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TEXTILE PRINTING EMULSIONS COMPRISING THERMOPLASTIC RESIN LATICES DISPERSED IN SOLUTIONS OF THERMOSETTING RESINS IN ORGANIC SOLVENTS

Edward F. Armatys, New York, N. Y., assignor to Sun Chemical Corporation, Long Island City, N. Y., a corporation of Delaware

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The present invention relates to coloring compositions for textile materials, and relates more particularly to pigmented emulsions especially adapted for imprinting textile fabrics.

The art of decorating and coloring textile fabrics by printing processes was formerly restricted almost completely to the use of various dyestuff materials. However, due to the high cost of many dyes, the involved and rather expensive processes required to imprint and fix the dyes upon the fabrics, the lack of clarity or sharpness of line in the finished print, and the deficiencies of many dyestuffs as regards light fastness, resistance to washing, etc., it was sought to employ the less costly and more light fast insoluble pigment materials as the coloring matter in coloring compositions suitable for imprinting textile fabrics.

However, the use of such coloring materials for textile printing presented many new problems not encountered in the use of dyestuffs. Since pigments, unlike dyestuffs, are insoluble materials and have no affinity for textile fabrics, it is necessary that these materials be employed in printing compositions which contain therein a material which has the ability to adhere to the fibers of textile fabrics and which, in the presence of pigment materials, acts so as to bind the pigment particles to the said fibers. It was therefore attempted to imprint fabrics with printing compositions containing pigment materials dispersed in a solution, in a sutable solvent therefor, of a film forming resinous material, the solvent usually being of such character as to be readily removable from the imprinted fabric as by rapid evaporation thereof. Such coloring systems, however, were found to be unsuitable as printing compositions for textile materials since they adversely affected the character of the fabric by cementing the fibers together and, in many cases, by filling in the interstices between the fabric fibers with a solid film of binder and pigment, thereby imparting an undesirable stiffness and harshness of feel to the fabric. Further, prints made with such printing compositions were not too resistant towards the action of various dry cleaning fluids customarily employed in such cleaning operations.

The deficiencies present in the imprinted fabric occasioned by the use of such pigmented printing compositions as above described has been largely

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overcome by the use, as printing compositions for textile materials, of pigmented emulsions containing film forming resinous materials as the binder component thereof, which resinous materials are characterized by their abiilty to set to a solvent insoluble condition by a suitable thermal treatment. These compositions are usually made and employed in the form of water-in-oil or oil-in-water emulsions, the oil phase generally comprising a pigmented solution or dispersion of a film forming thermosetting resinous material in solvents substantially immiscible with water. Since these compositions are applied to textile fabrics in the form of an emulsion, the resinous binder material which carries the pigment is deposited upon the fabric in the form of a discontinuous film, so that instead of completely covering the fabric structure with a continuous film of binder and pigment, only the individual fibers which make up the fabric structure are found to be coated with a film of binder and pigment. Upon application of such pigmented emulsions to textile fabrics by the conventional printing processes, and upon subsequent treatment of the imprinted fabrics at temperatures sufficient to effect setting of the resinous binder material upon the fabric to a solvent insoluble condition, a printed fabric is obtained which is lacking in the stiffness obtained by the use of pigmented resin solutions alone and which has a hand or feel to the touch substantially the same as the unprinted fabric.

However, fabrics printed or colored with such pigmented emulsions usually had one deficiency which caused serious concern among textile printers. This is the effect known as crocking, or the tendency of the color of the printed fabric to rub off onto other materials, such as other fabrics, when a sliding contact is made therebetween. As is evident, this is a highly objectionable characteristic in colored fabrics since in washing and cleaning operations, or even in ordinary use, such fabrics would tend to discolor other fabrics which came into contact therewith. Since such condition in the imprinted fabric tended to offset the advantages derived from the use of such pigmented emulsions as printing and coloring compositions for textile materials, it was desired to eliminate this condition as far as possible without sacrificing any of the other advantages obtained by the use thereof.

