United States Patent Office 3,002,939 Patented Oct. 3, 1961

3,002,939 COMPOSITIONS FOR PRINTING AND DYEING TEXTILES

Leslie L. Balassa, Madison, N.J., assignor to J. R. Geigy, S.A., Basel, Switzerland, a corporation of Switzerland

No Drawing. Filed Mar. 6, 1957, Ser. No. 644,195
11 Claims. (Cl. 260—6)

This invention relates to improved pigmented oil-in-water emulsion textile decorating compositions yielding improved resistance to abrasive laundering and to light, and to heat. The invention may be used to produce decorated pigment printed or pigment pad-dyed textiles having improved resistance to wet abrasion which is particularly characterized by the type encountered in severe hand laundering as on a washboard or as with other appliances which cause severe abrasion during washing or laundering operations.

Conventional pigmented oil-in-water textile printing emulsions yield color prints which, when properly ultimately used with conventional textile printing plant equipment, sometimes withstand repeated laundering in washing machines involving generally agitation, but do not withstand more severe types of laundering, such as using a washboard and/or scrubbing with stiff-bristled brushes or rubbing vigorously between the hands in the presence of detergents in the wash liquor. Previously improved pigmented oil-in-water emulsions which were developed to overcome the prior deficiency with respect to vigorous abrasion have been found to be deficient with respect to resistance to light and/or heat. The normal cycle of life of a washable garment involves wearing, followed by vigorous washing, followed by drying on a clothesline in the sunlight. Therefore, resistance to successive launderings interspersed with exposures to light, is a property to be greatly desired in the printed fabric.

The present invention exhibits improved characteristics over prior types of pigmented oil-in-water textile printing emulsions in that both resistance to light and resistance to strong or violent abrasion are developed and retained in textiles printed with the product of this invention with particular reference to the binder.

It has been found that under extreme or severe light conditions, textiles printed with the prior compositions exhibited a failure in light resistance within 20 to 30 hours, or less, in many instances. In other words, after 20 to 30 hours, or less, the pigment binder had, due to its lack of resistance to light, deteriorated even though the pigments themselves exhibited well over 100 hours light resistance.

The textile color compositions of the present invention maintain the dispersion of the pigments in combination with surface active agents and protective colloids, maintain the viscosity of the print pastes at a workable level for printing textiles, and provide a bond for the pigment particles to the textile substrate, while imparting desirable properties to the printed textile as to light-resistance and resistance to wet abrasion.

The compositions of the present invention utilize a pigment, a binder, and a carrier emulsion.

When printing textiles and other fibrous materials, the printing compositions should meet certain requirements with regard to performance, including the following: All three components of the print paste (i.e. pigment dispersion, binder and carrier emulsion) should be readily miscible by manual mixing devices or by high speed mechanical mixers without breaking the emulsion. The print paste should have a sufficiently high viscosity to be suitable for application by roller printing or screen printing. The print paste viscosity and the stability of the emulsion as well as the stability of the dispersion of the binder copolymer and of the pigments should be maintained under the conditions of high mechanical shear and violent agitation encountered during roller printing. The print pastes furthermore must be stable when exposed in a thin film to shear and partial loss of solvents and water such as occurs on screen printing. The pastes must uniformly and completely fill the cavities of the engraved rollers and readily pass through the interstices of printing screens. The print pastes also have to be readily and completely released from the engravings. The pastes have to form sharp, clear outlines without following the capillary forces of the fibrous substrate. The print paste has to lubricate the print roller and be cleaned off completely by the doctor blade without showing signs of "tarnish" which then would cause "facing" on the fabric. The print paste must not form gummy deposit behind the doctor blade which would cause interruptions in printing because of "snaps" or "streaks."

The print deposited on the substrate such as a textile fabric should dry rapidly under customary drying conditions; and the dried prints when folded into boxes or rolled up should not "mark off" on the unprinted or other parts of the fabric. The print is usually set, i.e. insolubilized, when heat treated at or below 300° F., e.g. for 3 to 10 minutes. The properly heat-set prints must be fast to laundering, scrubbing, dry cleaning as well as to cyclic aging; i.e. pass several cycles of alternate exposure to natural or artificial sunlight and abrasive laundering. The fastness to alternate light exposure followed by abrasive washing (AATCC–3A Test) is an extremely severe requirement especially if it is carried beyond 100 standard fading hours, in the Fade-Ometer testing machine. This requirement which was not met by prior art compositions, is met by the compositions of this invention.

Certain prior art binder compositions, both standing alone and in pigmented emulsions, exhibited degradation as by yellowing, embrittling, loss of adhesion by deposited film to the substrate, loss of adhesion between the pigment and the binder film, crocking and lowered resistance to washing and scrubbing. Certain elastomers used in prior binder compositions showed considerable resistance to sunlight when exposed in unpigmented clear films. Some of the same elastomers, in identical pigmented binder compositions, surprisingly exhibited relatively rapid degradation as to light-fastness in the presence of the pigments. The present invention overcomes these prior difficulties and exhibit a high degree of light-fastness upon exposure to sunlight for many months or to Fade-Ometer tests in excess of 120 hours.

The binder components of the present invention, preferably comprise a particular combination in aqueous dispersion or emulsion of a selected type of aminoaldehyde resin and of an acrylic interpolymer, both as hereinafter described. The interpolymer is preferably in latex form made from a monomer mixture comprising preferably from 30 to 80 parts of acrylonitrile, from 2 to 15 parts of an alpha-olefinic monocarboxylic acid selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, phenyl acrylic acid and crotonic acid, and from 15 to 65 parts of an ester of an alpha-olefinic monocarboxylic acid of the above group with a saturated aliphatic monohydric alcohol of 1 to 8 carbon atoms, for a total of 100 parts by weight. Preferred monomers are acrylonitrile, methacrylic acid, and butyl acrylate. While the foregoing range is suitable for the present invention, the preferred range is 30 to 50 parts of acrylonitrile. The interpolymers useful in the present invention are described in British Patent No. 761,928 and a preferred acrylic interpolymer latex is that described in Example 4 of that patent.

The binder composition also contains a suitable amino-aldehyde resin which in combination with the acrylic interpolymer is capable of forming a water-in-

soluble film which is also insoluble in those solvents customarily used in dry-cleaning textile fabrics, thereby to achieve dry-cleaning resistance together with increased scrubbing resistance in the finished film. The preferred resins of this type are solvent-soluble butylated condensation products of urea and formaldehyde or of melamine and formaldehyde. These resins are dissolved in organic solvent and are emulsified in water with the aid of an emulsifier and of protective colloids. The organic solvent-soluble resins are dissolved in water-immiscible solvents and emulsified in water with the addition of surface active agents and protective colloids before incorporating them into the composition containing the acrylic interpolymer latex referred to herein. Solvent-soluble resins of this type are preferable over the corresponding water-soluble amino-aldehyde resins because the latter render the printing compositions relatively unstable and adversely affect the viscosity of the printing compositions, thus making many normal pigments unduly susceptible to flocculation and causing loss of tinctorial strength. Furthermore, the solvent-soluble, substantially water-insoluble, resins maintain the requisite shear-stability, tub-stability and resistance to freeze-thaw cycles. Aminoaldehyde resins useful in this invention are:

