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DYEING OF POLYVINYL HALIDE-ACETATE COPOLYMER FIBERS AND FABRICS

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This invention relates to the dyeing of fibers and fabrics made from polyvinyl halide-acetate copolymers.

The new fibers and fabrics produced from polyvinyl halide-acetate copolymers and which are known under the trade name of "Vinyon" have shown important properties. However, the dyeing of this type of fibers or fabric has presented a serious problem because most dyes do not have any affinity for them.

It has been proposed in the Rugeley et al. U. S. Patent No. 2,161,766 to dye the fibers and fabric by the use of solvents for the resin of which the fibers are composed. This procedure results in dyeing of the material but the surface is affected by the solvent, and in many cases this effect is serious.

The present invention is directed to the dyeing of polyvinyl halide-acetate copolymer material with oil soluble colors in the absence of a solvent for the material but in the presence of a dyeing assistant which may be either an amine, a phenol, an ester, or an open chain ether. These compounds as used herein do not dissolve the resin. They may cause a swelling of the resin and it is possible that this property may in some cases be a factor in the excellent level dyeings which are possible by the use of the assistants of the present invention.

In the present invention, the term "solvent" is used in its common meaning. Theoretically some swelling agents, if used in extremely large quantities, are capable of dissolving a small amount of polyvinyl halide-acetate copolymers to form homogeneous liquids which might be termed solutions. For the purpose of the present invention, however, the term "solvent" is used in its ordinary restricted meaning of a material capable of dissolving considerable quantities of polyvinyl halide-acetate copolymer to form true solutions containing substantial percentages of the copolymer. It should be understood that this term is used throughout this specification and claims in this common sense only.

It is an advantage of the present invention that full shade, uniform dyeings are obtained without in any way damaging the fiber or the fabric, without causing shrinkage and with no substantial loss in strength. In general the dye baths of the present invention are aqueous solutions, the oil soluble colors and assistants being dispersed or emulsified in the bath. The present invention is not limited to any particular type of bath and it is an advantage that the dyeing technique which has been employed in the dyeing of cellulose acetate material can be followed except that temperatures should not exceed 70° C. and preferably should not exceed 65° C. Higher temperatures may be used but then a change occurs in the fabric such as shrinking.

The present invention depends on the use of a non-solvent or swelling assistant, the quantity being kept sufficiently low so that no objectionable effect on the material results. Minute quantities of solvent may of course be present without affecting the strength or desirable characteristics of the dyed material, but they should not be present in sufficient amounts to have any substantial solvent effect. In the specification and claims of the present case the term "substantial absence of solvents" is intended to cover all cases where there is no solvent at all, or, if any, it occurs in such minute quantities as to have no substantial effect on the material.

The method of forming a dye bath according to the present invention may vary within wide limits and is not critical, which is an advantage of the present invention. The dyes and assistants may be separately dispersed and emulsified and then added to a dye bath either in powder or paste form or the dye bath may be made up with the color and assistant or assistants dispersed therein afterwards. The results are substantially the same no matter how the baths are made up provided the same formula is used and this lack of critical procedure is a practical operating advantage of the present invention. A single assistant may be used in a particular dye bath, or a plurality of assistants may be employed. Frequently a dispersing agent may be added to the dye bath. The present invention, however, is not sensitive to the particular dispersing agent employed so long as it is not a solvent for the material to be dyed, but we have found that ammonium caseinate is useful and one of the preferred dispersing agents.

The present invention is applicable to oil soluble colors and more generally to those colors which can be used in dyeing cellulose acetate materials especially when the proper assistant is employed.

The present invention is not limited to any particular amount of assistant. However, the amount used should be sufficient to affect the surface of the material to be colored. Use of an assistant in amounts beyond this effective amount does not give improved results and may waste assistant. The particular amount to be used will depend somewhat with the assistant and with the dye bath. In general, it is of the order of

magntude of 1–3% calculated on the weight of the material to be dyed, but the invention is in no sense limited to these percents.

While the present invention can be used to dye polyvinyl halide-acetate copolymer material generally, it is desirable to either clean the material, for example by suitable scouring, or to assure a clean surface by precautions in manufacture. More rapid dyeing and more uniform and level results are thus obtained.

The invention will be described in greater detail in conjunction with the following specific examples which illustrate typical dye baths, but the invention is in no way liimted to the examples set forth.

Example 1

5 parts of "Vinyon" yarn is dyed as follows:

0.10 part of a dispersed oil-soluble color which is made by coupling diazotized p-nitroaniline on dimethyl aniline and reducing the nitro group, 0.10 part alpha naphthol, 0.05 part of benzophenone, and 0.30 part of a 10% ammonium caseinate solution are pasted together and added to 150 parts of water. The dyeing is carried out for 1 hour at 150° F. in this bath. The color is nearly completely exhausted to give a level, non-crocking dyeing.

Example 2

5 parts of "Vinyon" is dyed in the following manner:

A dye bath is prepared containing 0.10 part of a dispersed color which is made by coupling diazotized p-nitroaniline on phenyl ethyl ethanolamine, 0.05 part of diphenyl ether, 0.30 part of a 10% ammonium caseinate solution, and 150 parts of water. The dyeing is carried out for 1 hour at 150° F. The color is exhausted well and gives a level dyeing which does not crock or sublime.

