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PROCESS FOR DISTRIBUTING A RESIN IN A FABRIC

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ABSTRACT OF THE DISCLOSURE

In the dyeing of textile fabrics, particularly glass fiber textiles, uniformity and penetration of the coloring material throughout the fabric or yarn is achieved by providing a uniform distribution of resinous material throughout the fabric or yarn by the process comprising mixing a neutralized polyamide with said resinous material, applying the mixture so obtained to said fabric or yarn, and subsequently heating the fabric or yarn which contains the resinous material thereon to cause said polyamide to revert to an unneutralized state, whereby said resinous material is coagulated.

This invention relates to the treatment of textile fabrics. The invention is of particular importance in the dyeing of glass textiles.

BACKGROUND OF THE INVENTION

Prior art processes for dyeing glass textiles involve the use of pigments which are dispersed in resin emulsions, the dispersion being applied to the fabric by padding. One such prior art process is described in the Hamiter et al. Patent, No. 3,108,897, issued Oct. 27, 1963, the disclosure of which is hereby incorporated by reference. The Hamiter et al. patent uses a dye bath containing an anionic resinous binder and a flocculated pigment. After the dye bath is padded onto the fabric, the fabric is heated to cure the resin, thereby affixing the pigment onto the glass fabric.

The prior art has recognized the desirability in the dyeing of glass textiles, that is, glass fabrics or yarns made from glass fibers or filaments, that each filament of the fabric should be coated with pigmented resin to achieve a uniform coloring effect.

The Hamiter et al. process and other prior art processes for dyeing and finishing glass textiles do not achieve uniform color throughout the glass textile because the pigments and resins coated on the glass yarns tend to migrate to the surface of the textile during the drying step. This migration of pigments and resins tends to leave the interstices of the fabrics and the inside of the filament bundles of the individual yarns uncolored. When the yarns in the fabric are shifted, such as by abrasion during normal wear or use or on washing, the uncolored portions of the fabric or the yarn may be exposed to produce an objectionable effect.

Various agents, such as Kelsize, cellulose ethers or esters, natural gums, acrylic polymers, etc., have been employed in an effort to control migration of pigments in the dyeing process. These agents apparently derive their anti-migration effect by increasing the viscosity of the

padding liquor. However, when the viscosity of the padding liquor is thus increased, there is a corresponding decrease in the penetration power of the padding liquor, i.e., the higher the viscosity of the padding liquor, the less the inside surfaces of the fabrics and the yarns tend to be covered by the pigmented liquor.

OBJECTS OF THE INVENTION

It is an object of the present invention to provide a novel process for the treatment of textile materials.

It is another object of the present invention to provide a novel process for the penetration dyeing of textile fabrics.

It is yet another object of the present invention to provide a novel process for the penetration dyeing of glass textiles.

It is a further object of the present invention to provide a novel process for the dyeing of glass fabrics which results in increased uniformity in the distribution of the coloring material throughout the fabric.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

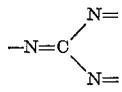
SUMMARY OF THE INVENTION

In accordance with the present invention, the above objects are accomplished by including neutralized polyamides in the resinous dye bath. During a heating step, subsequent to a dye bath padding step, which is conventionally used to cure the resins present in the dye bath, the neutralized polyamide is converted into the original polyamide compound, which fixes the pigment/resin dispersion. Such fixing of the pigment/resin dispersion fixes the position of the pigment within the fiber bundles, thereby eliminating subsequent pigment migration.

DESCRIPTION OF THE INVENTION

The process of the present invention provides for the inclusion of a neutralized polyamide in a pigmented dye bath or an unpigmented resinous bath. By the term "polyamide," when used in the present application, it is meant those cation active polyelectrolytes or cationic resinous compounds which are also amino-functional. These compounds are chemically identifiable as low molecular weight water-soluble polyamine acrylamides, e.g., the reaction product of a low molecular weight polymethacrylate or polyethylacrylate with a polyamine such as triethylene tetramine, having two or more amino groups, at least one of which is a primary amino. This type of reaction product is disclosed in U. S. Patent 2,675,359. Molecular weights in the rage of 2000 to 5000 may be mentioned as illustrative although products of higher molecular weights, e.g., 10,000 or above, may also be used. Compounds of this type which are commercially available include the products known as Nalco 600 (National Aluminate Corporation) and QR–419 (Rohm & Haas). Other cationic resinous compounds useful herein include the water-soluble, cationic condensation products of formal-

dehyde and dicyandiamide or similar compounds containing the grouping



wherein the free valences are satisfied by hydrogen, lower alkyl, phenyl or other aryl radicals. A typical example of such a condensation product useful herein is methylol guanidine.