Manufacturer	Trade Name	Solids	Solvent
Rohm & Hass Co.	Uformite F210 (butylated urea-formaldehyde resin).	50	Xylol-Butanol.
	Uformite F226 (coprylated and butylated urea-formaldehyde resin).	50	Capryl-Alcohol-Butanol.
	Uformite F240N (butylated urea-formaldehyde resin).	60	High Flash Butanol.
Reichhold Chemicals Inc.	Beckamine 3520 (butylated urea-formaldehyde resin).	50	Do.
American Cyanamid Co.	Beetle 230-8 (butylated urea-formaldehyde resin).	50	Do.
	Melmac 245-8 (butyl modified melamine-formaldehyde resin).	50	Do.
Monsanto Chemical Co.	Resimene 877 (butylated melamine-formaldehyde resin).	50	Butanol-Mineral Spirits.
	Resimene 878 (butylated malamine formaldehyde resin).	50	Butanol-Butyl Cellosolve.
	Resimene 883 (butylated melamine formaldehyde resin).	60	Butyl Cellosolve-Mineral Spirits.
Allied Chemical & Dye Corporation.	Plaskon 3382 (butylated melamine resin).	55	Xylol-Butanol.

The organic solvents or liquids which are used in accordance with this invention are substantially water-immiscible whether they serve as a solvent for the organic-solvent-soluble resin or whether they be used in the carrier emulsion. These organic liquids are volatile and substantially water-insoluble: e.g., they are less than 3% soluble in water by weight. The organic liquid imparts to the carrier emulsion and to the printing paste desirable structural characteristics which enhance the color value and hand of the final print. Improvement in hand is believed to be achieved by the evaporation of the solvent which interrupts the continuity of the film. They are preferably petroleum hydrocarbons, such as petroleum naphthas, mineral spirits or others. Other such liquids, such as aromatic hydrocarbons, like toluol, xylol, high flash naphtha, octyl acetate or terpene hydrocarbons such as turpentine, may also be used. Such liquids with Kauri-Butanol values of between 30 and 98½, have been found entirely satisfactory. The printing properties, and the color value of the print pastes are affected to some degree by the rate of evaporation of the solvents used. Low boiling solvents, having low flash point, may be used but they present a fire hazard. Medium boiling solvents having a flash point of over 70° F. are preferred in continuous printing operation. High boiling solvents such as kerosene or pine oil may be used; however, due to their slow rate of evaporation they require special handling.

When kerosene is used in print paste compositions of this invention, it may remain in the print even after drying and heat setting, and may somewhat retard the setting of some resins. The residual odor of kerosene is also sometimes objectionable but may be removed by prolonged heating with good ventilation or by washing.

Aliphatic hydrocarbons in the following ranges are useful:

Spec. grav. at 60° F	0.6900 to 0.8100
Flash point (tag closed cup)° F	below 0 to 125
Initial boiling point° F	150 to 350
End point° F	150 to 462
K-B value (ASTM D 1133—50 T)	30 to 50

Aromatic hydrocarbons in the following ranges are useful:

Spec. grav. at 60° F	0.8650 to 0.9250
Flash point (tag closed cup)° F	40 to 160
Initial boiling point° F	176 to 370
End point° F	176 to 550
K-B value (ASTM D 1133—50 T)	80 to 110

Solvent fractions having at least 80° F. flash point are preferred.

The preferred protective colloids as used in this invention are methyl-cellulose, ranging from low to high viscosity grades (15 cps. to 7000 cps.) and casein and combinations thereof. Other protective colloids which may be used are: egg albumin, blood albumin, gelatin, bone glue, zein, gluten, alkali metal or ammonium salts of polyacrylic acids, carboxymethyl cellulose, pre-gelatinized starch, carboxymethyl starch, hydroxyethyl cellulose, alkali-metal and ammonium salts of alginic acids, water-soluble salts of maleic adduct of styrene, gum tragacanth, carragheen moss, dextrin, starch, locust bean gum, hydroxypropyl starch, guar gum, polyvinyl pyrrolidone and polyvinyl alcohol.

The surface active agents, i.e., emulsifiers, wetting agents and dispersing agents used in practicing this invention serve to disperse the pigments as well as the polyacrylic latices and the thermo-setting resins. They also serve to emulsify and to maintain the emulsion of the water-immiscible solvents.

The following surface active agents are representative members of the group which were found suitable for use in the preparations within the scope of this invention:

The ammonium, morpholine, ethanolamine (mono-, di-, or tri-), or alkali metal salts of the following fatty acids: oleic acid, stearic acid, lauric acid, undecylenic acid and palmitic acid; in general, fatty acids with a straight or branched carbon chain length of 10 to 22 carbon atoms;

Hydroxy fatty acids with one or more hydroxyl groups in the chain, such as alpha hydroxy stearic acid, dihydroxy stearic acid and the fatty acids derived from castor oil;

Unsaturated fatty acids with one double bond such as oleic; with multiple double bonds such as the fatty acids derived from linseed oil, soya bean oil and fish oil;

Ammonium or alkali metal salts of mono esters formed from sulfuric acid and fatty alcohols having a carbon chain length of 8 to 22 carbon atoms such as prepared by the reduction of the carboxyl groups of the fatty acids named above; the preferred of these are lauryl-, cetyl-, stearyl-, and oleyl-sulfuric acids;

Ammonium or alkali metal salts of benzene, or a

naphthalene-sulphonic acid with one or more aliphatic chains on the aromatic ring and their condensation products; of these compounds, the preferred ones are alkyl-benzene sulphonic acids and alkyl-naphthalene-sulphonic acids or their formaldehyde condensation products;

Non-ionic agents; polyoxyethylene derivatives of fatty acids, of fatty alcohols, and of substituted phenols; examples of these products are ethylene oxide condensates of nonylphenol, which are variously known by the trade names of Igepals;

Non-ionic or anionic surface active agents are preferred, but it is to be understood that in a cationic emulsion system, a cationic surface active agent may be employed under appropriate operating conditions.

The carrier emulsions used in the printing compositions of this invention are designed to maintain printing viscosity, while at the same time maintaining the dispersion of the pigments and of the resin binder. These carrier emulsions in the printing of textiles also supply additional binder composition in some instances to replace or augment the binder lost to the substrates through absorption. The carrier emulsion also has an effect in controlling the hand of the print by breaking up the continuity of deposited film.

Pigments suitable for use in printing with compositions of this invention are discrete particles of solid colored materials which are substantially insoluble in water, mild alkalis, hydrocarbon solvents, as well as in the solvents used customarily in dry cleaning textiles. Some of these pigments are inorganic materials, but the majority are organic compounds, mostly insolubilized dyestuffs, metal complexes and the like. The preferred pigments have high tinting power. Some of the useful pigments for this invention are: (carbon black being herein defined as an organic pigment)

Carbon blacks	Pigment Green B.
Iron oxides	Benzidine Orange.
Titanium dioxides	Molybdate Orange.
Zinc oxides	Red ITR/AS–ITR coupling.
Chrome yellow	Rhodamine Toner Y.
Phthalocyanine blue	Red PNOA/AS–BS coupling (naphthol).
Chlorinated phthalocyanine blue	Red PNOT/AS–D coupling (naphthol).
Indanthrene blue CE	Scarlet G Salt/ASD coupling (naphthol).
Dianisidine blue	Scarlet PNOT/AS coupling (naphthol).
Ultramarine blue	Indanthrene Red Violet RRN.
Metallized azo brown	Indomaroon (Harmon).
Indanthrene Brown RRD	Indanthrene Brilliant Violet RR.
Phthalocyanine green	Benzidine Yellow.
Aniline black pigment	Lithosol Fast Yellow 3GD.

