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LOW TEMPERATURE PIGMENT BINDER COMPOSITIONS FOR TEXTILE FABRICS

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This invention relates to an improved composition for use in the printing and padding of textile fabrics, in particular synthetic textile fabrics or mixtures of natural and synthetic fabrics. The novel compositions of the invention are employed in the formation of print pastes and padding liquors for the coloring of textile fabrics. The invention also relates to a method of using said compositions.

It is an object of the invention to provide a binder component for a finished print paste or padding liquor, which binder component permits the curing of the printed or padded fabric at generally lower temperatures than heretofore practiced. Prior binder components have required curing of the colored fabric at higher temperatures for longer periods of time than the binder components according to the present invention. For example, in the past it has been common to subject the printed fabric to a temperature of about 300° F. to about 350° F. for from 2 to 10 minutes. Often the process of curing at such temperatures requires special handling of the textile goods and added operations. According to the present invention, however, the printed goods are dried and cured on hot cans in the same operation at from about 180° F. to about 250° F. for from about 0.5 to about 5 minutes. The prior method requires separate drying and curing steps and higher temperatures, as well as more time to accomplish the curing of the print. Thus, the use of the low temperature pigment binder compositions of the present invention results in a saving of valuable time, heat energy and manpower. Other advantages of the invention will appear from the specification and examples which follow hereinafter.

The low temperature cure according to the present invention has been devised to solve a problem raised by the advent of the many heat-sensitive synthetic fabrics and blends of synthetic with natural fabrics. The curing of colored fabrics which are at least partially synthetic at temperatures of 300° F. to 350° F. for periods in excess of 2 to 3 minutes, may result in some cases in shrinkage of up to 15% of the original dimensions of the fabric. High temperatures, such as those above 300° F. often cause considerable distortion of the printed design, particularly in blended fabrics. This heat sensitivity is characteristic of such diverse synthetics as the polyamides, polyesters, polyacrylics, and also some of the acetate fabrics. In addition, it is known that application of high temperatures to various fabrics causes loss of tensile strength with resultant reduction of durability in articles of clothing or other consumer goods manufactured with the aforesaid heat-treated fabrics.

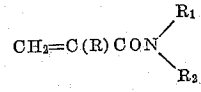
The binder component of the invention is composed of two elements: a hard latex and a soft latex. An additional agent which is required for the successful operation of the invention in the finished print paste is a latent acid catalyst. The inventive concept, thus, extends to a binder composed of from 10 to 90% by weight of a component, e.g. a hard latex, as defined hereinbelow, and from 90 to 10% of a soft latex consisting essentially of from 2 to 10% of methacrylic acid, from 60 to 85% of butadiene, and from 38 to 5% of either acrylonitrile or styrene, said soft latex being a polymerization product having the composition by weight indicated. The binder component, when used in combination with the latent

acid catalysts defined below, is successful in forming print pastes and padding liquors which produce textile colored fabrics which are wash- and rub-fast, as well as resistant to dry cleaning solvent and to dry and wet crocking.

One or more latent acid catalysts may be employed in the compositions of the invention. Any suitable latent acid catalyst may be used, i.e. any catalyst may be used whose basic element is volatile on heating and may be removed to leave an acid catalytic element. Thus, for example, ammonium nitrate, ammonium thiocyanate, ammonium sulfate, ammonium chloride, and diammonium hydrogen phosphate are all useful. Amine salts of mineral acids are also employable, as are the morpholine and/or pyridine salts thereof, etc.

The latent acid catalyst is used in an amount of from about 2 to about 10% by weight, based upon the quantity of binder component used in the finished coloring composition. On the basis of the total weight of the finished print paste or padding liquor, from about 0.025 to about 2% by weight of latent acid catalyst is used.

The hard latex element of the binder component comprises several types of latex which lend themselves to setting at lower temperatures when combined with the soft latex defined above, and when in the presence of the acid catalyst above mentioned. In one aspect of the invention, the hard latex is a water-insoluble linear polymer of a mixture comprising (i) from about 1% to about 25% by weight of a monomer of the formula



wherein

R is either hydrogen or lower alkyl, preferably methyl, R_1 and R_2 are each independently either hydrogen or alkyl, preferably alkyl having from 1 to 10 carbon atoms, and

(ii) 99% to 75% by weight of at least one alkyl ester of acrylic and/or methacrylic acid, the alkyl group of said ester containing from 1 to 8 carbon atoms. The aforesaid water-insoluble linear polymer is preferably mixed with an auxiliary crosslinking agent. The crosslinking agent is dissolved in an aqueous composition or in a clear extender in which the pigment is dispersed together with the water-insoluble linear polymer defined above. The ratio between the weights of the linear polymer and the crosslinking agent is in the range of 6:1 to 1:6, preferably 5:2 to 2:5.