The preferred polyamide is the compound commercially available as Nalco 600. This compound and other polyamides can be neutraized by the addition of a strong volatile organic acid under conditions which favor the reaction of the polyamide and the acid. Generally, the materials will react at room conditions but heating to a temperature of 100 to 120° F. for a time of 1 to 5 minutes is preferred. The final product should have a pH within the range of 2.5 to 6, and preferably the pH is within the range of 4 to 5. Acetic acid is the preferred neutralizing acid, but formic acid and acrylic acid may be used in lieu thereof, as well as other strong, volatile acids which will neutralize the primary amine groups within the polyamide.

Before the polyamides are neutralized, they possess the ability to flocculate pigments and to aid in the coagulation in the binder resins in the dye bath. This flocculating and coagulating property of the polyamides is inhibited by the neutralization step, but the property can be regenerated when heat causes the neutralized compound to revert back to the acid and the polyamide. Generally, it is preferred for the neutralizing acid to be evaporated during the heating, or fixing, step. Although the neutralized polyamides will function at any acid pH, a pH of 4 to 5 is preferred.

In dyeing glass fibers, a binder is commonly employed to cause a physical adherence between the coloring agent and the glass. The binder is generally a resinous material such as polyacrylic latex, certain of the silicones, polyvinyl alcohol or polyvinyl acetate, etc. Additional resinous materials which may be used in the process of this invention are disclosed in the Hamiter et al. Patent, 3,108,897.

It has been found highly advantageous to include in the pad composition a silane crosslinking agent containing a reactive grouping. The function of this crosslinking agent is to anchor the resin to the glass surface. Additionally, however, the silane serves as an anchoring agent and catalyst for a subsequently applied top finishing binder system. The silane crosslinking agent used herein may be an aminolykyl trialkoxy silane containing at least one amino group and up to about 10 carbon atoms, exclusive of those in the alkoxy groups attached to the silicon atom, each alkoxy group containing from 1–3 carbon atoms. Best results are obtainable with aliphatic silanes containing one or more secondary groups or both primary and secondary groups. Typical examples of such compounds are those represented by the formula:

$$R_1HN(CH_2)_mNH(CH_2)_nSi(OR)_3$$

wherein m and n are integers from 1 to 4, preferably 2 to 3, R is alkyl containing from 1 to 3 carbon atoms and R_1 is hydrogen, methyl or ethyl. An especially preferred silane is N-(2-aminoethyl)-3-propylamino trimethoxy silane represented structurally as

$$H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$$

and commercially available as Z–6020 or A–1100. An acrylic modification of Z–6020, available as XZ–8–4032, may also be mentioned as a specific illustration of a silane useful, as well as gamma-aminopropyl triethoxy silane.

It has also been found desirable to include an epoxy resin and/or epoxy oil compounds in the pigmented coating composition. Epoxy resins generally are suitable for this purpose but the preferred epoxies are those which can react with the silane crosslinking agent. Examples of suitable epoxies include the bisphenolepichlorhydrin type and epoxidized oils, e.g. epoxy soybean oil or the like.

The pigment to be used in the process of the present invention must be selected from those which are stable throughout the processing steps, i.e. the pigment must be able to withstand the curing temperature without change. These pigments are well known to those skilled in the art. Examples of the inorganic pigments which can be used are the oxides, sulfites and sulfates of cobalt, chromium, iron, zinc and cadmium, etc. Examples of organic pigments are the azo coupling dyes, anthraquinone, phthalocyanine, indanthrene vat dyes and carbon black, etc. The dye bath generally contains about 0.5 to 5% by weight of pigment but more or less pigment can be used as desired. The pigment is usually employed in the form of an aqueous dispersion, which includes water, pigment and a dispersing agent, as is known to the prior art.