The pigments are usually employed in aqueous dispersion. The dispersions are prepared, preferably, by treating the dry pigment or the pigment presscake with suitable surface active agents and protective colloids, to obtain the desired dispersion and paste characteristics. Coarse pigments are usually ground in suitable mills, such as pebble mills or roller mills, in the presence of surface active agents and protective colloids to obtain the desired particle size and dispersion. The pigment dispersions require substantial amounts of surface active agents and protective colloids to be present for proper use in the compositions of this invention without flocculation of the pigments or premature coagulation of the dispersed solids.

Parts are by weight unless otherwise stated:

EXAMPLE 1.—ACRYLIC CO-POLYMER LATEX A

	Parts by weight
Polymerizable monomers:	
Acrylonitrile	30.0
Methacrylic acid	5.0
Butyl acrylate	65.0
Sodium lauryl sulfate: dispersing agent	0.5
Water	200.0
Polymerization initiators:	
Sodium bisulfite	0.1
Potassium persulfate	0.3

The polymerization reaction is carried out as described in British Patent 761,928 under an atmosphere of an inert gas such as nitrogen in a suitable polymerization vessel equipped with stirrer, reflux column, thermometer and an inert gas inlet. Before the polymerizable monomers (in this case the acrylonitrile, the methacrylic acid and the butyl acrylate) are added to the water it is deoxygenated by refluxing for about 15 minutes under an atmosphere of nitrogen and then cooled to about 150° F. The emulsifying agent, sodium lauryl sulfate, is added to the deoxygenated water along with the sodium bisulfite after which the mixture of polymerizable monomers is added, while mixing to form an emulsion, followed by the addition of an aqueous solution of potassium persulfate. The aqueous polymerization charge is maintained at about 140° F. for about 2 hours or until the polymerization reaction is complete. After the polymerization reaction has run to completion, the heated aqueous co-polymer dispersion is freed of residual monomers by blowing with air.

The polymerization may be carried out at room temperature or as high as the refluxing temperature of the polymerization charge.

The methacrylic acid may be replaced by other alpha-olefinic monocarboxylic acids, such as, acrylic, ethacrylic, phenylacrylic and crotonic acids.

In place of the butyl acrylate, other alkyl esters of monocarboxylic acids, such as methyl-, ethyl-, octyl acrylates as well as other esters of the above mentioned alpha olefinic monocarboxylic acids with saturated aliphatic monohydric alcohols of 1 to 8 carbon atoms may be used.

The tripolymers found useful in this invention are preferably derived from mixtures of monomeric components varying within the following quantitative ranges:

	Parts by weight
Acrylonitrile	30–80
Alpha-olefinic mono-carboxylic acid	2–15
Alkyl ester of alpha olefinic mono-carboxylic acid	15–65

The acrylic co-polymers used in this invention are prepared by emulsion polymerization in an aqueous medium and the binder and extender compositions are preferably prepared therefrom while the co-polymer is still in latex form.

A suitable binder composition for preparing the printing pastes is as follows:

EXAMPLE 2.—BINDER EMULSION

	Parts by weight
Casein solution (18% casein in water)	8.0
Ammonium lauryl sulfate (30% solution in water)	1.0
Butylated melamine formaldehydre resin (BMF) (60% solution in butanol-xylol)	6.5
Mineral spirits	6.5
Acrylic co-polymer latex A—Example 1	77.0
Ammonia	1.0
	100.0

Directions

Dissolve casein, preferably lactic acid precipitated casein, in hot water and 1% ammonia. Add the ammonium lauryl sulfate solution, cool to room temperature. In a separate container, dilute the BMF resin solution with equal weight of mineral spirits and then add to the above casein solution with constant mixing. Continue mixing until a uniform emulsion is obtained. Adjust with ammonia the pH of the acrylic co-polymer latex A of Example 1 to pH between 7.5 and 10 and add it to the BMF resin emulsion while mixing. Mix until a uniform product is obtained. The BMF used here was Uformite MM-47 of Rohm & Haas Co.

EXAMPLE 3

Similar to Example 2 but the butylated melamine-formaldehyde resin (BMF) used therein is replaced by the same quantity of butylated urea-formadlehyde resin (BUF) solution.

EXAMPLE 4.—BINDER EMULSION

Similar to Example 2 but the butylated melamine-formaldehyde resin solution contained dissolved therein 2% of soya lecithin to make it more readily emulsifiable in the casein solution.

EXAMPLE 5.—BINDER EMULSION

Similar to Example 2 with one-third of the solids of acrylic co-polymer latex A substituted by an equal amount of acrylonitrile-butadiene elastomer solids (Goodrich Hycar 1571).

EXAMPLE 6.—BINDER EMULSION

	Parts by weight
Casein solution (18% casein in water)	10.0
Ammonium lauryl sulfate (30% solution in water)	2.0
Butylated melamine formaldehyde resin (BMF) (60% solution in butanol-xylol)	12.0
Octyl acetate	2.0
Lecithin	0.2
Acrylic co-polymer latex A—Example 1	72.8
Ammonia	1.0
	100.0

EXAMPLE 7.—BINDER EMULSION

Similar to Example 6 with the casein replaced by a 10% aqueous solution of an albumin.

EXAMPLE 8.—BINDER EMULSION

Similar to Example 6 with the casein replaced by the same quantity of soya protein solution of the same concentration.

EXAMPLE 9.—BINDER EMULSION

Similar to Example 6 with the casein solution replaced by a 5% aqueous solution of a low viscosity methylcellulose (15 c.p.s. grade).

EXAMPLE 10.—PADDING BINDER

	Parts by weight
Casein solution (18% casein in water)	8.00
Ammonium lauryl sulfate (30% solution in water)	1.00
Polyoxyethylene condensation product (Igepal CO-880 polyoxyethylated nonylphenol, pale yellow wax, specific gravity 1.17, M.P. 104° F.)	2.00
Acrylic co-polymer latex A—Example 1	88.00
Ammonia	1.00
	100.00

Examples 11 and 12 illustrate, for comparative purposes, compositions analogous to the present invention, but with conventional synthetic latices instead of the acrylic latex.

EXAMPLE 11.—CONTROL BINDER COMPOSITION

Analogue of Example 2 with an acrylonitrile-butadiene copolymer latex (Hycar 1571—B. F. Goodrich) substituted for the acrylic latex of Example 1.

EXAMPLE 12.—CONTROL BINDER COMPOSITION

Analogue of Example 11 but the latex used was Chemigum 245 AHS of Goodyear Chem. Co., another butadiene-acrylonitrile copolymer latex (butadiene to acrylonitrile ratio 67 to 33) instead of that of Example 1.

