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FINISHING PIGMENT-RESIN COLORED FABRICS

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This invention relates to the permanent finishing of textiles dyed or printed with pigment-colored compositions.

Printing and dyeing of fabrics by the use of pigment-containing compositions has achieved an important position in the textile finishing trades. This is due to the fact that certain colors and effects can be obtained with pigments that are impossible or impractical with true dyes. Unfortunately, however, these pigments themselves must be applied to the fabric in conjunction with some material which serves as a vehicle in applying the pigments and a binder to fix the pigments in place after they are applied.

One of the earlier proposed procedures was to combine the pigment with a lacquer, that is to say a solution of one or more natural resins, synthetic resins, or cellulose esters or cellulose ethers in an organic solvent in which the pigment was dispersed. In use, this lacquer-pigment process was found to avoid many of the disadvantages of ordinary printing with dyes and to enable the production of sharp prints using substantially any desired pigment.

However, the process was not found to be as universally practicable as had been anticipated. Lacquer-coloring was found to have a serious defect, inherent in the nature of the product, which prevented the process from becoming very widely used. The lacquer film which was formed on evaporation of the solvent was so stiff that it bound the textile fibers together to produce a colored fabric which was not flexible and had a harsh feel. In addition, the use of lacquer also produced a surface gloss which in many cases was highly undesirable. It was found that these lacquer prints could be improved in pliability if a sufficient amount of plasticizer was used. But this impaired the fastness properties without producing any decrease in the continuity in the lacquer film and increased the expense of carrying out the process.

In order to overcome the objectionable features associated with the use of lacquers, particularly the stiff hand or harsh feel of the finished product, emulsion-coloring was developed. These emulsions are commonly of two types, the oil-in-water and the water-in-oil types. Each of these has certain advantages over the other but both enable the production of sharp prints and fixed coloring without forming the continuous film which appears to be responsible for the undesirable stiffness and gloss inherent in lacquer-pigment colored fabrics. As a result, the use of emulsions, particularly in printing, has to a large extent replaced other types of compositions where the color or effect produced is due to the use of a pigment.

Unfortunately, however, emulsion prints and dyes, while superior to those produced from lacquer-type compositions, were also found to possess certain defects which are objectionable from a commercial point of view. Emulsion-deposited pigments, particularly those from a water-in-oil type emulsion, are quite subject to both wet and dry crocking.

Nor were the fabrics which had been colored by emulsion-deposited pigments as washfast as is desirable in materials to be used for many purposes. For example, fabrics colored by the use of pigments in this way, when subjected to standard wash and crock tests were still found to be inferior as compared with fabrics colored with vat dyes, stabilized azoic dyes or the like.

In the past, considerable effort has been expended in attempting to overcome these objectionable tendencies of emulsion-deposited pigments to crock and wash down. These proposed solutions to the problem have generally proceeded along one or the other of two lines. In some cases, attempts were made to pre-treat the fabric with a material, such as a resin, which would mechanically or chemically bond the pigment to the fabric. In other cases, attempts were made to include some similar bonding agent in the composition from which the color was deposited.

Many of these procedures were at least partially successful in accomplishing their intended object in that they did somewhat improve the wash and crock-fastness when they were used. However, these expedients were found to have definite limitations. In some cases, the proposed procedures were too expensive for practical purposes. In others, the feel or hand of the finished product was impaired so that the fabric no longer retained its normal pliability. A compromise was therefore usually adopted, using only so much of the pigment-fixing agent as would not interfere with the hand, even though this did not give the desired color-fastness.

Fabrics colored by emulsion-deposited pigments using one of these modified compositions or by pre-treating the fabric have fair wash-fastness under some conditions. For example, the best colored fabrics which can be prepared without impairing their hand according to these procedures will pass a standard wash test if not previously exposed to light. A standard wash test as used in the present specification and claims refers to the American Association of Textile Chem-

ists and Colorists Test No. 3, as set forth in their 1941 Yearbook.