The glass fibers treated herein may be of any conventional composition. Typically suitable fibers are those made from glass of the following approximate composition wherein parts are by weight.

	Parts
Silicone dioxide	52–56
Calcium oxide	16–25
Aluminum oxide	12–16
Boron oxide	8–13
Na_2O sodium oxide	0–1
Magnesium oxide	0–6

Other suitable glass compositions are shown, for example, in U.S. Patents 2,582,919 and 3,011,929.

While the present invention is not to be limited to any particular theory of reaction or mechanism, it is believed that the heating step causes water and acetic acid to evaporate from the textile material, thus causing the pH of the remaining liquid in the fabric to rapidly rise. Due to the loss of acetic acid, with the consequential regeneration of the primary amine groups in the free state, the cationic nature of the polyelectrolyte is restored and causes a coagulation of the resin and/or flocculation of the pigment within the filament bundles of the glass yarns. This coagulation and/or flocculation prevents the migration of the resin and any pigments present during subsequent operations, thereby producing a level dyeing throughout each individual glass yarn in the fabric.

The invention is illustrated but not limited by the following examples wherein parts and percentages unless otherwise stated, are by weight.

Example I

A fabric woven with glass "E" yarn in both warp and filling was first heat cleaned using the process shown in U.S. Patent 2,970,934. The heat cleaning process of U.S. Patent 3,012,848 could also be used with equal effect.

The heat cleaned fabric was then immersed in a dye bath made up as follows:

To a small quantity of water was added the following materials:

½% silicone XZ8–4032
1% Nalco 600 (neutralized to pH 5 with acetic acid)
4½% acrylic resin emulsion
1% epoxy resin emulsion
4% epoxy soybean oil emulsion
2% acetic acid (final bath pH of 4)

The neutralized Nalco 600 was prepared by reacting the Nalco 600 with an amount of acetic acid sufficient to give a final reaction product pH of 5. The reaction occurred at atmospheric pressure by heating the admixed materials to a temperature of 110° F. for 3 minutes.

All percentages in this example were based on the final weight of the dye bath. To the above mixture was then added 1% of an aqueous dispersion of pigment padding Brown R (Interchemical Corporation). The pig-

ment dispersion was added to the mixture with vigorous stirring and additional water was added to bring the dye bath mixture to the final composition (total solids of 9% by weight).

The above dye bath was then padded onto heat cleaned glass cloth and the fabric was then dried with sufficient heat to cure the resins (340° F. for 2 minutes).

After the fabric was treated with dye bath composition it was given a top finish. The composition used for top finish was:

1% XZ8–4032 silicone
8% Acrylic resin emulsion
8% Epoxy oil emulsion
3% Epoxy resin emulsion
2½ Quilon
Water to make 100%

Quilon is a chrome complex such as described in U.S. Patents 2,356,161 and 2,273,040. This finish was also padded onto the fabric and dried and cured.

The glass fabric dried according to the above procedure was found to have good dye penetration, good dye fixation, and good color fastness through repeated washing.

Although the preferred embodiment of the present invention is in the penetration dyeing of glass textiles, it is clear that the process of this invention may be used whenever a uniform distribution of a resinous material is desired throughout a textile fabric. The process of the present invention was found to give excellent dye penetration, dye fixation and wash fastness on fabrics other than fiber glass, for example, on cotton and rayon fabrics, etc. The process of the present invention was also effective in preventing the migration of unpigmented resins applied upon glass textiles and other types of fabrics.

The dried glass fabric may be given a dulling treatment with oxalic acid prior to the top finishing step. The dulling treatment with oxalic acid is described in co-pending application Ser. No. 266,013 now U.S. Patent 3,259,517 assigned to Burlington Industries, the disclosure of which is hereby incorporated by reference. This dulling treatment produces the desired degree of dullness or opacity in the fabric. This treatment also improves the abrasion resistance and tensile strength of the dried fabric. The dulling treatment is preferably applied to the fabric after the dyeing step but before the top finishing process.