By the present invention there are provided

pigmented emulsions especially adapted for imprinting and coloring textile materials by the conventional printing processes employed in the textile industry whereby crocking in the finished print is substantially eliminated. The use of the pigmented emulsions of the present invention in the printing of fabrics does not materially change the hand of the fabric imprinted, nor does it cause any stiffening or excess weighting in the printed fabric. When the imprinted fabric is subjected to a subsequent thermal treatment as hereinafter set forth, the imprinted fabric is highly resistant toward fading or discoloration as, for example, by the loss of pigment due to the effect of washing or laundering operations thereon, or due to the effect which the solvents ordinarily employed in dry cleaning operations may have upon the fabric.

The textile printing compositions of the present invention are pigmented water-in-oil emulsions in which the discontinuous or aqueous phase comprises a latex of a synthetic thermoplastic resinous material, and in which the continuous or oil phase comprises a solution of a thermosetting resinous material in organic solvents which are substantially non-solvents for the resinous materials of the aqueous phase, the said emulsion also containing a plasticizer for the resinous material of the aqueous phase in certain definite proportions as hereinafter outlined.

The term "latex" as employed in the present invention refers to stable colloidal dispersions of a thermoplastic resinous material in water, the dispersed resin being present therein in the form of finely divided discrete particles. The resins which have been found to be particularly useful in providing the textile printing compositions of the present invention when employed in the form of a latex are the polymers of vinyl chloride, the copolymers of vinyl chloride and vinyl acetate, and the copolymers of vinylidene chloride and acrylonitrile.

The most satisfactory binder materials for utilization as the binder material of the oil phase of the emulsions of the present invention are the alcoholated melamine-formaldehyde thermosetting resinous condensates which comprise the reaction product of melamine, formaldehyde and an alcohol such as butyl alcohol or capryl alcohol, reacted to a point where the condensate is soluble in organic solvents or in mixtures thereof, such as a mixture of equal parts of mineral spirits and butyl alcohol. Also suitable for such use are alkyd-modified melamine-formaldehyde thermosetting resinous condensates, as for example, a melamine-formaldehyde resinous condensate modified with a drying oil-modified glycerol-phthalate resin.

The solvent medium of the oil phase of the printing emulsions of the present invention may comprise any of the ordinary hydrocarbon solvents, both aliphatic and aromatic, and also any of the common terpene solvents, and usually comprises mixtures of these solvents together with certain of the lower aliphatic alcohols since the thermosetting resinous materials mentioned above are usually provided and employed as solutions of the resins in mixtures of either aliphatic or aromatic solvents with various alcohols such as butanol or capryl alcohol.

The plasticizers for the resinous material of the aqueous phase of the emulsions are non-volatile liquid organic compounds which are immiscible with water and generally miscible with the common organic solvents and thinners employed in the emulsions of the present invention. Examples of plasticizers which may be employed in the compositions of the present invention, are tricresyl phosphate, triphenyl phosphate, dibutyl phthalate, dioctyl phthalate and dibutyl sebacate. The plasticizers are employed in the compositions of the present invention in certain definite amounts such amounts being based upon the amount of resinous material present in the aqueous phase of the emulsion. For best results, the plasticizer is employed in the ratio of from approximately one to approximately two parts by weight of plasticizer to approximately one part by weight of the resinous material of the aqueous phase; that is, the resinous material of the latex dispersion. The use of plasticizer in amounts substantially beyond the limits specified has an adverse effect upon the end results obtained in the finished product, too small an amount of plasticizer resulting in a rather stiff and brittle film of binder and pigment, and too large an amount of plasticizer providing a binder-pigment film which is too soft to prevent rub-off of the pigment particles from the imprinted fabric.

As pigment coloring material there may be utilized either dry colors or dispersed colors; that is, colors wherein the pigment has been dispersed in a solvent suitable for use as a part of the solvent medium of the oil phase of the emulsion. In practicing the present invention, it has been found that the amount of pigment coloring material utilized in the compositions of the present invention should not exceed a ratio of approximately 1.5 parts by weight of pigment to one part by weight of combined resinous binders; that is, the weight of both the thermosetting resinous binder of the oil phase and that of the thermoplastic resinous material of the aqueous phase combined. Further, the ratio of the thermoplastic resinous material to the thermosetting resinous binder of the oil phase of the printing compositions of the present invention should preferably be maintained within a range of from approximately one to approximately two parts by weight of the said thermoplastic resinous material to one part by weight of the said thermosetting resinous binder of the oil phase of the emulsions.