But if these same colored fabrics are first exposed to light, as, for example, in a standard fadeometer test, and then given the same wash test they wash down badly even though the pigments used are of such a nature that the fadeometer test alone does not appreciably alter the shade. Since most fabrics in ordinary use are subject to light as well as washing these colorings are not entirely commercially satisfactory. Consequently there still remains a demand for a suitable method of improving the wash and crock-fastness of emulsion-deposited pigments.

Obviously the length of exposure to light which may be made without producing fading will vary with the pigment used. With some of the poorer pigments fading on exposure to light occurs after only such a relatively short exposure that colorings with these pigments are impractical regardless of whether or not the color may wash down. The present invention is not concerned with such materials but has reference to the use of those pigments which are themselves light fast for periods of exposure longer than is required for the action of the light to cause that change in the materials which appears during the subsequent wash test.

It is, therefore, the object of this invention to provide a novel, simple and effective process whereby textile fabrics which have been dyed or printed with pigment-resin emulsions may be rendered more nearly permanently washfast and highly resistant to crocking and sloughing. It is also an object of this invention to accomplish this result without producing a harsh feel or hand in the fabric analogous to that produced by the older lacquer-printing process.

In general these objects are attained by after-treating the printed or dyed fabric with an aqueous solution of a water-soluble amidealdehyde type resin which has been etherified with a polyhydric alcohol. This treatment may be concluded by drying the treated fabric and setting and/or curing the resin to eliminate its water-soluble characteristics. Fabrics so treated possess excellent washfastness and marked improvement in both wet and dry crockfastness without undergoing any appreciable change in the pliability or hand of the fabric.

A notable feature of the present invention is that its applicability is not limited to the use of any one particular resin. An aqueous solution of substantially any water-soluble amide-aldehyde type resin which has been etherified with a polyhydric alcohol may be used. The term "amide-aldehyde" resin as used in the present specification and claims is intended to include aldehyde condensation resins derived from an aldehyde and amides such as urea, thiourea, guanidine, biuret, dicyandiamide or melamine which when etherified with a polyhydric alcohol are soluble in aqueous media. However, in some cases, it has been found that certain types of resins when given specific etherification treatments are particularly useful on specific fabrics. The choice of a particular resin, therefore may depend on the use to which it is to be put.

While most of the commercial resins are made by condensing the amide or imide with formaldehyde, the present invention is not necessarily so limited. Condensation resins made from other aldehydes are also suitable for use. The limiting factors for all practical purposes is that they be water-soluble and they be adapted to further condensation or etherification with a polyhydric alcohol.

It is a still further advantage of the present invention that since it comprises a protective after-treatment, it requires no special modification of the dyeing and printing technique used in coloring the fabric. Nor does it require any modification of the coloring compositions used in processing the fabric. Thus, the fabric may be dyed or printed using coloring compositions and techniques currently available. As an illustration of this feature it may be noted that most dyeing and printing emulsions make use of some resin to bond the pigment and fabric. These resins must be developed in some way to insure the bond. The after treatment of the present invention may be used after printing with the emulsion and developing the resin in the usual way.

It is also a still further advantage of the present invention that the resin need not have been etherified with any particular polyhydric alcohol. Illustrative examples of polyhydric alcohols which are useful in preparing the after-treating resin of the present invention include dihydric alcohols such as the glycol, trihydric alcohols such as glycerine and polyhydric alcohols such as pentaerythritol, di - pentaerythritol, sorbitol, mannitol containing more than three hydroxy groups.

The effectiveness of the treatment of the present invention in eliminating crocking and washing difficulties encountered with pigment colors is even more unexpected when the nature of the pretreating resins that have been used in the previous attempts to solve the problem are considered. For example, amide resins that have been alkylated with monohydric alcohols of low molecular weight have been employed both in pretreating compositions and as a component of the coloring composition without satisfactorily overcoming the crocking tendency or improving the washfastness of pigment-colors. When these same materials are used in the after-treating process of the present invention they do not produce the desired improvement in color fastness. Therefore it would appear that the success of the present invention is due, in some way which is not wholly understood at the present time, to the use of a polyhydric alcohol and the resultant presence of one or more terminal hydroxy radicals.