Although the amounts of the various constituents in the dye bath may be varied over wide ranges, generally the dye bath will contain about 2 to 15% by weight of binder resin, and about 0.5 to 3% by weight of pigment. The amount of pigment used is only limited by the carrying ability of the resin system. In order for larger amounts of pigment to be used, an increase in the resin content of the dye bath is generally necessary. Such resin content increase in the dye bath affects the hand and drape of the final product.

The amount of neutralized polyamide which can be used in the dye bath will vary over very wide ranges. It is generally preferred to use an amount of the polyamide which, in the unneutralized state, will be in excess of the amount required to flocculate the pigment in the dye bath, but a great excess over this preferred minimal amount of neutralized polyamide may be used. Generally, it is preferred that the amount of neutralized polyamide used be within the range of 0.5 to 1.5% by weight of the dye bath, although it is to be understood that this range is only to indicate the most desirable range and is not by the way of limitation.

Since the neutralized Nalco **600** is preferably used at a pH of 4 to 5, it is preferred to use pigment dispersions and resin emulsions which are stable at these pH values in order to give best results.

By the process of the invention dried glass fabrics were obtained which had a good hand, excellent wash fastness, excellent hem-line abrasion resistance and excellent dye penetration throughout the fabrics. When the threads in the fabrics were shifted, there were exposed no objectionable undyed areas such as would happen with conventional dyeing processes. Examination of yarn dyed according to the present process shows the dye-resin mixture to have penetrated the yarn bundles and the fabric throughout. Furthermore, the dye/resin mixtures which have penetrated the yarn bundles showed no appreciable migration during the curing step, thus yielding a product having excellent pigment distribution. Equally good results were obtained when the process was tried on fabrics other than fiber glass, e.g. cotton and rayon goods, etc.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A process for uniformly distributing a resinous material throughout fabric or yarn, said process comprising mixing a neutral salt of a polyamino-polyamide and a volatile organic acid with a dispersion of a coagulable resinous material and water, applying the mixture obtained to said fabric or yarn, and subsequently heating the fabric or yarn which contains the aforesaid mixture of resinous material and polyamino-polyamide salt therein to a temperature of at least 250° F. to regenerate the free polyamino-polyamide thereby causing the coagulation of the resinous material.

2. The process as claimed in claim **1** wherein said mixture of a neutral salt of a polyamino-polyamide and a volatile organic acid and a coagulable resinous material contains a pigment and a liquid vehicle.

3. The process as claimed in claim 2 wherein said textile material is selected from the group consisting of cotton and rayon.

4. The process as claimed in claim **2** wherein said mixture of a neutral salt of a polyamino-polyamide and a volatile organic acid and a coagulable resinous material containing a pigment and a liquid vehicle additionally includes a reactive amino-silane.

5. The process as claimed in claim **4** wherein said mixture of a neutral salt of a polyamide-polyamide and a volatile organic acid and a coagulable resinous material containing pigment and a liquid vehicle additionally includes an epoxy compound.

6. The process as claimed in claim **2** wherein said fabric or yarn is a glass textile.

7. The process as claimed in claim **6** further comprising treating said glass textile, after the cogaulated resin has been cured thereon, with an oxalic acid-dulling treatment and thereafter coating said dulled glass fabric with a top finish composition.

8. The process as claimed in claim **6** further comprising treating said glass textile after said resin had been cured thereon with a top finish composition.

9. The process as claimed in claim **2** wherein said neutralized polyamide is prepared by reacting a polyamino-polyamide with a strong, volatile organic acid.

10. The process as claimed in claim **9** wherein said polyamide is a water-soluble cation active polyelectrolyte.

11. The process as claimed in claim **9** wherein said polyamide is a water-soluble polyamino-polyamide.

12. The process as claimed in claim **9**, wherein said polyamino-polyamide is reacted with a sufficient amount of said acid to result in a salt with a final pH of about 4 to about 5.

13. The process as claimed in claim 12 wherein said volatile acid is selected from the group consisting of acetic acid, formic acid and acrylic acid.

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