In providing compositions in accordance with the present invention, it has been found to be completely satisfactory and economical to furnish a concentrate which subsequently can be diluted prior to use to furnish a composition with the desired body for the particular operation by which such materials are applied to the fabric. In operations where a concentrate is furnished the user may dilute such concentrate with a suitable colorless emulsion, until a composition of the necessary flow properties and containing the amount of coloring material necessary for a particular printing operation has been obtained. Therefter such printing may be effected by utilization of the equipment ordinarily employed in textile printing operations. When printing is completed, the colored fabric then is treated at elevated temperatures of the order of 300–350° F. for approximately one minute to effect removal of the volatile material present and to complete the setting of the coloring material upon the fabric.

A colorless water-in-oil emulsion (clear), suitable for diluting the pigment concentrate of the present invention, is provided as follows. A clear concentrate is prepared by emulsifying, as by stirring under high speed agitation conditions,

the following materials in the proportions set forth.

Example 1

	Parts by weight
Drying oil-modified glycerol-phthalate resin (40% resin solids in mineral spirits)	70
Xylol	5
Ammonium sulfate	10
Dialyzed waste sulfite liquor of U. S. P. No. 2,201,812	10
Water	5
	100

The clear concentrate provided as in Example 1 is then diluted and emulsified with Varsol and water in the proportions set forth in Example 2 to provide a water-in-oil emulsion suitable for diluting the pigment concentrate hereinafter set forth to the degree of printing consistency and shade of color desired.

Example 2

	Parts by weight
Clear concentrate of Example 1	2.5
Varsol	22.5
Water	75.0
	100.0

The pigment concentrates of the present invention are water-in-oil emulsions in which the aqueous phase comprises an aqueous colloidal dispersion of a thermoplastic resinous material in latex form and in which the oil phase comprises a solution of a thermosetting resinous binder material in substantially water-immiscible organic solvents. The pigment concentrates also contain a plasticizer for the resinous material of the aqueous phase and, depending upon the manner in which the emulsions are prepared, may take two distinct forms. That is, the plasticizer may be a component of the oil phase of the emulsion since the plasticizers employed are miscible with the organic solvents constituting the oil phase of the emulsion, or the plasticizer may be present in the aqueous phase of the emulsion in dispersed form. The first form of emulsion, wherein the plasticizer constitutes a part of the oil phase, may be had by incorporating the plasticizer in the materials which constitute the oil phase of the emulsion before emulsification of the same with the latex is accomplished. The second form of emulsion, wherein the plasticizer is present in dispersed form in the aqueous phase thereof, is had when a plasticizer-water emulsion is emulsified with the remainder of the materials constituting the oil phase of pigment concentrates of the present invention.

Illustrative examples of the pigment concentrates of the present invention are given below. In preparing such concentrates, satisfactorily all of the material may be charged to a high speed mixer and agitated until the requisite dispersion and emulsification is completed. To obtain the required degree of pigment dispersion when a dry color is employed as the coloring material of the emulsion, the mixture should be passed through a roller mill or preferably be admixed and milled in a ball mill or pebble mill.

Example 3

	Parts by weight
Latex containing polyvinyl chloride (55% resin solids in water)	10.0
Tricresyl phosphate	11.0
Butylated melamine-formaldehyde resinous condensate (50% resin solids in 25 mineral spirits, 25 butanol)	10.0
Amyl alcohol	10.0
Turpentine	46.0
Phthalocyanine blue pigment	13.0
	100.0

Example 4

	Parts by weight
Latex containing a vinyl chloride-vinyl acetate copolymer, containing approx. 3% vinyl acetate (55% resin solids in water)	10.0
Dioctyl phthalate	12.0
Butylated melamine-formaldehyde resinous condensate (50% solids in 25 mineral spirits, 25 butanol)	6.0
Amyl alcohol	10.0
Turpentine	50.0
Phthalocyanine blue pigment	12.0
	100.0

Example 5

	Parts by weight
Latex containing a vinylidene chloride-acrylonitrile copolymer (56% resin solids in water)	10.0
Tricresyl phosphate	5.0
Butylated melamine-formaldehyde resinous condensate (50% resin solids in 25 mineral spirits, 25 butanol)	6.0
Turpentine	67.0
Phthalocyanine blue pigment	12.0
	100.0