The invention will be described in greater detail in conjunction with the following specific examples which are meant to be merely illustrative and do not in any way limit the invention. The parts are by weight unless otherwise noted.

Example 1

A pigmented resin color base was prepared by blending together 45 parts of iron oxide yellow pigment, 14 parts of an oil modified alkyd resin, 7 parts of a 50% solution of butylated dimethylol urea in a mixture of xylene and butanol, 24 parts of steam distilled pine oil, 5 parts of oleic acid and 5 parts of 26° Bé. ammonia on a 3 roller ink mill.

Concurrently, a reducing oil-in-water emulsion was prepared by dissolving 0.4 part of a 4000 centipoise grade of methyl cellulose in 81.6 parts of water to which 0.7 part of 26° Bé. ammonia had been added. To this solution was added a solution consisting of 0.3 parts of oleic acid dissolved in 17 parts of a petroleum distillate fraction boiling between 160–250° C. and containing

about 16% aromatics, the remainder being predominantly paraffinic and naphthenic hydrocarbons. By mixing the two solutions while subjecting the mixture to high speed stirring a fluid oil-in-water emulsion was produced.

9 parts of the pigmented resin base was then thoroughly mixed with 91 parts of the reducing emulsion. A fabric strip was padded by passing it through this mixture and then between rubber squeeze rolls to remove the excess color, air-drying the treated fabric and heat curing it for 3 minutes at 120° C.

A strip of the fabric, colored in this way, was then passed through a finishing solution comprising 8 parts of a 50% aqueous solution of a urea formaldehyde resin etherified with ethylene glycol, 91.5 parts of water and 0.5 parts of 85% orthophosphoric acid. The treated strip was passed between rubber squeeze rolls to remove the excess finishing solution, dried for 2 hours at 60° C. and heat cured for 3 minutes at 120° C.

The untreated dyeing showed a good hand, fair washfastness and fair dry and wet crock resistance, whereas the treated dyeing was found to possess an unchanged hand, an excellent washfastness, excellent dry crock resistance and good wet crock resistance.

An intaglio print made from the same formulation as that used above in the dyeing operation was found to have resultant properties comparable to those described for the dyed fabric.

Example 2

The pigmented resin color base and the reducing oil-in-water emulsion were prepared as in Example 1. The procedure of Example 1 was followed, passing the strip of colored fabric through a finishing solution comprising 8 parts of a 50% solution of a urea formaldehyde resin alkylated with glycerine, 91.5 parts of water and 0.5 part of 85% orthophosphoric acid.

The untreated dyeing showed a good hand, fair washfastness and fair dry and wet crock resistance, whereas the treated dyeing possessed a good hand, excellent washfastness and good dry and wet crock resistance.

Example 3

A pigmented resin color base was prepared by mixing 25.5 parts of a solution of an oil modified alkyd resin consisting of 15.3 parts of the oil modified alkyd in 10.2 parts of a petroleum fraction boiling between 160–250° C. containing about 16% aromatics, the remainder being predominantly paraffinic and naphthenic, with 11.5 parts of a solution comprising 3.12 parts of low viscosity ethyl cellulose, 6.68 parts of the said petroleum fraction and 1.7 parts of butanol. This mixture was blended with 1.8 parts of tricresyl phosphate, 7 parts of copper phthalocyanine pigment and 3.6 parts of aluminum hydrate and ground on a 3 roller ink mill until a fine and uniform dispersion was obtained. The pigmented material was then blended together with 16 parts of a 50% solution of a butylated dimethylolurea in a mixture of xylene and butanol, 17.3 parts of a petroleum fraction boiling between 135–175° C. with an aromatic content of about 90% and 17.3 parts of a petroleum fraction boiling between 160–250° C. and containing about 16% aromatics, the remainder being predominantly paraffinic and naphthenic hydrocarbons.