The following carrier emulsions serve as examples. Others may be formulated along similar lines:

EXAMPLE 13.—CARRIER EMULSION

	Parts by weight
Water	29.7
Methyl cellulose (high viscosity grade—4000 cps.)	.3
Ammonia	.3
Ammonium lauryl sulfate (30% H_2O solution)	2.0
Binder composition (Ex. 2)	12.0
Mineral spirits	55.7
	100.0

Preparation.—The methyl cellulose is first dispersed in the water by mixing with a suitable high speed mixer. The ammonia and ammonium lauryl sulfate is added, followed by the binder. The mineral spirits is added under constant mixing. The mixing is continued until a uniform and homogeneous emulsion is obtained.

EXAMPLE 14.—CARRIER EMULSION

Analogue of Example 13 with the methyl collulose replaced by the same quantity of sodium alginate.

EXAMPLE 15.—CARRIER EMULSION

Analogue of Example 13 with the methyl collulose replaced by a high viscosity grade of polyvinyl alcohol.

EXAMPLE 16.—CARRIER EMULSION

Analogue of Example 13 containing 3% of a pregelatinized corn starch in combination with the methylcellulose.

EXAMPLE 17.—CARRIER EMULSION

Analogue of Example 13 with the mineral spirits reduced to 45% of the composition.

EXAMPLE 18.—CARRIER EMULSION

Analogue of Example 13 with the ammonium lauryl sulfate replaced by sodium lauryl sulfate.

EXAMPLE 19.—CARRIER EMULSION

Analogue of Example 16 with the mineral spirits reduced to 30% of the total composition of the carrier emulsion.

EXAMPLE 20.—CARRIER EMULSION

Analogue of Example 13 with the binder composition of Example 2 increased to 25% of the composition with the corresponding lowering of the mineral spirits used.

EXAMPLE 21.—CARRIER EMULSION

	Parts by weight
Water	30.00
Methylcellulose (4000 cps. viscosity)	.30
Ammonia	.30
Binder of Ex. 2	10.00
Butylated melamine formaldehyde resin	2.00
Soya lecithin	.04
Mineral spirits	56.36
	100.00

The water, methyl cellulose and ammonia are mixed, then the binder composition is added and mixed. The

soya lecithin is first dissolved in the BMF which then is emulsified in the aqueous binder dispersion, followed by the mineral spirits. (The BMF used here was Uformite MM–47 of Rohm & Haas Co.)

EXAMPLE 22.—CONTROL CARRIER EMULSION

Analogue of Example 13 with the binder composition of Example 2 replaced by binder composition of Ex. 11.

EXAMPLE 23.—CONTROL CARRIER EMULSION

Analogue of Example 22 with binder composition of Ex. 12.

EXAMPLE 24.—ELASTOMER-FREE CARRIER EMULSION

	Parts by weight
Water	47.3
Methyl cellulose (4000 cps. viscosity)	.4
Ammonia	.3
Ammonium lauryl sulfate (30% H_2O solution)	2.0
Mineral spirits	50.0
	100.0

The methyl cellulose, ammonia, and ammonium lauryl sulfate are dissolved in the water, then the mineral spirits is emulsified with suitable mixing.

Suitable pigment dispersions for formulation with the carrier emulsions of this invention to produce satisfactory print pastes follow:

EXAMPLE 25.—PIGMENT DISPERSION

	Parts by weight
Phthalocyanine blue (press cake 25% dry content)	60.00
Naphthalene sulfonic acid formaldehyde condensate sodium salt	.50
Sodium lauryl sulfate	3.00
Casein	2.00
Methyl cellulose (15 cps. viscosity grade)	2.20
Water	32.30
	100.00

In this example the sodium lauryl sulfate could be advantageously increased up to double of the quantity used above in relationship to the dry pigment content. The phthalocyanine blue presscake used was Monastral Blue BCF of E. I. du Pont de Nemours Co. The naphthalene sulfonic acid formaldehyde condensate sodium salt was Tamol N of Rohm & Haas Co. The sodium lauryl sulfate was Duponol ME of Du Pont Co. The casein was PMX grade obtained from Borden Co. The methyl cellulose was Methocel 15 cps. from Dow Chemical Co. The naphthalene sulfonic acid condensate is added to the pigment presscake in 25% aqueous solution. The sodium lauryl sulfate was added dry. The presscake was then mixed slowly until its structure broke down to a water slurry. The casein was added as a 20% aqueous dispersion. The slurry was then mixed with a high speed turbine mixer, and passed through a colloid mill with a four-inch diameter rotor operated with an approximate setting of 0.010 inch between rotor and stator and at about 17,500 r.p.m.

The methyl cellulose was then added as a 10% aqueous dispersion and finally the remainder of the water was added.

All additions were made while mixing with the high speed turbine mixer. The mixing was continued until a homogeneous product resulted.

This example illustrates one of the satisfactory methods of dispersing pigments used in this invention. The same process may be used in dispersing a variety of other pigments in practicing this invention.

A finished print paste with excellent performance and fastness properties was made up as follows:

EXAMPLE 26.—PRINTING COMPOSITION

	Parts by weight
Color dispersion of Ex. 25	10.0
Binder of Ex. 2	10.0
Carrier emulsion of Ex. 13	80.0
	100.0

EXAMPLE 27.—PRINT PASTE

Color dispersion—Ex. 25	10.0
Binder—Ex. 2	10.0
Carrier emulsion—Ex. 21	80.0
	100.0

EXAMPLE 28.—PRINT PASTE CONTROL

Color dispersion—Ex. 25	10.0
Binder—Ex. 11	10.0
Carrier emulsion—Ex. 22	80.0
	100.0

EXAMPLE 29.—PRINT PASTE CONTROL

Color dispersion—Ex. 25	10.0
Binder—Ex. 12	10.0
Carrier emulsion—Ex. 23	80.0
	100.0

The color dispersions, binders and carrier emulsions of Examples 26 through 29 were mixed thoroughly by a turbine mixer and the resulting print pastes were printed on a well prepared (scoured and bleached) cotton print cloth (thread count 80 x 80). The prints were made with a conventional print machine using engraved rolls.

The prints were dried over heated copper cylinders (dry cans) and then heat set at 300° F. for 8 minutes.

Description of tests and equipment used

In evaluation of the print pastes herein described, equipment and methods were used which are described in the "1956 Technical Manual and Year Book of the American Association of Textile Chemists and Colorists (A.A.T.C.C.), Volume XXXII." In many tests for abrasive washfastness, the A.A.T.C.C. Standard Test Method 3A (Accelerated Washfastness Tests) was used, described on pages 82 and 83 of the said technical manual and year book. This test is carried out with the Launder-Ometer which is illustrated on page 83 of the said technical manual and year book.

In judging the resistance to alternate light exposure and washing, the tentative test method "Colorfastness to Alternate Light Exposure and Washing," described on page 85 of the said Technical Manual and Year Book was used for exposure to light. The Fade-Ometer was used which is illustrated on page 87 of the said Technical Manual and Year Book.

In addition, a scrubbing test was used before and after exposure to light with the "Gardner Washability and Abrasion Testing Machine," Model 105 (which machine is manufactured by the Institute of Paint and Varnish Research—Henry A. Gardner Laboratory, of Bethesda 14, Maryland) using a nylon brush being weighted to one pound.

The expressions and the nomenclature used conform in general with that adopted by the A.A.T.C.C. Accordingly, where "satisfactory fastness to washing" is indicated, the printed swatches, after drying and curing, passed the accelerated washfastness test number 3A. By "resistance to crock" it is meant that the dried and heat set prints have passed the A.A.T.C.C. Standard Test Method 8–52, for color fastness to rubbing. The tests were carried out with a standard A.A.T.C.C. crockmeter.