The auxiliary crosslinking agent is a bivalent or bifunctional organic compound, such as one having one or more reactive carbonyl groups, as e.g. formaldehyde, glyoxal, propanediol, etc. Low molecular weight condensation polymers are also useful. Monomeric reaction products of an aldehyde, e.g. formaldehyde, with urea, thiourea or biuret, or homologues or derivatives thereof, may be used. Thus, the following may be used as auxiliary crosslinking agents: aldehyde condensates with N,N-ethyleneurea, N,N' - ethyleneurea, N,N' - dimethylurea, N,N' - diethylurea, N,N' - dimethoxymethylurea, N,N-dimethoxymethylurea, N,N'-diethoxyethylurea, tetramethoxymethylurea, tetraethoxyethylurea; formaldehyde condensates with triazines, e.g. to yield melamines, also N,N-dimethylmelamine, alcohol-modified melamine-formaldehyde thermosetting resin condensates, e.g. of methyl and ethyl alcohols, such as dimethoxymethyl monomethylolmelamine. Other crosslinking agents may be formed from reaction of formaldehyde with mixtures of triazines with urea, biuret or other urea derivatives.

In another aspect of the invention, the hard latex component may be replaced by the crosslinking agent alone, as defined above.

In still another aspect of the invention, the hard latex comprises an integrated chemical composition having been copolymerized in a free radical emulsion polymerization from the following monomers:

Ethyl acrylate (I)
Methyl methacrylate (II)
Styrene (III)

Preferred proportions of said composition are from about 65% to about 75% ethyl acrylate, from about 10% to about 15% methyl methacrylate and from about 15% to about 10% styrene. A particularly preferred composition comprises about 67% (I), about 12.5% (II) and about 12.5% (III) plus other agents, such as minor amounts of wetting agents and alkali to adjust pH, as well as small amounts of copolymers of (I), (II) or (III) with:

Methacrylic acid (IV) and/or
Methacrylamide (V)

The proportions of copolymers formed from (IV) and (V) may be from about 0.5% to about 10%, preferably about 4%. (All foregoing percentages by weight are based on the total composition.) Not more than abount 2% to about 4% by weight (on total composition) of other materials (such as wetting agents, alkali) is contemplated. These materials are inert for the purposes of this invention and do not play a significant role therein. Examples of wetting agents are e.g. the alkaryl sodium sulfonates, ethylene oxide condensates with octyl or nonyl phenols, etc.

The invention is illustrated, but not limited, by the examples which follow. In the examples, unless otherwise noted, parts are by weight and temperature is in degrees Fahrenheit.

Example 1

This example illustrates various components useful in making the compositions for printing and padding textile fabrics according to the invention, the employment of some of which is further illustrated in Examples 2 through 7.

Part A—Color concentrate:	Parts
Phthalocyanine Blue Pigment	15.0
Water	57.6
Sodium lauryl sulfate	2.8
Sodium diisopropyl naphthalene sulfonate	2.4
Casein	1.5
Methyl cellulose, 15 cps.	1.5
Solvent soluble butylated melamine formaldehyde	7.5
Anti-foam agent	0.2
Xylol	7.5
Mineral spirits	4.0
	100.0

Part B—Extender concentrate:	
Water	30.0
Casein	1.5
Sodium lauryl sulfate	10.0
Ammonium lauryl sulfate	7.5
Solvent soluble butylated melamine formaldehyde	12.0
Methyl cellulose, 4000 cps.	14.0
Ammonium hydroxide	2.0
Solvent	23.0
	100.0

Part C—Printing extender:	
Extender concentrate (Part B)	2.0
Water	43.0
Mineral spirits	55.0
	100.0

Part D—Low temperature curing binder:

(*a*) Hard Polymers—

(1) 8 parts methacrylamide, 32 parts of methyl methacrylate and 60 parts of ethyl acrylate with 17 parts of dimethoxymethyl monomethylol melamine.

(2) 10 parts N,N-dimethylacrylamide, 90 parts of n-butyl acrylate and 20 parts of dimethyl-N,N'-ethyleneurea.

(3) 15 parts of acrylamide, 30 parts of methyl methacrylate and 55 parts of ethyl acrylate with 40 parts N,N'-dimethoxymethylurea.

(4) 3 parts of N-methyl methacrylamide, 17 parts of methyl methacrylate and 80 parts of ethyl acrylate with 30 parts of dimethoxymethyl monomethylol melamine.

