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METHOD OF COLORING MATERIAL

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This invention relates to printing and coloring of materials and more particularly, to the coloring and printing of textile fabrics.

The printing and dyeing of fabrics has usually been effected by treatment of the fabric with a printing paste or a dye bath in which a soluble or insoluble form of coloring matter is dispersed. Another procedure is to print or impregnate a fabric with one component capable of forming a color and then printing with the other component which reacts therewith under suitable conditions to produce the color. These processes are generally wasteful of color since usually only a portion thereof adheres to the fiber. Frequently, these processes do not give as sharp outlines as might be desired due to creeping or bleeding of the print. In the case where a dye bath is used, it is difficult to exhaust all of the color from the bath.

It has been proposed in the past to print materials with lacquers, that is to say, solutions of various resins either natural or synthetic in organic solvents, coloring matter being dispersed through the solution or dissolved therein. Lacquer printing avoids some of the disadvantages of ordinary printing procedures in that sharp prints are possible and there is little or no waste of coloring matter. This also permits the use of pigment colors which cannot be printed in the ordinary manner. While lacquer printing has the above advantages, it has not been very widely used because of several defects, one being that the film which is formed on evaporation of the lacquer solvent is so stiff that it binds fibers of textile fabrics together to produce a final product that is not flexible and has a harsh feel. The lacquer also produces a surface gloss which is undesirable in many cases. The organic solvents used in the lacquers also add to the expense and introduce a fire hazard.

It has also been proposed to color textile fabrics by means of a colored dispersion or emulsion of the water-in-oil type in which the aqueous dispersed phase is in the form of relatively coarse droplets materially larger than 50 microns. When such a water-in-oil emulsion is used, it is possible to obtain printing or coloring but this procedure is subject to similar disadvantages as are inherent in lacquer printing, that is to say, there is a bridging from fiber to fiber which renders the textile fabric relatively stiff and with a harsh feel.

The colored emulsion of the present invention should not be confused with stiff pastes which are of the water-in-oil dispersion type which have been used for stencil purposes. These pastes are so stiff that while they can be brushed or forced through a stencil and give sharp stencil designs, they cannot be used satisfactorily on textile printing equipment or in dyeing equipment.

According to the present invention we have found that it is possible to color or print fabrics by means of water-in-oil emulsions in which a resin or organic pigment or mixture is dissolved in a suitable solvent and coloring matter or pigment uniformly dispersed therein, followed by emulsification of the water, preferably with the aid of suitable emulsifying agents, to produce an extremely fine emulsion which can be still further improved by homogenizing with a colloid mill. The emulsion thus produced has aqueous droplet size of less than 50 microns and in the preferred compositions, less than 5 microns. Where a water-soluble color is used this may be introduced with the water phase instead of in the resin solution.

When textile fabrics are colored or printed with the extremely fine water-in-oil emulsions of the present invention, uniform level coloring or sharp prints are obtained but the dispersing medium is so uniformly separated by minute droplets of aqueous phase that on drying and coloring there is little or no bridging from fiber to fiber and as a result the fabric remains flexible and with a desirable soft hand. It is an important advantage of the present invention that the color can be fixed in or on the fibers of the fabric by simply drying at moderate temperatures. No chemical development is required, nor is it necessary to use a very high temperature. This permits a coloring of practically all textile fibers which will withstand moderate temperatures such as for example, animal fibers of the character of wool or silk, synthetic fibers, cellulose fibers, and the like. The present invention can also be applied to fibers which are relatively heat sensitive such as vinyl halide-vinyl acetate copolymers. In the case of such fibers, however, care should be taken that a lower temperature and longer time of curing be employed in order to prevent damage to the fiber by the use of a temperature as high as would be safe with other fibers which are less heat sensitive.

Another important advantage of the present invention is that the range of coloring matter is extremely wide. Thus it is possible to use insoluble inorganic or organic pigments which can be uniformly dispersed and which would otherwise be inapplicable to printing or coloring of fabrics or fibers. Organic soluble dyes may be used or water-soluble dyes may be used. In every case sharp outlines in the case of prints, or uniformity and levelness in the case of coloring is obtained without stiffness or harsh hand. These advantages are obtained with important saving of steps over the ordinary dyeing and printing procedures which involve such steps as ageing, development of color, washing after development, and the like. At the same time finishes are obtained which show good light fastness and a resistance to crocking, washing, drycleaning, and the like.