Some of the tests described herein have been made by continuously exposing the prints to the Fade-Ometer for the number of hours given and abrasively laundering, following such exposure.

The test ratings used were as follows:

CROCK TESTS

Rating:

1–3 ---------- Considerable transference of color.
4–6 ---------- Medium transference of color.
7–9 ---------- Slight transference of color.
10 ---------- Complete absence of transference of color.

LIGHT FASTNESS—FADE-OMETER TESTS

Y ---------- Yellowing.
F ---------- Fading.
10 ---------- No change or loss of color.

ALTERNATE LIGHT AND WASH FASTNESS (CYCLIC AGING)

Fade-Ometer light test followed by abrasive wash test

Rating:

1–3 ---------- Considerable loss of color.
4–6 ---------- Medium loss of color.
7–9 ---------- Slight loss of color.
10 ---------- No loss of color.

This last (alternate l. and w.) test serves to determine the light fastness of the pigment and the resistance to degradation of the binder due to exposure to light. The ratings are based on the difference of the loss of color of the unexposed print vs. the print exposed in the Fade-Ometer for 48, 72 and 120 hours.

TEST RESULTS

Example	26	27	28	29
Dry crock	8	8	8	8
Wet crock	8	9	6	6
Dry clean	8	8	8	8
Wash	8	9	8	8
Fade-Ometer 48 hrs.	10	10	y	y
Alternate l. and w. 48 hrs.	9	9	4	4
Alternate l. and w. 120 hrs.	8	8	1	1

The above results show that while the conventional control binders gave results comparable to the binders of this invention with regard to dry crock and resistance to dry cleaning and washing, the control binders showed more pronounced wet crock and yellowing already after 48 hours exposure in a Fade-Ometer. The most surprising difference however showed up in the alternate light and wash tests where the composition of Examples 26 and 27 were still in excellent condition after 120 hrs. exposure followed by abrasive washing. The compositions of Examples 28 and 29 representing some of the best of the prior art failed in less than 40 hours and were completely destroyed at the end of the test of 120 hours.

The results with regard to fastness properties were identical when the above compositions were applied by screen printing.

On roller printing the compositions of Examples 26 to 29 were about equally satisfactory in mechanical printability; however, on screen printing the composition of Examples 26 and 27 showed much greater stability enabling the printer to operate continuously for prolonged periods of time, whereas with the control pastes 28 and 29 the screens had to be frequently cleaned of the rubbery deposit formed, with resultant loss of time and material and an even more serious loss due to the necessity of replacing the screens at relatively short intervals as the rubbery deposit could not always be completely removed from the screens.

Test examples illustrating the effect of variations in the carrier compositions:

EXAMPLE 30

The carrier emulsions of Examples 14 to 21 were tested in the same manner as Examples 26 and 27, in 10% cuts (dilutions) with the ratio of pigment dispersion binder carrier emulsion of 1:1:8. The pigment dispersion was Ex. 25, the binder Example 2, the variations being only in the carrier emulsion.

Example 30	A	B	C	D	E	F	G	H
Carrier Emulsions, Ex.	14	15	16	17	18	19	20	21

The above compositions were printed simultaneously on cotton print cloth with an engraved test roller. The print was dried and heat set at 300° F. for 6 minutes. All the print pastes printed equally well insofar as mechanical performance in the printing machine was concerned.

Results of tests.—The dry crock was between 3 and 9 and about equal for all compositions.

The wet crock showed some differences. Example 30–E was noticeably the weakest in this respect indicating that the sodium lauryl sulfate was somewhat inferior to the ammonium compound.

Example 30–G showed the best wet crock results in the range of 9, demonstrating that increasing the binder and increasing somewhat the butylated melamine formaldehyde at the expense of the acrylic copolymer latex A improves the wet crock.

Abrasive washing.—All the compositions of Example 30 showed excellent resistance in the range of 7 to 9 with Examples 30–G–H somewhat superior for the same reasons as explained above.

Alternate light and wash tests.—All the compositions of Example 30 (with the Exception of G) rated 8 after 120 hours. Ex. 30G rated 9. This again shows that with everything else held constant, the resistance to sunlight and abrasive washing are improved with increased amount of the acrylic binder present.

In addition to the above observations, it was noted that the prints were more brilliant in shade and the hand of the fabrics softer in the case of Ex. 30, A, B, C, D, E, H, while with 30F and 30G the handle was noticeably stiffer showing that the handle of the fabric may be controlled by the ratio of emulsified solvent used in the carrier emulsion.

Example 31	A	B	C	D	E	F
Pigment Dispersion, Ex. 25	10	10	10	10	10	10
Acrylic Copolymer latex A, Ex. 1	17	17	17	17	17	17
Carrier Emulsion, Ex. 24	70	70	70	70	70	70
BMF	3	----	----	----	----	----
BUF	----	3	----	----	----	----
MMF	----	----	3	----	----	----
MUF	----	----	----	3	----	----
AF	----	----	----	----	3	----
PF	----	----	----	----	----	3

This example demonstrates the use of a variety of thermo-setting resins in heat setting prints containing as the binder the latex of Ex. 1. The following resins were used.

BMF—butylated melamine formaldehyde resin—60% solution in xylol-butanol containing also 5% of soya lecithin.

BUF—butylated urea formaldehyde resin—60% solution in xylol-butanol containing also 5% soya lecithin.

MMF—melamine-formaldehyde resin—60% solution in water.

MUF—urea-formaldehyde resin—60% solution in water.

AF—acetone-formaldehyde resin—60% solution in water.

PF—phenol-formaldehyde resin—60% solution in water.

The compositions were applied and tested as described above. The color value of prints made with pastes 30–C, –D and –F is substantially lower than those obtained with 30–A and –B.

The fastness properties of the compositions 31 A–F were nearly alike when heat set for 8 minutes at 300° F. The stability or "pot life" of Compositions A and B, however, was much greater than Comps. C, D, E and F. Compositions A and B could be reprinted with fastness properties about equal to the fresh pastes after storing them at room temperature for over two months, while C, D, E, and F gave prints with unsatisfactory appearance after storing the pastes for less than 12 days.

Example 32	A	B	C	D	E
Pigment dispersion, Ex. 25	25	10	5	1	1
Binder, Ex. 2	25	10	5	1	----
Carrier Emulsion, Ex. 13	50	80	90	98	199

This example demonstrates the use of a range of pigment concentrations with the preferred binder composition. The fastness properties of prints when applied and heat-set as in Ex. 30, made with Compositions A to E were all excellent and essentially alike even with very low pigment concentration. Note that carrier emulsion of Ex. 32 contains 12% binder, thereby resulting in substantial binder concentration even in Ex. 32 E.

Example 33	A	B	C	D	E
Pigment dispersion, Ex. 25	10	10	10	10	10
Binder, Ex. 2	30	30	30	30	30
Carrier Emulsion, Ex. 24 (binder free)	60	70	80	85	90

This example demonstrates the effect of decreasing the binder content upon the fastness to crocking and to abrasive washing.

The print pastes were applied and heat set as in Ex. 30.