A reducing water-in-oil emulsion was prepared by dissolving 8 parts of sodium lignin sulfonate in 12 parts of water and emulsifying this in 80 parts of a solution consisting of 48 parts of an oil modified alkyd resin and 32 parts of toluene by means of a homogenizing type of stirrer. 2 parts of the finished emulsion, 15 parts of a petroleum fraction boiling between 135–175° C. with an aromatic hydrocarbon content of about 90%, 15 parts of a petroleum fraction boiling between 160–250° C. containing about 16% aromatics, the remainder being predominantly paraffinic and naphthenic hydrocarbons, are then mixed after which 66 parts of water and 2 parts of glacial acetic acid are stirred in with a homogenizing type of stirrer. A creamy water-in-oil emulsion resulted.

10 parts of the pigmented resin base was thoroughly mixed with 90 parts of the reducing emulsion and the composition printed on the fabric by means of an intaglio printing roll. The print was air dried, and then heat cured for 3 minutes at 120° C.

A strip of the printed fabric was passed through a finishing solution consisting of 5 parts of an 80% aqueous solution of a melamine formaldehyde resin etherified with ethylene glycol, 94.5 parts of water and 0.5 parts of 85% orthophosphoric acid. The treated strip was passed between rubber squeeze rolls to remove the excess finishing solution, dried for 2 hours at 60° C. and heat cured for 3 minutes at 120° C.

The untreated print showed a good hand, good washfastness and poor dry and wet crock resistance, whereas the treated print possessed a good hand, very good washfastness and fairly good dry and wet crock resistance.

A dyeing made from the same formulation as that used above for the intaglio printing was found to have improved crock resistance and washfastness properties comparable to those described for the print.

Example 4

A pigmented resin color base was prepared by deflocculating 50 parts of dichlorobenzidine yellow presscake containing 20% solids with 0.4 part of the sodium salt of disulfodinaphthyl methane and then given one pass through a colloid mill. 0.6 part of bentonite were stirred into the dispersed color and the mixture was given one pass through a colloid mill. To this mixture were added 24 parts of dimethoxymethyl urea, 16 parts of a 25% aqueous solution of trimethylolmelamine, 6 parts of the 15 centipoise grade of methyl cellulose and 4 parts of water. After stirring for 60 minutes the mixture was given one pass through a colloid mill.

A reducing oil-in-water emulsion was obtained by stirring 6 parts of a 5% aqueous solution of the 4000 centipoise grade of methyl cellulose into a solution consisting of 0.6 part of the trimethylolmelamine and 25.4 parts of water. 68 parts of a petroleum fraction boiling between 160–250° C. and containing about 16% aromatics, the remainder being predominantly paraffinic and naphthenic hydrocarbons were emulsified in the solution by means of a homogenizing type of stirrer.

10 parts of the pigmented resin base was then thoroughly mixed with 89.5 parts of the oil-in-water reducing emulsion followed by the addition of 0.5 part of 85% orthophosphoric acid. A fabric strip was padded by passing it through this mixture and then between rubber squeeze rolls to remove the excess color, air-drying the treated fabric and heat curing it for 3 minutes at 120° C.

A strip of the fabric colored in this way was then passed through a finishing solution comprising 8 parts of a 50% aqueous solution of a urea formaldehyde resin etherified with ethylene glycol, 91.5 parts of water and 0.5 part of 85% orthophosphoric acid. The treated strip was passed between rubber squeeze rolls to remove the excess finishing solution, dried for 2 hours at 60° C. and heat cured for 3 minutes at 120° C.

The untreated dyeing showed a fair hand, good washfastness, poor dry crock resistance and very poor wet crock resistance. The treated dyeing, on the other hand, showed a fair hand, excellent washfastness and surprisingly good dry and wet crock resistance.

An intaglio print made from the same formulation as that used above in the dyeing operation was found to have resultant properties comparable to those described for the dyed fabric.

It is also another important advantage of the present invention that it can be readily employed in conjunction with other dyeing and printing operations in which no pigment coloring is used. For example, one portion of the fabric surface may be colored with any suitable organic dyestuff such as a vat dye, a stabilized azoic dye or the like or with an ingrain mineral color, the remainder of the surface may be printed or dyed with an emulsion-deposited pigment and the after-treatment of the present invention employed to improve the color fastness of the pigment colored portion. Similarly an emulsion-deposited pigment may be used to overprint a portion of a fabric surface which has been previously colored by the use of some organic or inorganic dyestuff and the after-treament again employed to improve the color fastness of the pigment colored portion.