The present invention is not concerned with the use of any particular pigment, organic-soluble or water-soluble dye and this is one of the outstanding advantages because it opens up the field of textile coloring and printing to many coloring matters which could not be successfully employed hitherto. Thus, for example, ultramarine, phthalocyanine pigments, lake colors such as phosphotungstic and phosphomolybdic lakes of basic dyestuffs, azo pigments such as diazo compounds coupled onto anilides of beta-hydroxy naphthoic acid, and similar coloring materials which do not have anaffinity for the fiber can be employed, whereas in the procedures which have been customary up to the present time such materials were not applicable. At the same time coloring matters which do have affinity for the fibers of the textiles may be employed and the advantages of the coating of the individual fibers with thin film of the resin are retained. Another advantage of the present invention is that it is possible to use otherwise incompatible colors. For example, in the prior processes it would not be possible to use mixtures of colors which must be developed with pigments which do not need development. In the present case any suitable mixture may be employed provided only that it can be satisfactorily dispersed in the finely homogenized water-in-oil emulsions which are employed in the present invention. It is also possible to use mixtures of organic-soluble colors and water-soluble colors, the one dispersing in oil phase, the other dispersed in the water phase. Many valuable new coloring effects can be produced in this manner.

The present invention is not limited to any particular resins. On the contrary, any suitable resins or organic polymerides which can be dissolved in organic solvents and which will set or cure at moderate temperatures are useful. Thus, for example, drying oil acid modified alkyd resins may be employed as can organic soluble urea aldehyde, and other resins.

In general it is desirable to effect dispersion or formation of the water-in-oil emulsion with the aid of emulsifying agents because in this manner it is easier to produce homogeneous emulsions with many types of material. The invention is not limited to the use of emulsifying agents, however, much less is it limited to the use of any particular emulsifying agents. We have found, however, that emulsifying agents of the ammonium or amine soap type are very suitable such as for example the oleates of ammonia or amines, but other types of emulsifying agents capable of producing water-in-oil emulsions may be employed such as, for example, diamyl ethoxyaspartate hydrochloride or distearylethoxy propanolamine acetate.

The invention will be described in greater detail in conjunction with the following specific examples which are typical illustrations of the invention but which are not intended to limit the invention to the details therein set forth. In the following examples, all parts are by weight.

Example 1

33 parts of a polymer of chloroprene are dissolved in 157 parts of toluene. This solution is mixed by means of a small high speed stirrer with 118 parts of a dispersion consisting of 12 parts copper phthalocyanine, 12 parts of diethanolamine oleate and 94 parts of water. The resulting mixture is homogenized by high speed stirring and passage through a colloid mill, which results in a water-in-oil type of emulsion. 150 parts of this emulsion are then diluted, using high speed agitation, with 75 parts of toluene. A uniform blue colored emulsion results which pours easily, possesses an aqueous dispersed phase with all particles 5 microns or smaller, and is of good printing viscosity. This emulsion is now placed in the paste well of a print machine and applied to an engraved copper roll. Cotton fabric is then passed over the engraved roll and clear, strong, blue prints obtained have an excellent hand. These cotton prints are dried for one-half hour at a temperature of approximately 50° C. and heat-treated for 5 minutes at a temperature of 120° C. The resulting prints are resistant to both wet and dry crocking and show remarkable washfastness to Test No. 4 of the American Association Textile Color and Chemists Year Book 1939 (AATCC).

Example 2

160 parts of an oxidizing oil-modified glycerol phthalate resin are dissolved in 110 parts of a light, highly-aromatic, hydrogenated petroleum fraction, boiling range 275°–346° F. This solution is intimately mixed on a three-roller ink mill first with 160 parts of a 50% solution of an alkylated urea resin prepared by refluxing octyl alcohol with dimethyl urea and then with a wet presscake, containing 80 parts of real pigment made by coupling 4-nitro-2-amino anisol with m-nitranilide of 2-hydroxy-3-naphthoic acid. In this process of mixing, the water in the color press cake separates and is run off. 100 parts of the resulting pigment color base are mixed by means of a small rapid stirrer with 100 parts of the hydrogenated petroleum solvent described above and with a solution made up by dissolving 1.6 parts of morpholine oleate in 100 parts of water. The crude emulsion thus prepared is homogenized to give a uniform, blue emulsion that pours easily. It possesses an aqueous dispersed phase with all particles well under 5 microns in diameter.

This emulsion gives clear, strong, red prints on both cotton and regenerated cellulose, the latter delustered with titanium dioxide (pigmented rayon). These prints are dried for one-half hour at a temperature of approximately 50° C. and heat-cured for 5 minutes at a temperature of 150 C. The resulting prints are resistant to both wet and dry crocking and show excellent washfastness to Test No. 4 of the AATCC.