Example 6

	Parts by weight
Latex containing a vinyl chloride-vinyl acetate copolymer, containing approx. 3% vinyl acetate (55% resin solids in water)	12.0
Tricresyl phosphate	7.0
Butylated melamine-formaldehyde resinous condensate (50% resin solids in 25 mineral spirits, 25 butanol)	10.0
Amyl alcohol	10.0
Turpentine	39.0
Water	10.0
Phthalocyanine blue pigment	12.0
	100.0

Following the procedure hereinbefore outlined, the pigment concentrates of the above illustrative examples provide water-in-oil emulsions in which the plasticizer constitutes a part of the continuous or oil phase of the emulsion. These emulsions may be diluted to any degree desirable with the clear emulsion of Example 2 to provide the printing compositions of the present invention.

As stated hereinbefore, pigment concentrates of the water-in-oil type of emulsion may be had by incorporating the plasticizer into the mixture to be emulsified in the form of an oil-in-water emulsion. That is, an oil-in-water emulsion is prepared in which the plasticizer constitutes the dispersed or inner phase and in which water constitutes the outer phase. The plasticizer, in emulsion form, is then admixed with the remainder of the material employed in preparing

the pigment concentrates of the present invention and the whole is emulsified by the procedure hereinbefore outlined for preparing the said concentrates. By this method, the plasticizer remains dispersed in the water phase of the finished emulsion.

In preparing a pigment concentrate of the type above described, a plasticizer emulsion is first prepared. A plasticizer emulsion suitable for use in the pigment concentrates of the present invention is prepared, for example, by mixing, under high speed agitation conditions, a solution of 1.25 parts by weight of oleic acid in 65 parts by weight of dioctyl phthalate with a solution of 0.25 part by weight of ammonia in 33 parts by weight of water. The resultant product is an oil-in-water emulsion in which the plasticizer constitutes the dispersed phase. Such emulsion may then be employed together with the material set forth in the following illustrative example to form a pigment concentrate in accordance with the disclosure of the present invention.

Example 7

	Parts by weight
Latex containing polyvinyl chloride (55% solids in water)	10.0
Dioctyl phthalate plasticizer emulsion as described above	15.0
Butylated melamine-formaldehyde resinous condensate (50% resin solids in 25 mineral spirits, 25 butanol)	5.0
Amyl alcohol	12.0
Turpentine	46.0
Phthalocyanine blue pigment	12.0
	100.0

The above concentrate may also be diluted with the clear emulsion of Example 2 to provide printing compositions for textile materials having the characteristics of those of the present invention.

By the use of a latex dispersion of the thermoplastic resinous materials herein set forth as the aqueous phase of the pigmented emulsions of the present invention, printing compositions for textile materials are provided whereby crocking in the finished print is substantially eliminated. Apparently the use of such materials in the form employed in the compositions of the present invention in some manner improves the pigment binding properties of those emulsion systems. Just why the latex dispersion should have such effect upon the finished print may possibly be explained by the fact that since the resinous material of the latex dispersion is not only present in the printing composition in a colloidally suspended form, but is also part of the discontinuous phase of the said compositions, upon application of the said printing compositions to textile fabrics as by the conventional printing processes, the thermoplastic resinous material is deposited upon the fabric in the form of finely divided discrete particles interspersed throughout the pigmented thermosetting resinous film. It may be that upon subsequent heat treatment of the imprinted film, the plasticizer present in the imprinted film acts as a flux whereby the dispersed thermoplastic resin softens and flows together to form a protective film over or about the pigment particles and the thermosetting resinous binder materials which bind the pigment particles to the fabric. However, such explanation is merely theoretical and is not to be construed as a teaching of the actual manner in which the improved pigment binding properties are secured with the compositions of the present invention.

While the above products and processes constitute preferred embodiments of the present invention, changes may be made therein without departing from the scope of the present invention as defined in the appended claims.

What is claimed is:

1. A coloring composition for textile materials comprising pigment dispersed in an emulsion containing a discontinuous phase comprising an aqueous colloidal dispersion of a thermoplastic resinous material selected from the group consisting of a homopolymer of vinyl chloride, a copolymer of vinyl chloride and vinyl acetate, and a copolymer of vinylidene chloride and acrylonitrile, and a continuous phase comprising a thermosetting resinous binder selected from the group consisting of alcoholated melamine-formaldehyde resinous condensates and alkyd-modified melamine-formaldehyde resinous condensates in organic solvents which are substantially non-solvents for the resinous material of the aqueous phase, said emulsion containing a non-volatile liquid plasticizer for the resinous material of the discontinuous phase, the ratio of plasticizer to the resinous material of said discontinuous phase being within the range of from approximately 1 to approximately 2 parts by weight of plasticizer to 1 part by weight of said resinous material.