Example 3

5 parts of "Vinyon" yarn is dyed as follows:

0.10 part of a dispersed oil-soluble color prepared by coupling diazotized p-nitroaniline on p-xylidine, 0.10 part of diamyl phthalate and 0.30 part of a 10% ammonium caseinate solution are pasted together and then added to 150 parts of water. The yarn is dyed in this bath for 1 hour at 150° F. The color is exhausted very well to give a level dyeing which does not crock or sublime.

Example 4

5 parts of a skein of "Vinyon" is dyed in the following manner:

A dye bath is prepared containing 0.05 part of xylene azo betanaphthol, 2 parts of aniline, 0.10 part of dioctyl sodium sulfosuccinate which issued as the wetting agent, and 150 parts of water. The skein is dyed for 30 minutes at 130° F. The bath is exhausted and the fiber is uninjured. The dyeing obtained is level and does not crock.

Example 5

5 parts of "Vinyon" staple fiber is dyed as follows:

0.10 part of dispersed 1-ethylamino-4-ethanolamino anthaquinone are pasted with 0.10 part n-butyl-phenyl acetate, 0.30 part of a 10% ammonium caseinate solution, and 0.30 part of a 10% ammonium linoleate solution. This paste is diluted with 100 parts of water at 100° F. The fiber is dyed in this bath for 1 hour at 150° F. The bath is exhausted and the fiber is dyed a bright blue.

Example 6

5 parts of "Vinyon" yarn is dyed as follows:

.18 part of a dispersible powder which is prepared by pasting .10 part of a dispersed red dye (prepared by coupling diazotized p-nitroaniline with phenyl ethyl ethanolamine) with 0.05 part of triphenyl phosphate, 0.10 part of a 15% ammonium caseinate solution, 0.01 part soap and 0.05 part of a 10% solution of dioctyl sodium sulfosuccinate and drying this paste in the vacuum oven below 50° C., is pasted with 0.5 cc. of a 5% soap solution and diluting with 150 parts of water. The yarn is dyed in this bath for 1 hour at 150° F. The color is exhausted and the yarn is dyed a bright scarlet which does not crock or sublime.

Example 7

5 parts of a "Vinyon" knit goods are dyed as follows:

0.10 part of dispersed 1-ethylamino-4-ethanolamino anthraquinone and 0.05 part of a dispersed yellow dye, made by coupling cresidine diazo with p-amino acetanilide and saponifying, are pasted with 0.05 part of n-butyl-phenyl-acetate, 0.30 part of a 10% solution of ammonium caseinate and 0.30 part of a 10% solution of ammonium linoleate. This paste is diluted with 150 parts of water. The knit goods are dyed for 1 hour at 150° F. This procedure gives a bright green dyeing which does not crock or sublime.

The present invention not only provides an improved process for dyeing materials containing polyvinyl halide-acetate copolymers, but it also produces new colored products. The dyed products of the present invention differ from those of the prior art as described in the Rugeley patent above referred to, by the fact the surface of the material shows no detectable deterioration as compared with the corresponding undyed material, whereas in the prior art processes, unless extreme precautionary measures are taken, a surface deterioration and loss of strength can be detected. The dyed material of the present invention contains at least one oil soluble color, a small amount of the dyeing assistant used, and is free from solvents for the polyvinyl halide-acetate copolymers.

What we claim is:

1. A method of dyeing polyvinyl halide-acetate copolymer containing materials which comprises subjecting the material to the action of a dye bath containing an oil soluble color and from 1 to 3% of a phthalate ester based on the weight of the copolymer.

2. A method of dyeing polyvinyl halide-acetate copolymer containing materials which comprises subjecting the material to the action of a dye bath containing an oil soluble color and from 1 to 3% of an alkyl phenyl acetate based on the weight of the copolymer.

3. A method of dyeing polyvinyl halide-acetate copolymer containing materials which comprises subjecting the material to the action of an aqueous bath containing a dispersed oil-soluble color and from 1–3% of at least one ester which is a non-solvent for the copolymer and liquid at temperatures below 70° C., the dyeing taking place in the substantial absence of organic solvent for the material.

4. A method of dyeing poyvinyl halide-acetate copolymer containing materials which comprises subjecting the material to the action of an aqueous bath containing a dispersed oil-soluble color and from 1–3% of at least one ester which is a non-solvent for the copolymer and liquid at tem-

peratures below 70° C., the dyeing taking place at temperatures not exceeding 75° C. and in the substantial absence of organic solvent for the material at that temperature.

5. A method of dyeing polyvinyl halide-acetate copolymer containing materials which comprises subjecting the material to the action of an aqueous bath containing a dispersed oil-soluble color and from 1–3% of at least one ester which is a non-solvent for the copolymer and liquid at temperatures below 70° C., the dyeing taking place at temperatures not exceeding 65° C. and in the substantial absence of organic solvent for the material at that temperature.

6. A colored polyvinyl halide acetate copolymer containing material showing no detectable deterioration as compared with the corresponding uncolored material, the colored material containing an oil-soluble color and from 1 to 3% of an ester which is a non-solvent for the copolymer and a liquid below 70° C., the colored material being further substantially free from organic solvents for the copolymer.

7. A colored polyvinyl halide-acetate copolymer ester containing material showing no detectable deterioration as compared with the corresponding uncolored material, the colored material containing an oil color and from 1 to 3% of a phthalate ester based on the weight of the copolymer.

8. A colored polyvinyl halide-acetate ester containing material showing no detectable deterioration as compared with the corresponding uncolored material, the colored material containing an oil color and from 1 to 3% of an alkyl phenyl acetate based on the weight of the copolymer.

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