(*b*) Soft polymers—

(1) 7 parts of methacrylic acid, 73 parts of butadiene and 20 parts of acrylonitrile.

(2) 8 parts of methacrylic acid, 62 parts of butadiene and 30 parts of styrene.

(3) 10 parts of methacrylic acid, 80 parts of butadiene and 10 parts of acrylonitrile.

(4) 3 parts of methacrylic acid, 77 parts of butadiene and 20 parts of styrene.

(5) 5 parts of methacrylic acid, 85 parts of butadiene and 10 parts of acrylonitrile.

(6) 8 parts of methacrylic acid, 72 parts of butadiene and 20 parts of acrylonitrile.

(*c*) Some especially advantageous crosslinking agents—

(1) N,N,-dimethyl melamine.

(2) Dimethoxymethyl monomethylol melamine.

(3) Diethoxymethyl monomethylol melamine.

(4) N,N'-dimethylurea.

(5) N,N-dimethoxymethylurea.

Example 2

A print paste is made with:

20 parts of phthalocyanine blue color concentrate (Example 1, Part A),
20 parts of stabilized 40% aqueous emulsion binder combination containing 50% of hard polymer (Example 1, Part D, *a*–1) and 50% of soft polymer (Example 1, Part D, *b*–1),
58 parts of printing extender (Example 1, Part C),
2 parts of 50% solution of ammonium nitrate

100 parts

Prints are made on cotton, polyamide fabric (nylon), polyester fabric (Dacron) and cotton and acrylic fabric (Orlon blend) and dry-cured on hot cans for approximately 2 minutes at 200 to 230°. The prints obtained have high brilliancy, good handle and very good fastness to washing (AATCC No. 3 Wash Test), dry cleaning (AATCC Test Method) and wet and dry crocking (AATCC Test Method).

Example 3

A print paste is prepared with:

20 parts of color concentrate (Example 1, Part A)
15 parts of a stabilized 43% solids aqueous emulsion binder containing 35% of hard polymer (Example 1, Part D, *a*–3) and 65% soft polymer (Example 1, Part D, *b*–2)
62 parts of printing extender (Example 1, Part C)
3 parts of a 50% solution of ammonium thiocyanate

100 parts

Prints are made on Dacron batiste, nylon shear, and a cotton acetate blend. They are dry-cured on a bank of hot cans at 180° to 210° for approximately 3 minutes.

Excellent fastness is obtained as evidenced in the conventional AATCC fastness tests. The printed and cured fabrics, moreover, all retain their dimensional stability.

Example 4

A print paste is prepared with:

20 parts of blue color concentrate (Example 1, Part A)
20 parts of a stabilized 45% solids aqueous emulsion binder containing 40% of hard polymer (Example 1, Part D, *a*–4) and 60% of soft polymer (Example 1, Part D, *b*–1)
58 parts of printing extender (Example 1, Part C)
2 parts of a 40% solution of diammonium phosphate

100 parts

Prints are made on cotton, acetate blend, silk, and nylon batiste. They are dried and cured for 2 minutes at 200°. Good handle and good wash fastness are obtained.

Example 5

A print paste is prepared with:

20 parts of an aqueous dispersion containing 20 parts of an azo red pigment
15 parts of a stabilized binder containing 8 parts of a water-soluble polymethylated melamine formaldehyde condensate and 33 parts of soft polymer (Example 1, Part D, *b*–4)
2 parts of a 40% aqueous solution of diammonium phosphate
63 parts of printing extender (Example 1, Part C)

100 parts

Prints made on nylon pongee, Dacron sand crepe and cotton show excellent crock and wash resistance on being cured for 2 minutes at 210°. No dimensional instability or print distortion is evident on the synthetic fabrics so printed and so cured.

Example 6

A print paste is prepared with:

30 parts of phthalocyanine green color concentrate made in a manner analogous to Example 1, Part A
25 parts of a 40% aqueous emulsion binder containing (1) 50% of a hard polymer of 71 parts of ethyl acrylate, 12.5 parts of methyl methacrylate, 12.5 parts of styrene, 2 parts of methacrylic acid and 2 parts of methacrylamide, and (2) 50% of a soft polymer (Example 1, Part D, *b*–1)
4 parts of a 50% solution of ammonium nitrate
41 parts of printing extender (Example 1, Part C)

100 parts

Prints made on rayon crepe, nylon challis, Dacron shear and a 60–40 Dacron-cotton blend exhibit good to excellent fastness properties upon being cured at 190° to 210° for 2 minutes.