2. A coloring composition for textile materials comprising pigment dispersed in an emulsion containing a discontinuous phase comprising an aqueous colloidal dispersion of a homopolymer of vinyl chloride, and the continuous phase comprising a thermosetting resinous binder selected from the group consisting of alcoholated melamine-formaldehyde resinous condensates and alkyd-modified melamine-formaldehyde resinous condensates in organic solvents which are substantially non-solvents for the said polymer of vinyl chloride, said emulsion containing a non-volatile liquid plasticizer for said polymer of vinyl chloride, the ratio of plasticizer to said polymer of vinyl chloride being within the range of from approximately 1 to approximately 2 parts by weight of plasticizer to one part by weight of said polymer of vinyl chloride.

3. A coloring composition for textile materials comprising pigment dispersed in an emulsion containing a discontinuous phase comprising an aqueous colloidal dispersion of a copolymer of vinyl chloride and vinyl acetate, and a continuous phase comprising a thermosetting resinous binder selected from the group consisting of alcoholated melamine-formaldehyde resinous condensates and alkyd-modified melamine-formaldehyde resinous condensates in organic solvents which are substantially non-solvents for the said copolymer of vinyl chloride and vinyl acetate, said emulsion containing a non-volatile liquid plasticizer for said copolymer of vinyl chloride and vinyl acetate, the ratio of plasticizer to said copolymer of vinyl chloride and vinyl acetate being within the range of from approximately one to approximately two parts by weight of plasticizer to one part by weight of said copolymer of vinyl chloride and vinyl acetate.

4. A coloring composition for textile materials comprising pigment dispersed in an emulsion containing a discontinuous phase comprising an aqueous colloidal dispersion of a copolymer of vinylidene chloride and acrylonitrile, and a continuous phase comprising a thermosetting resinous binder selected from the group consisting of alcoholated melamine-formaldehyde resinous

condensates and alkyd-modified melamine-formaldehyde resinous condensates in organic solvents which are substantially non-solvents for the said copolymer of vinylidene chloride and acrylonitrile, said emulsion containing a non-volatile liquid plasticizer for said copolymer of vinylidene chloride and acrylonitrile, the ratio of plasticizer to said copolymer of vinylidene chloride and acrylonitrile being within the range of from approximately one to approximately two parts by weight of plasticizer to one part by weight of said copolymer of vinylidene chloride and acrylonitrile.

5. A coloring composition for textile materials comprising pigment dispersed in an emulsion containing a discontinuous phase comprising an aqueous colloidal dispersion of a thermoplastic resinous material selected from the group consisting of a homopolymer of vinyl chloride, a copolymer of vinyl chloride and vinyl acetate, and a copolymer of vinylidene chloride and acrylonitrile, and a continuous phase comprising a butylated melamine-formaldehyde resinous condensate in a solvent mixture comprising mineral spirits and butanol, said emulsion containing a non-volatile liquid plasticizer for the resinous material of the discontinuous phase, a ratio of plasticizer to the resinous materials of said discontinuous phase being within the range of from

approximately 1 to approximately 2 parts by weight of plasticizer to 1 part by weight of said resinous material.

6. A coloring composition for textile materials comprising pigment dispersed in an emulsion containing a discontinuous phase comprising an aqueous colloidal dispersion of a copolymer of vinyl chloride and vinyl acetate, and a continuous phase comprising a butylated melamine-formaldehyde resinous condensate in a solvent mixture comprising mineral spirits and butanol, said emulsion containing a non-volatile liquid plasticizer for said copolymer of vinyl chloride and vinyl acetate, the ratio of plasticizer to said copolymer of vinyl chloride and vinyl acetate being within the range of from approximately 1 to approximately 2 parts by weight of plasticizer to 1 part by weight of said copolymer of vinyl chloride and vinyl acetate.

EDWARD F. ARMATYS.

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