air-dried and ironed at a low temperature, i.e., at the "synthetic fabrics" setting. The polyester swatch had an even, rose pink color which is colorfast for more than 80 hours in the Fade-O-Meter, is colorfast on washing with detergent in hot water, is colorfast to dry cleaning solvents such as naphtha and perchlorethylene, and is colorfast to rubbing with a white cloth. The multifiber test cloth is quite uniformly colored to a very acceptable shade of rose pink.

EXAMPLE 15

A dye bath is prepared by adding 2 ounces of the concentrate of Example 1 (blue) to 15 gallons of water at 80°F in an automatic washing machine. A 1-ounce swatch of fiberglass fabric, a 4-ounce swatch of cotton terry towel, and a 2-ounce swatch of cotton fabric, all previously washed and rinsed, are added damp to the dye bath and agitated for 24 minutes, then rinsed for 3 minutes in cool water, and spun damp dry. The swatches are dried in an electric dryer. Each swatch is colored a uniform blue which is colorfast to light for 80 hours in the Fade-O-Meter, is colorfast to laundering with detergent in hot water, is colorfast to the above dry cleaning solvents and is colorfast to rubbing with a white cloth.

EXAMPLE 16

A dye bath is prepared by adding two ounces of the concentrate of Example 10 to 2.5 gallons of water at 77°F. A beige wool sweater weighing 9 ounces and wet with water is added to the dye bath and stirred for 30 minutes. The sweater is removed, rinsed thoroughly in cool water and air-dried. Its uniform green color is colorfast to light for 40 hours in the Fade-O-Meter, colorfast to dry cleaning solvents, colorfast to cool water wash with a mild detergent and colorfast to rubbing with a white cloth.

EXAMPLE 17

A dye bath is prepared by adding 4 ounces of the concentrate (yellow) of Example 11 to 2 gallons of water at 180°F. A white shirt (65% dacron and 35% cotton) weighing 6 ounces is wet with water, then added to the dye bath and stirred for 15 minutes. The shirt, now yellow, is rinsed in cool water, squeezed to remove excess water and dried in an electric dryer. The yellow color is fast to light for 60 hours in the Fade-O-Meter, fast to dry cleaning solvents, fast to laundering in an aqueous detergent solution and fast to rubbing with a white cloth.

EXAMPLE 18

A dye bath is prepared by adding 3.7 ml. of the concentrate of Example 4 (blue) to 1 l. of water at 140°F in a Terg-O-Tometer. A 7 × 12 inch swatch of white polyester fabric, previously wetted and rinsed, and a pre-wetted multi-fiber as above are added. These fabrics are agitated in the bath for 20 minutes, then rinsed in cold water, air-dried, and ironed with a hand iron set at a low temperature, i.e., at the synthetic fabrics setting. The polyester swatch has a uniform, medium blue color, which is color-fast for more than 80 hours in the Fade-O-Meter, is color-fast upon washing with detergent in hot water, is color-fast to dry cleaning solvents such as naphtha and perchchlorethylene, and is color-fast to rubbing with a white cloth. The multi-fibered test cloth is uniformly blue on all six fibers.

EXAMPLE 19

The procedure of Example 18 is followed, using the concentrate of Example 6 instead of that of Example 4. The results are the same as those observed in Example 18.

EXAMPLE 20

The procedure of Example 18 is followed, except that the concentrate of Example 13 is used instead of that of Example 4. The results are the same as those observed in Example 18.

All parts and percentages herein are by weight, unless otherwise expressly stated.

What is claimed is:

1. An aqueous dye composition having a pH of from about 1.0 to about 9.0 comprising in combination (a) about 0.01–10% of a water insoluble pigment, (b) about 0.01–10% of a cationic starch and (c) about 0.01–5% of a nonionic, anionic or zwitterionic dispersant.

2. The dye composition of claim **1** wherein the water-insoluble pigment is an organic pigment.

3. The dye composition of claim **1** wherein the water-insoluble pigment has a particle size of from about 0.01 to about 40 microns.

4. The dye composition of claim **1** wherein the cationic starch has a degree of substitution of from about 0.005 to about 0.5.