Results (of Example 33)	A	B	C	D	E
Dry Crock	9	9	6	4	1
Wet Crock	9	8	6	3	1
Abrasive washing	9	8	6	4	1
Alt. light and Washing, 120 hours	9	8	6	2	1

These results show that with decreasing binder content the fastness properties fell off steeply.

EXAMPLE 34

To demonstrate the performance of the binder compositions with a variety of pigments, the following pigment dispersions were made up along the lines of Ex. 25, all containing 15% dry pigment in the dispersion.

A—Ex. 25 ..... Phthalocyanine blue.
B ..... Phthalocyanine green.
C ..... Red ITRA/AS-ITR coupling.
D ..... Lithosol Fast-Yellow 3 GD (naphthol).
E ..... Indanthrene Red Violet RRN.

These pigment dispersions were formulated in the following manner into a print paste.

	Parts by weight
Pigment dispersion	10.0
Binder, Ex. 2	10.0
Carrier emulsion, Ex. 13	80.0
	100.0

All the compositions containing pigment dispersion from Ex. 34A to E performed well in printing and had about equal resistance to crocking and to abrasive washings. In the alternate light and wash test the performances of all the compositions were about equal after 48 hours Fade-Ometer test, but after 120 hrs. exposure only A and B remained essentially intact with C, D and E showing some loss of color due to fading of the pigment, but no essential destruction of the binder film.

EXAMPLE 35.—PRINT PASTE

	Parts by weight
Pigment dispersion—Ex. 25	10.0
Binder—Ex. 6	10.0
Carrier emulsion	80.0
	100.0

The carrier emulsion used here was made up as follows:

Carrier Emulsion

	Parts by weight
Water	34.0
Mineral spirits	52.0
Emulsifier composition (see below)	2.0
Binder composition of Ex. 6	12.0
	100.0

The carrier emulsion was prepared by dispersing the emulsifier composition in the water followed by the binder of Example 6 and finally the mineral spirits was emulsified under constant mixing and mixed until a homogeneous emulsion resulted.

The emulsifier composition consisted of the following ingredients:

	Parts by weight
Methylcellulose (4000 cps.)	15.00
Casein	6.40
2-methyl-2,4-pentane-diol	13.56
Ammonium lauryl sulphate (30% solution in water)	58.00
Orthphenylphenol sodium salt	.31
Pentachlorophenol sodium salt	.06
Ethylenediamine tetraacetic acid sodium salt	.09
Ammonia (28% in water)	1.65
Stearic acid	4.93
	100.00

The emulsifier was prepared by mixing the ingredients.

EXAMPLE 36.—PRINT PASTE

Analogue of Example 36 except that phthalocyanine green pigment dispersion was substituted for the phthalocyanine blue pigment dispersion used in Example 35.

EXAMPLE 37.—PRINT PASTE

Analogue of Example 36 except that the blue pigment was replaced by a red pigment ITR/AS–ITR prepared by coupling.

These last three print paste compositions were tested by roller printing on 80 x 80 cotton print cloth using an engraved roller. All three compositions printed well and with the drying and heating setting at 8 minutes at 300° F. gave prints with excellent fastness properties.

RATINGS

Dry crock	8
Wet crock	7
Abrasive wash 3A	7
Alternate light and wash tests (48 hour light exposure)	7

On the same tests, the controls made by substituting an acrylonitrile-butadiene latex for the acrylic co-polymer latex of Example 1 failed completely by giving in the alternate light and wash tests ratings of 2 to 3. Print pastes using the binder of Example 5 showed ratings between 4 and 6 in the alternate light and wash tests.

The following are formulations of practicable print pastes.

Printpastes prepared with—	Example 38 Phthalocyanine Blue Pigment Dispersion, Parts by Wgt.	Example 39 Phthalocyanine Green Pigment Dispersion, Parts by Wgt.	Example 40 Red Pigment, ITR/AS-ITR Dispersion, Parts by Wgt.
Pigment, dry	1.4250	1.6393	1.4500
Sulfonated Naphthalene Condensation Product Free Acid (33% nonvolatile)	.1069	.1229	.1088
Sodium Lauryl Sulfate (dry)	.2850	.3279	.4350
Ammonium Lauryl Sulfate (30% active)	1.9660	1.9606	2.0884
Stearic Acid (dry)	.1443	.1443	.1327
Casein (dry)	.5744	.5766	.7707
Methylcellulose 15 cps. (dry)	.2669	.2669	.1973
Methylcellulose 4000 cps. (dry)	.2413	.2400	.2400
Ammonia (28%)	.6514	.6564	.6597
Octyl Acetate	.5884	.5884	.6928
Orthophenylphenol Sodium Salt	.0296	.0298	.0412
Pentachlorophenol Sodium Salt	.0069	.0069	.0091
Ethylenediamine Tetraacetic Acid	.0080	.0080	.0106
Glycerine	.0577	.0567	.0467
Butylated Melamine Formaldehyde Resin (Uformite MM-47—60% solution in xylene butanol)	1.5586	1.5576	1.3875
Butylated Melamine Formaldehyde Resin (Cymel 245-8—50% solution in xylene butanol)	trace		
Xylene	.1525	.1525	.0916
Mineral Spirits	43.6178	44.1542	42.8760
Soya Lecithin	.1994	.1994	.1778
Sodium Tertiary Octyl Phenoxy Polyether Sulphonate (Triton 770—Rohm & Haas)	.0001		
2-Methyl-2,4-Pentane-Diol	.2170	.2170	.2170
Water	33.3850	32.5768	33.8493
Polyoxyethylene Condensation Product (Igepal CO 880—G.D.C.)	.3842	.3842	.3842
Acrylic Co-Polymer Latex A (40% Solids: Example 1)	14.1336	14.1336	14.1336
	100.0000	100.0000	100.0000

Several of the binders herein described are suitable for use as binders in the pigment pad dye system.

In pad dyeing, the textile fabric is impregnated with the dye liquor, and then passed between two squeeze rolls (one dip, one nip padding), or impregnated twice by exposing it twice to the squeeze rolls between the two impregnations as well as after the second impregnation (two dip, two nip padding).

The following example illustrates the use of the binders and pad dye compositions to produce dyeings with fastness to washing as well as fastness in alternate light and wash tests (cyclic aging).

EXAMPLE 41.—BLUE PAD DYE LIQUORS

	Percent by Weight	
	41-A	41-B
Pigment Dispersion Example 25	2.5	2.5
Padding Binder Example 10	7.5	
Binder Emulsion Example 6		9.5
Ammonium Lauryl Sulphate	2.5	
Polyoxyethylene Condensation Product (Igepal CO-880)	.2	.2
Phosphoric Acid	.4	.4
Ammonia	.4	.4
M.M.F. (60%) (water-soluble)	2.0	
Sodium Alginate (2%)	2.5	2.5
Silicone Antifoam	.1	.1
Water	81.9	81.9
	100.0	100.0

The printpastes of this invention have the following preferred proportion limits based on 100 weight parts of printpaste.

	Percent
1. Total surface active agent	0.7–2.0
Including:	
Fatty alcohol sulphate	0.3–1.30
2. Total protective colloid	0.5–1.5
Including:	
(a) Methylcellulose	0.25–0.8
Including:	
1. L.V	0.0–0.6
2. H.V	0.15–0.3
(b) Casein	0.3–0.7
3. Total binder	3.5–10.0
Including:	
(a) Acrylic latex A	3.0–9.0
(b) Amino-aldehyde resin	0.4–2.5
4. Pigment	0.05–4.0

The binder emulsions of this invention, based on 100 weight parts of binder emulsion have the following preferred proportion limits.