Both pigmented rayon and cotton fabrics can be colored by immersing the fabrics in the emulsion and then passing through suitable squeeze rolls. After drying, the impregnated fabrics for one-half hour at approximately 50° C. and heating for an additional 5 minutes at 150° C., uniformly red colored fabrics are obtained that show unusual washfastness.

Example 3

75 parts of chlorinated rubber the 10 centipoises

grade, are dissolved in 168 parts of xylene. This solution is intimately mixed on a three-roller ink mill with 112 parts of an alkyd resin solution of an oxidizing oil-modified glycerol phthalate resin which contains 75 parts of alkyd resin, 28 parts of the hydrogenated petroleum solvent described in Example 2 and 9 parts of butanol and finally with 50 parts of a yellow pigment, ortho nitro para toluene azo acetoacetanilide (Schultz 84). 100 parts of the resulting colored base are further diluted with a solution composed of 1.5 parts of aluminum stearate in 70 parts of xylene. This cut base is then mixed, by means of a small high speed stirrer, with a solution containing 0.5 part of cobalt chloride and 80 parts of water. The resulting crude emulsion is further thoroughly homogenized by a suitable colloid mixer to give a water-in-oil system that pours easily.

To illustrate the wide variation in water content and viscosity which it is possible to attain with this system and still be useable for textile purposes, 100 parts of the emulsion described above and designated as A, are homogenized with 28 parts of water. 85 parts of the resulting emulsion, which is designated as B, are homogenized with 27 parts of water to given emulsion C. All three emulsions are water-in-oil systems that pour easily. The particle size of the dispersed phase in all three emulsions is well under 5 microns. All give clear, well-defined, strong, yellow prints on both pigmented rayon and cotton. When all the prints are dried at a temperature between 40°–60° C. for one-half hour and heat-treated at 150° C. for 5 minutes, the resulting prints are resistant to both wet and dry crocking, and show good washfastness.

Example 4

100 parts of low viscosity cellulose acetopropionate are dissolved in 315 parts of butyl acetate. 180 parts of this solution are further diluted with a solution containing 1.5 parts of triethylene tetramino oleate dissolved in 75 parts of butyl acetate. The resulting solution is thoroughly mixed by means of a small high speed stirrer with a solution containing 15 parts of a water soluble color prepared by coupling 4-amino azo benzene-4′-sodium sulfonate to the sodium salt of 6-benzoyl amino-1-naphthol-3-sulfonic acid (C. I. 278) dissolved in 100 parts of water. This crude emulsion is homogenized with a suitable colloid mixer to give a water-in-oil emulsion that pours easily. Clear, strong, pink prints are produced by this emulsion on both pigmented rayon and cotton.

To reduce the cellulose acetopropionate content of the emulsion, 100 parts of water and 50 parts of butyl acetate are further homogenized with 100 parts of the emulsion. This diluted emulsion is a water-in-oil system that also pours easily. The particle size of the dispersed phase is 1 micron or less. It gives clear, strong, pink prints on both pigmented rayon and cotton. Both pigmented rayon and cotton fabrics are colored by immersing the fabrics in the emulsion and then passing them through suitable squeeze rolls. Both the prints and the completely colored fabrics have a good hand and, after being dried for one-half hour at a temperature of approximately 50° C. and heat-treated for 5 minutes at a temperature of 150° C. are practically untouched by dry cleaning.

Example 5

89 parts of milled rubber are dissolved in 815 parts of toluene. 240 parts of this solution are intimately mixed on a three-roller ink mill with 44 parts of a wet presscake containing 8 parts of a yellow pigment prepared by coupling 2 molecules of 2-amino-4-chlorotoluene with one molecule of bis-acetoacetbenzidide until homogeneously pigmented. 124 parts of the pigmented base are then diluted with a solution containing 336 parts of toluene and 3 parts of aluminum stearate. This diluted base is stirred by means of a small high speed stirrer with 350 parts of water and the resulting crude emulsion homogenized to give a water-in-oil emulsion that pours easily. The particle size of the dispersed phase of the emulsion is well under 50 microns. It gives clear, strong, yellow prints on both pigmented rayon and cotton that have an excellent hand. After being dried for one-half hour at a temperature of approximately 50° C. and heat-treated for 5 minutes at 150° C., the prints are resistant to both wet and dry crocking and show excellent washfastness to Wash Test No. 4 of the AATCC.