Where emulsion-deposited pigments have been used to color only a portion of a surface of a fabric, the after-treatment of the present invention may be applied either to the whole fabric or to the pigment colored area only. The after-treatment of the present invention produces such a slight change in the hand of the fabric that substantially no change is perceptible to the touch to distinguish the treated areas from those which are not. This may be of particular importance in those cases in which the pigmented area comprises only a small portion of the total surface and therefore a considerable saving in material can be effected by after-treating only those portions which are pigment colored.

We claim:

1. A textile fabric, at least a portion of the surface of which is colored by an emulsion-deposited pigment, said pigment being attached the fibers comprising the fabric by a cured resinous binder selected from the group consisting of the heat-curable alkyd and heat-curable alkylated amide-aldehyde type resins, at least the portions colored by said pigment and said cured binder being overlaid by protective coating comprising an amide-aldehyde resin which resin has been etherified with a polyhydric alcohol.

2. A textile fabric, at least a portion of the surface of which is colored by an emulsion-deposited pigment, said pigment being attached the fibers comprising the fabric by a cured resinous binder selected from the group consisting of the heat-curable alkyd and heat-curable alkylated amide-aldehyde type resins, at least the portions colored by said pigment and said cured binder being overlaid by protective coating comprising an urea-formaldehyde resin which resin has been etherified with a polyhydric alcohol.

3. A textile fabric, at least a portion of the surface of which is colored by an emulsion-deposited pigment, said pigment being attached the fibers comprising the fabric by a cured resinous binder selected from the group consisting of heat-curable alkyd and heat-curable alkylated amide-aldehyde type resins, at least the portions colored by said pigment and said cured binder being overlaid by protective coating comprising a melamine-formaldehyde resin which resin has been etherified with a polyhydric alcohol.

4. In making textile fabrics colored by emulsion-deposited pigments, the method of improving the wash-fastness, dry crock resistance and wet crock resistance of the pigmented surfaces which comprises the steps of treating at least portions of the fabric surface with an emulsion containing a light-fast pigment and a binder selected from the group consisting of the heat-curable alkyd and heat-curable alkylated amide-aldehyde type resins; curing said binder by heating, whereby the pigment is adhere to the fibers comprising the fabric; treating at least the pigmented portions with an aqueous solution of an uncured water-soluble, heat-curable, amide-aldehyde resin, which resin has been etherified with a polyhydric alcohol; drying the treated fabric and heating said dried fabric to cure the heat-curable, amide-aldehyde resin.

5. In making textile fabrics colored by emulsion-deposited pigments, the method of improving the wash-fastness, dry crock resistance and wet crock resistance of the pigmented surfaces which comprises the steps of treating at least portions of the fabric surface with an emulsion containing a light-fast pigment and a binder selected from the group consisting of the heat-curable alkyd and heat-curable alkylated amide-aldehyde type resins; curing said binder by heating, whereby the pigment is adhered to the fibers comprising the fabric; treating at least the pigmented portions with an aqueous solution of an uncured water-soluble, heat-curable, urea-formaldehyde resin, which resin has been etherified with a polyhydric alcohol; drying the treated fabric and heating said dried fabric to cure the heat-curable, urea-formaldehyde resin.

6. In making textile fabrics colored by emulsion-deposited pigments, the method of improving the wash-fastness, dry crock resistance and wet crock resistance of the pigmented surfaces which comprises the steps of treating at least portions of the fabric surface with an emulsion containing a light-fast pigment and a binder selected from the group consisting of the heat-curable alkyd and heat-curable alkylated amide-aldehyde type resins; curing said binder by heating, whereby the pigment is adhered to the fibers comprising the fabric; treating at least the pigmented portions with an aqueous solution of an uncured water-soluble, heat-curable, melamine-formaldehyde resin, which resin has been etherified with a polyhydric alcohol; drying the treated fabric and heating said dried fabric to cure the heat-curable, melamine-formaldehyde resin.

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