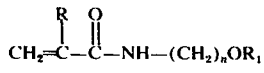
5. An aqueous resinous dye composition having a pH of from about 1.0 to about 9.0 comprising

a. a water insoluble pigment in an amount of about 0.01–10%,

b. a cationic starch in an amount of about 0.01–10%,

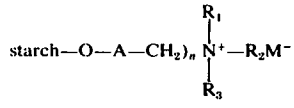
c. a nonionic, anionic or zwitterionic dispersant in an amount of about 0.01–5%, and

d. a polymer which is self-cross-linking at low temperatures in an amount of about 0.1–10%, said polymer being obtained from a monomer mixture containing about 0.1–3.0% of an N-alkylol or N-alkoxyalkyl amide of the formula:

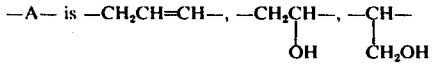


wherein R is hydrogen or an alkyl group having 1–4 carbon atoms, R_1 is hydrogen or an alkyl group having 1–8 carbon atoms and *n* is an integer from 1 to 4.

6. The resinous dye composition of claim **5** wherein the cationic starch conforms to the formula:



wherein



or $-CH_2-$; *n* is zero or 1; R_1 and R_2 are each alkyl having 1–22 carbon atoms, phenyl, lower alkyl phenyl, halophenyl or together form a morpholinyl, pyrrolidyl or piperidinyl ring, which ring may contain one or more methyl or ethyl groups; R_3 is hydrogen or lower alkyl; M is halogen, sulfate, phosphate, or RCOO—, and R is hydrogen or lower alkyl.

7. The resinous dye composition of claim **5** wherein the cationic starch is prepared by the reaction of starch with a cationic reagent which is in turn prepared by the reaction of trimethyl amine with epichlorohydrin.

8. The resinous dye composition of claim **7** wherein the starch is a modified starch.

9. The resinous dye composition of claim **7** wherein the starch is a thick boiling starch.

10. The resinous dye composition of claim **5** wherein the polymer is a copolymer of an acrylate ester.

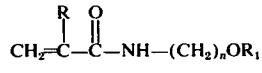
11. The resinous dye composition of claim **10** wherein the acrylate ester is an alkyl acrylate.

12. A dye concentrate having a pH of from about 1.0 to about 7.0 comprising an aqueous dispersion of (a) from about 0.01 to about 10% of a water insoluble pigment, (b) from about 0.01 to about 10% of a cationic starch, and (c) from about 0.01 to about 5% of a nonionic, anionic or zwitterionic dispersant.

13. The dye concentrate of claim **12** wherein the cationic starch has a D.S. of from about 0.005 to about 0.5.

14. The dye composition of claim **12** wherein the cationic starch is prepared by the reaction of starch with a cationic reagent which in turn is prepared by the reaction of epichlorohydrin and trimethylamine.

15. The dye concentrate of claim **12** is characterized further in that it contains from about 0.1 to about 10% of a binder resin which is self-cross linking at low temperatures, said binder resin being a copolymer which is prepared from a monomer mixture containing from about 0.1 to about 3.0% of an N-alkylol or N-alkoxyalkyl amide of the formula:



wherein R is hydrogen or an alkyl radical having 1–4 carbon atoms, R_1 is hydrogen or an alkyl radical having 1–8 carbon atoms, and n is an integer from 1 to 4.

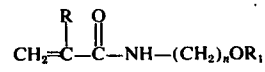
16. A dye bath having a pH of from about 1.0 to about 9.0 comprising an aqueous dispersion of

a. from about 0.00006 to about 0.1% of a water insoluble pigment,

b. from about 0.00006 to about 0.1% of a cationic flocculent,

c. from about 0.00006 to about 0.03% of a nonionic, anionic or zwitterionic dispersant and

d. from about 0.00006 to about 0.25% of a binder resin, said binder resin being obtained from a monomer mixture containing about 0.1-3.0% of an N-alkyl or N-alkoxyalkyl amide of the formula:



wherein R is a hydrogen or an alkyl group having 1–4 carbon atoms, R_1 is hydrogen or an alkyl group having 1–8 carbon atoms and *n* is an integer from 1 to 4.

17. The dye bath of claim **16** wherein the cationic flocculant is a cationic starch.

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