Example 7

A padding liquor for pigment dyeing is prepared with:

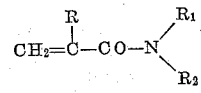
10 parts of a phthalocyanine blue pigment dispersion
10 parts of a 48% aqueous emulsion binder of a copolymer containing 50% of soft polymer (Example 1, Part D, *b*–4) and 50% of the crosslinking agent dimethoxymethyl monomethylol melamine
2.5 parts of a 2% solution of sodium alginate
2.8 parts of a 30% solution of diammonium phosphate
74.7 parts of water

100.0 parts

Fabric blends of cotton and silk, and Dacron and cotton are padded with this liquor to a pick-up of 50% and dry-cured at 220° for 2 minutes. Wash fastness and crock fastness test results are very good.

What is claimed is:

1. A method for coloring textile material, which comprises the steps of applying to a fabric of said material an aqueous composition containing from about 0.025% to about 2% by weight of the total composition of a latent acid catalyst and comprising a water-insoluble pigment intimately mixed with a binder, said binder being composed substantially of the following elements: (*a*) from about 90% to about 10% by weight of a soft latex component consisting essentially of a polymerization product having from about 2% to about 10% of methacrylic acid, from about 60% to about 85% of butadiene and from about 38% to about 5% of a member selected from the group consisting of acrylonitrile and styrene, and (*b*) from about 10% to about 90% by weight of a mixture composed of (1) a hard latex component consisting essentially of a water-insoluble linear polymer of a mixture comprising (i) from about 1% to about 25% by weight of a monomer of the formula



wherein

R is a member selected from the group consisting of hydrogen and lower alkyl,
R_1 and R_2 are each independently selected from the group consisting of hydrogen and alkyl, and

(ii) from about 99% to about 75% by weight of at least one alkyl ester of a member selected from the group consisting of acrylic acid, methacrylic acid and a mixture of methacrylic and acrylic acid, the alkyl group of said ester containing from 1 to 8 carbon atoms, and (2) a water-soluble resinous condensate selected from the group consisting of polymethylated melamine-formaldehyde, polymethylated urea-formaldehyde and polymethylated ethylene-urea-formaldehyde, said condensate being dissolved in the aqueous composition and the copolymer and pigment being dispersed therein, the ratio of the weights of the copolymer to the crosslinking agent being from about 6:1 to about 1:6, and then simultaneously drying and heating said fabric at a temperature of from about 180° F. to about 250° F. for from about 0.5 to about 5 minutes.

2. A method for coloring textile material, which comprises the steps of applying to a fabric of said material an aqueous composition containing from about 0.025% to about 2% by weight of the total composition of a latent acid catalyst and comprising a water-insoluble pigment intimately mixed with a binder, said binder being composed substantially of the following elements: (*a*) from about 90% to about 10% by weight of a soft latex component consisting essentially of a polymerization product having from about 2% to about 10% of methacrylic acid, from about 60% to about 85% of butadiene and from about 38% to about 5% of a member selected from the group consisting of acrylonitrile and styrene, and (*b*) from about 10% to about 90% by weight of a hard latex component comprising a polymerization product of from about 65% to about 75% by weight of ethyl acrylate, from about 10% to about 15% by weight of methyl methacrylate and from about 15% to about 10% by weight of styrene, and then simultaneously drying and heating said fabric at a temperature of from about 180° F. to about 250° F. for from about 0.5 to about 5 minutes.

3. A composition of matter for coloring textile material, which comprises an aqueous composition containing from about 0.025% to about 2% by weight of the total composition of a latent acid catalyst and a water-insoluble pigment intimately mixed with a binder, said binder

being composed substantially of the following elements: (*a*) from about 90% to about 10% by weight of a soft latex component consisting essentially of a polymerization product having from about 2% to about 10% of methacrylic acid, from about 60% to about 85% of butadiene and from about 38% to about 5% of a member selected from the group consisting of acrylonitrile and styrene, and (*b*) from about 10% to about 90% by weight of a hard latex component comprising a polymerization product of from about 65% to about 75% by weight of ethyl acrylate, from about 10% to about 15% by weight of methyl methacrylate and from about 15% to about 10% by weight of styrene.