Example 6

150 parts of a wet presscake containing 60 parts of a phosphotungstic lake of methyl violet (C. I. 680) are intimately mixed until completely homogeneous on a three-roller ink mill with:

113 parts of a solution of a drying oil-modified glycerol phthalate resin which contains 90 parts of alkyd resin, 16 parts of the hydrogenated petroleum solvent described in Example 2, 180 parts of an alkylated urea resin prepared by refluxing dimethylol urea with butyl alcohol and dissolved in butanol and xylene, and 30 parts of dibutyl phthalate.

Sixty-four parts of this colored resin base are handstirred with a solution prepared by dissolving 1.5 parts of morpholine oleate in 70 parts of the hydrogenated petroleum solvent described in Example 2, and the resulting mixture then stirred by means of a small high speed stirrer with 165 parts of water. The final mixture is homogenized with an Eppenbach Homo-mixer to give a water-in-oil emulsion that pours easily. The particle size of the dispersed phase of this emulsion is well under 5 microns. It produces beautiful, violet prints on both pigmented rayon and cotton that are strong and well-defined and of good hand.

Both pigmented rayon and cotton fabrics can also be completely colored with this emulsion by passing the fabrics through the emulsion and then through rubber squeeze rolls. After drying the printed and colored fabrics for one-half hour at a temperature of approximately 50° C. and then heat-curing for at least 5 minutes at a temperature of 150° C., finished products are obtained that are resistant to both wet and dry crocking and show good washfastness to Wash Test No. 4 of the AATCC.

Example 7

22 parts of an oxidizing oil acid modified alkyd resin are dissolved in 60 parts of xylene. To this solution are added 0.5 part of a solution containing 33 parts of ethyl cellulose, 90 parts of pine oil and 16.7 parts of dibutyl phthalate. To the resulting mixture are added 1 part of aluminum stearate and 5 parts of an oil soluble color prepared by condensing benzaldehyde with ortho-toluidine and tetrazotizing and coupling this product with beta-naphthol and with phenyl-

methyl pyrazolone. This final solution is then mixed with 185 parts of water by means of a small high speed stirrer and the resulting mixture homogenized. The resulting emulsion is a water-in-oil system that is very fluid. To increase the viscosity, 50 parts of water are further homogenized with 150 parts of the emulsion and the result is still a water-in-oil system that pours easily. This emulsion produces clear, strong red prints on both pigmented rayon and cotton that have a good hand. The prints can be dried and set by employing temperatures up to 150° C. The finished prints are resistant to both wet and dry crocking and show fair washfastness.

In the claims the term "coloring" is used in the generic sense to include applying color to a textile material either over the whole surface thereof or on restricted portions when it is desired to print a design.

We claim:

1. A method of producing a colored emulsion of the water-in-oil type suitable for coloring of textiles which comprises dispersing a film forming material capable of setting or curing at moderate temperatures in an organic solvent, dispersing therein coloring matter, adding an aqueous material and effecting emulsification with sufficient completeness so that the droplets of dispersed aqueous phase do not exceed 5 microns in diameter.

2. A method of producing a colored emulsion of the water-in-oil type suitable for coloring of textiles which comprises dispersing a film forming material capable of curing at moderate temperatures in an organic solvent, dispersing therein coloring matter, adding an aqueous solution of a water-soluble coloring matter and effecting emulsification with sufficient completeness so that the droplets of dispersed aqueous phase do not exceed 5 microns in diameter.

3. A color emulsion of the water-in-oil type suitable for coloring of textiles comprising a continuous phase of a dispersion of film forming material capable of setting or curing at moderate temperatures and a coloring matter in an organic solvent and a disperse phase of aqueous material, the droplets of the disperse phase not exceeding 5 microns in diameter.

4. A color emulsion of a water-in-oil type suitable for coloring of textiles comprising a continuous phase of a dispersion of an alkyd resin capable of setting or curing at moderate temperatures and a coloring matter in an organic solvent and a disperse phase of aqueous material, the droplets of the disperse phase not exceeding 5 microns in diameter.

5. A color emulsion of the water-in-oil type suitable for coloring of textiles comprising a continuous phase of a dispersion of an organic soluble aminoplast capable of setting or curing at moderate temperatures and a coloring matter in an organic solvent and a disperse phase of aqueous material, the droplets of the disperse phase not exceeding 5 microns in diameter.

6. A color emulsion of the water-in-oil type suitable for coloring of textiles comprising a continuous phase of a dispersion of an organic soluble urea formaldehyde resin capable of setting or curing at moderate temperatures and a coloring matter in an organic solvent and a disperse phase of aqueous material, the droplets of the disperse phase not exceeding 5 microns in diameter.

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