1. Total surface active agents	2.25–5.7
Including:	
Fatty alcohol sulphate	0.29–4.1
2. Casein	1.20–1.50
3. Total binder	30.00–33.00
Including:	
(a) Acrylic latex A	19.0–30.0
(b) Amino-aldehyde resin	3.40–6.70

The binder emulsions of this invention, based on 100 non-volatile weight parts of the acrylic latex A, have the following preferred proportion limits.

1. Total surface active agent	5–24
Including:	
Fatty alcohol sulphate	3–17
2. Casein	1–5
3. Amino-aldehyde resin	5–28

Wherever ammonium fatty alcohol sulphate is present in the Binder Emulsion, the preferred proportion for each non-volatile 100 weight parts of organic solvent-soluble melamine formaldehyde resin is 8–60 weight parts of the ammonium fatty alcohol sulphate.

The carrier emulsions of this invention, based on 100 weight parts of carrier emulsion, have the following preferred proportion limits.

1. Total surface active agent	0.70–2.5
Including:	
Fatty alcohol sulphate	0.35–2.10
2. Total protective colloid	0.5–0.8
Including:	
Methylcellulose—H.V	0.2–0.3
3. Casein	0.2–0.5
4. Acrylic latex A N.V	2.3–4.0
5. Amino-aldehyde resin	0.4–1.0
6. Mineral spirits	50.0–60.0

In the carrier emulsion, there is preferably present an ammonium salt of a fatty alcohol sulphate. The preferred ratio per 100 weight parts of organic solvent-soluble melamine formaldehyde resin is 80–100 weight parts of the ammonium fatty alcohol sulphate.

The carrier emulsions of this invention, based on 100 non-volatile weight parts of the Acrylic Latex A, have the following preferred proportion limits.

1. Total surface active agent	16–28
Including:	
Fatty alcohol sulphate	11–17
2. Protective colloid	16–22
3. Methylcellulose H.V	7–10
4. Casein	8–14 (5–14)
5. Amino-aldehyde resin	12–28

In the print pastes of this invention, based on 100 weight parts of pigment the following are the preferred proportions by weight parts.

1. Total surface active agents	57–125
2. Total protective colloid	42–84
Including:	
(a) Methylcellulose	30–38
(b) Casein	20–54
3. Total binder	273–570
Including:	
(a) Acrylic latex A	230–480
(b) Amino-aldehyde resin	43–90

In general, these are the preferred ranges of components in the print paste compositions on a solids weight basis. A useful preferred weight ratio range of interpolymer to pigment is 1:1 to 5:1.

All the proportions above are weight parts and relate to non-volatile (dry) ingredients.

The combination of the binder emulsion and carrier emulsion components of the print pastes of this invention, based on 100 weight parts of acrylic latex A solids, has the following preferred proportions.

1. Total surface active agents	5–22
Including:	
Fatty alcohol sulphate	2–17
2. Casein	0.5–14
3. Total protective colloid	0.5–22
4. Melamine resin	5–30

The methods and product formulations of this invention accomplish the following results:

(1) Fastness to alternate exposure to light and brasive laundering;

(2) Achieve proper toughness of the printed deposit, required to withstand abrasive laundering, and resistance to dry crock and wet crock;

(3) Provide a soft feel of the printed fabric;

(4) Provide for conversion of the printed deposit to an irreversibly thermoset stage with equipment available at textile printing plants, thereby providing resistance not only to abrasive laundering but also to abrasive dry cleaning;

(5) Provide for emulsion stability, including shear-stability, pot-stability and passage of freezing cycles;

(6) Provide the achievement of maximum color value from the pigments used;

(7) Provide for simplest and least expensive means of insolubilization of the protective colloids and/or surface active agents present in the printed composition, after the prints have been deposited, and

(8) Provide for proper carrier emulsions to achieve proper printing viscosity.

In formulations where other fastness requirements are reduced, except the requirement to withstand light exposure and subsequent laundering, the acrylic latex A solids content may be reduced to as low as 0.3% of the print paste. In such cases the amino-aldehyde resins BMF (solids) ratio to 100 latex solids may increase up to 70 weight parts.

While I have illustrated various embodiments of the invention, it is to be understood that the scope of my invention is as stated in the accompanying claims.

What is claimed is:

1. An oil-in-water textile printing and pad-dyeing emulsion composition consisting of an admixture of (*a*) a pigment in aqueous dispersion, (*b*) a water-immiscible and organic-solvent-soluble thermosetting emulsified amino-aldehyde resin selected from the group consisting of butylated melamine-formaldehyde and butylated urea-formaldehyde resins and mixtures thereof, in organic solvent solution, said aminoaldehyde resins being per se in the emulsified state, (*c*) a protective colloid selected from the group consisting of methyl cellulose, casein, egg albumin, blood albumin, gelatin, bone glue, zein, gluten, alkali metal salts of polyacrylic acids, ammonium salts of polyacrylic acids, carboxymethyl cellulose, pre-gelatinized starch, carboxymethyl starch, hydroxyethyl cellulose, alkali metal salts of alginic acids, sodium and ammonium salts of alginic acids, water-soluble salts of maleic adduct of styrene, gum tragacanth, carragheen moss, dextrin, starch, locust bean gum, hydroxypropyl starch, guar gum, polyvinyl pyrrolidone, polyvinyl alcohol, and mixtures thereof, (*d*) a surface active agent selected from the group consisting of ammonium, morpholine, ethanolamine, and alkali metal salts of fatty acids having 10 to 22 carbon atoms, of hydroxy fatty acids having one or more hydroxyl groups attached to the carbon chain, of unsaturated fatty acids derived from naturally occurring oils, ammonium and alkali metal salts of mono-esters formed from sulfuric acid and fatty alcohols having a carbon chain length of from 8 to 22 carbon atoms, ammonium and alkali metal salts of benzene and naphthalene sulphonic acids having one or more aliphatic chains on the aromatic ring and condensation products thereof with formaldehyde, polyoxyethylene condensation products of fatty acids and of fatty alcohols and of substituted phenols, soya lecithin, and mixtures thereof, (*e*) a water-dispersion of an interpolymer of a monomer mixture comprising 30 to 80 parts of acrylonitrile and 2 to 15 parts of an alphaolefinic monocarboxylic acid selected from the group consisting of acrylic acid and methacrylic acid, ethacrylic acid, phenylacrylic acid and crotonic acid, and 15 to 65 parts of an ester of an alpha-olefinic monocarboxylic acid of the above group formed with a saturated aliphatic monohydric alcohol of 1 to 8 carbon atoms, said parts of said monomer mixture being based upon 100 parts by weight of total monomer mixture, (*f*) emulsified water-immiscible organic hydrocarbons having less than 3% solubility in water by weight, (*g*) and ammonia, the dry weight of said interpolymer being between 1 and 5 times the dry weight of said pigment, the proportion on a dry weight basis of the aminoaldehyde resin to 100 parts of said interpolymer being between 5 and 30.