4. A method for coloring textile material, which comprises the steps of applying to a fabric of said material an aqueous composition containing from about 0.025% to about 2% by weight of the total composition of a latent acid catalyst and comprising a water-insoluble pigment intimately mixed with a binder, said binder being composed substantially of he following elemens: (*a*) from about 90% to about 10% by weight of a soft latex component consisting essentially of a polymerization product having from about 2% to about 10% of methacrylic acid, from about 60% to about 85% of butadiene and from about 38% to about 5% of a member selected from the group consisting of acrylonitrile and styrene, and (*b*) from about 10% to about 90% by weight of a hard latex component comprising a polymerization product of the following monomers: from about 65% to about 74.5% ethyl acrylate, from about 10% to about 15% methyl methacrylate, from about 15% to about 10% styrene, and from about 10% to about 0.5% of at least one monomer selected from the group consisting of methacrylic acid and methacrylamide, all of the foregoing percentages being by weight and based upon the composition of the hard latex component, and then simultaneously drying and heating said fabric at a temperature of from about 180° F. to about 250° F. for from about 0.5 to about 5 minutes.

5. A method for coloring textile material, which comprises the steps of applying to a fabric of said material an aqueous composition containing from about 0.025% to about 2% by weight of the total composition of a latent acid catalyst and comprising a water-insoluble pigment intimately mixed with a binder, said binder being composed substantially of the following elements: (*a*) from about 90% to about 10% by weight of a soft latex component consisting essentially of a polymerization product having from about 2% to about 10% of methacrylic acid, from about 60% to about 85% of butadiene and from about 38% to about 5% of a member selected from the group consisting of acrylonitrile and styrene, and (*b*) from about 10% to about 90% by weight of a hard latex component consisting essentially of a polymerization product of the following monomers: about 71% ethyl acrylate, about 12.5% methyl methacrylate, about 12.5% styrene, and about 4% of at least one monomer selected from the group consisting of methacrylic acid and methacrylamide, all of said percentages being by weight based on the hard latex component, and then simultaneously drying and heating said fabric at a temperature from about 180° F. to about 250° F. for from about 0.5 to about 5 minutes.

6. A composition of matter for coloring textile material, which comprises an aqueous composition containing from about 0.025% to about 2% by weight of the total composition of a latent acid catalyst and a water-insoluble pigment intimately mixed with a binder, said

binder being composed substantially of the following elements: (*a*) from about 90% to about 10% by weight of a soft latex component consisting essentially of a polymerization product having from about 2% to about 10% of methacrylic acid, from about 60% to about 85% of butadiene and from about 38% to about 5% of a member selected from the group consisting of acrylonitrile and styrene, and (*b*) from about 10% to about 90% by weight of a hard latex component comprising a polymerization product of the following monomers: from about 65% to about 74.5% ethyl acrylate, from about 10% to about 15% methyl methacrylate and from about 15% to about 10% styrene, and from about 10% to about 0.5% of at least one monomer selected from the group consisting of methacrylic acid and methacrylamide, all of the foregoing percentages being by weight.

7. A composition of matter for coloring textile material, which comprises an aqueous composition containing from about 0.025% to about 2% by weight of the total composition of a latent acid catalyst and a water-insoluble pigment intimately mixed with a binder, said binder being composed substantially of the following elements: (*a*) from about 90% to about 10% by weight of a soft latex component consisting essentially of a polymerization product having from about 2% to about 10% of methacrylic acid, from about 60% to about 85% of butadiene and from about 38% to about 5% of a member selected from the group consisting of acrylonitrile and styrene, and (*b*) from about 10% to about 90% by weight of a hard latex component consisting essentially of a polymerization product of the following monomers: about 71% ethyl acrylate, about 12.5% methyl methacrylate, about 12.5% styrene, and about 4% of at least one monomer selected from the group consisting of methacrylic acid and methacrylamide, all of said percentages being by weight.

8. A method for coloring textile material, which comprises the steps of applying to a fabric of said material an aqueous composition containing (i) from about 0.25% to about 2% by weight of the total composition of a latent acid catalyst and (ii) an aqueous dispersion of a water-insoluble pigment intimately mixed with a binder, said binder being composed susbtantially of the following elements: (*a*) from about 90% to about 10% by weight of a soft latex component consisting essentially of a polymerization product having from about 2% to about 10% of methacrylic acid, from about 60% to about 85% of butadiene and from about 38% to about 5% of a member selected from the group consisting of acrylonitrile and styrene, and (*b*) from about 10% to about 90% by weight of a water-soluble resinous condensate selected from the group consisting of polymethylated melamine-formaldehyde, polymethylated urea-formaldehyde and polymethylated ethylene-urea-formaldehyde, said condensate being dissolved in the aqueous composition and the pigment being dispersed therein, and then simultaneously drying and heating said fabric at a temperature of from about 180° F. to about 250° F. for from about 0.5 to about 5 minutes.

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