2. A pigment dispersion for incorporation in the composition of claim 1 comprising (*a*) an organic pigment having high tinting power, (*b*) at least one surface acting agent selected from the group consisting of ammonium, morpholine, ethanolamine, and alkali metal salts of fatty acids having 10 to 22 carbon atoms, of hydroxy fatty acids having one or more hydroxyl groups attached to the carbon chain, of unsaturated fatty acids derived from naturally occurring oils, ammonium and alkali metal salts of mono esters formed from sulfuric acid and fatty alcohols having a carbon chain length from 8 to 22 carbon atoms, ammonium and alkali metal salts of benzene and naphthalene sulphonic acids having one or more aliphatic chains on the aromatic ring and condensation products thereof with formaldehyde, polyoxyethylene condensation products of fatty acids and of fatty alcohols and of substituted phenols, soya lecithin, and (*c*) at least one protective colloid selected from the group consisting of methyl cellulose, casein, egg albumin, blood albumin, gelatin, bone glue, zein, gluten, alkali metal salts of polyacrylic acids, ammonium salts of polyacrylic acids, carboxymethyl cellulose, pregelatinized starch, carboxymethyl starch, hydroxyethyl cellulose, alkali metal salts of alginic acids, sodium and ammonium salts of alginic acids, water-soluble salts of maleic adduct of styrene, gum tragacanth, carragheen moss, dextrin, starch, locust bean gum, hydroxypropyl starch, guar gum, polyvinyl pyrrolidone, and polyvinyl alcohol.

3. As a component of the composition of claim 1, a binder comprising an aqueous emulsion including casein, ammonium lauryl sulfate, butylated melamine formaldehyde resin, mineral spirits, a water-dispersion of an interpolymer of a monomer mixture comprising 30 to 80 parts of acrylonitrile and 2 to 15 parts of an alpha-olefinic monocarboxylic acid selected from the group consisting of acrylic acid and methacrylic acid, ethacrylic acid, phenylacrylic acid and crotonic acid, and 15 to 65 parts of an ester of an alpha-olefinic monocarboxylic acid of the above group formed with a saturated aliphatic monohydric alcohol of 1 to 8 carbon atoms, said parts

of said monomer mixture being based upon 100 parts by weight of total monomer mixture, and ammonia.

4. As a component of the composition of claim 1, a carrier emulsion comprising methylcellulose, casein, ammonium lauryl sulfate, 2-methyl-2,4-pentane-diol, orthophenylphenol sodium salt, pentachlorphenol sodium salt, ethylene diamine tetraacetic acid sodium salt, ammonia, stearic acid, mineral spirits and a binder comprising a water-dispersion of an interpolymer of monomer mixture comprising 30 to 80 parts of acrylonitrile and 2 to 15 parts of an alpha-olefinic monocarboxylic acid selected from the group consisting of acrylic acid and methacrylic acid, ethacrylic acid, phenylacrylic acid and crotonic acid, and 15 to 65 parts of an ester of an alpha-olefinic monocarboxylic acid of the above group formed with a saturated aliphatic monohydric alcohol of 1 to 8 carbon atoms, said parts of said monomer mixture being based upon 100 parts by weight of total monomer mixture, said mineral spirits comprising between about 26% and about 60% of the total weight of the said carrier emulsion.

5. The composition of claim 1, in which the interpolymer is the polymerization product of 30–80 weight parts acrylonitrile, 2–15 parts methacrylic acid, and 15–65 parts butyl acrylate.

6. The composition of claim 5, in which the weight part of acrylonitrile are 30–50.

7. The composition of claim 1, in which the interpolymer is the polymerization product of 30 weight parts acrylonitrile, 5 parts methacrylic acid and 65 parts butyl acrylate.

8. As a component of the composition of claim 2, an emulsifier consisting of methyl cellulose, casein, ammonium lauryl sulfate, 2-methyl-2,4-pentane-diol, orthophenylphenol sodium salt, pentachlorphenol sodium salt, ethylene diamine tetraacetic acid sodium salt, ammonia and stearic acid.

9. The composition of claim 1 in which said interpolymer dry weight content is between 0.3 to 9% of the composition and in which said amino-aldehyde resin solid content ratio to 100 parts of interpolymer solids content is increased up to 70 weight parts.

10. The composition of claim 1 in which the dry weight of said interpolymer is between about 2.3 and 5 times the dry weight of said pigment.

11. A pigment pad-dye liquor composition consisting essentially of an admixture of (*a*) a pigment in aqueous dispersion, (*b*) a water-immiscible and organic-solvent-soluble thermosetting emulsified amino-aldehyde resin selected from the group consisting of butylated melamine-formaldehyde and butylated urea-formaldehyde resins and mixtures thereof, in organic solvent solution, said amino-aldehyde resins being per se in the emulsified state, (*c*) a water soluble amino aldehyde resin, (*d*) a protective colloid selected from the group consisting of methyl cellulose, casein, egg albumin, blood albumin, gelatin, bone glue, zein, gluten, alkali metal salts of polyacrylic acids, ammonium salts of polyacrylic acids, carboxymethyl cellulose, pre-gelatinized starch, carboxymethyl starch, hydroxyethyl cellulose, alkali metal salts of alginic acids, sodium and ammonium salts of alginic acids, water-soluble salts of maleic adduct of styrene, gum tragacanth, carragheen moss, dextrin, starch, locust bean gum, hydroxypropyl starch, guar gum, polyvinyl pyrrolidone, polyvinyl alcohol, and mixtures thereof, (*e*) a surface active agent selected from the group consisting of ammonium, morpholine, ethanolamine, and alkali metal salts of fatty acids having 10 to 22 carbon atoms, of hydroxy fatty acids having one or more hydroxyl groups attached to the carbon chain, of unsaturated fatty acids derived from naturally occurring oils, ammonium and alkali metal salts of mono-esters formed from sulfuric acid and fatty alcohols having a carbon chain length of from 8 to 22 carbon atoms, ammonium and alkali metal salts of benzene and naphthalene sulphonic acids having one or more aliphatic chains on the aromatic ring and condensation products thereof with formaldehyde, polyoxyethylene condensation products of fatty acids and of fatty alcohols and of substituted phenols, soya lecithin, and mixtures thereof, (*f*) a water-dispersion of an interpolymer of a monomer mixture comprising 30 to 80 parts of acrylonitrile and 2 to 15 parts of an alpha olefinic monocarboxylic acid selected from the group consisting of acrylic acid and methacrylic acid, ethacrylic acid, phenyl acrylic acid and crotonic acid, and 15 to 65 parts of an ester of an alpha-olefinic monocarboxylic acid of the above group formed with a saturated aliphatic monohydric alcohol of 1 to 8 carbon atoms, said parts of said monomer mixture being based upon 100 parts by weight of total monomer mixture, (*g*) emulsified water-immiscible organic hydrocarbons having less than 3 percent solubility in water by weight, (*h*) and ammonia, the dry weight of said interpolymer being between 1 and 5 times the dry weight of said pigment, the proportion on a dry weight basis of the amino-aldehyde resin to 100 parts of said interpolymer being between 5 and 30.

References Cited in the file of this patent

UNITED STATES PATENTS

2,760,945	Bodenschatz et al.	Aug. 28, 1956
2,787,561	Sanders	Apr. 2, 1957
2,787,603	Sanders	Apr. 2, 1957
2,865,871	Johnson et al.	Dec. 23, 1958