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# UNITED STATES PATENT OFFICE

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## METHOD OF DYEING CELLULOSE ACETATE FIBERS IN A MIXED ACETATE-NYLON FABRIC USING AN AQUEOUS SOLUTION OF AN ACID DYE, ETHYL ALCOHOL, ACETIC ACID, AND EITHER SODIUM OR AMMONIUM THIOCYANATE

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1 Claim. (Cl. 8—24)

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This invention relates to the colouration of textile materials comprising both fibres of cellulose acetate or other cellulose ester or ether and fibres of a superpolyamide. The term "superpolyamide" is used as including in particular superpolyurethanes and the superpolyamides obtainable by the self-condensation of amino fatty acids or by the condensation of aliphatic or other diamines with aliphatic or other dicarboxylic acids. The invention is particularly concerned with the colouration of materials comprising on the one hand cellulose acetate fibres and on the other fibres of the superpolyamides obtainable by condensing adipic acid with hexamethylene diamine. The latter condensation product is hereinafter referred to as nylon 66.

It is an object of the present invention to colour the cellulose acetate of such a mixed material containing both cellulose acetate fibres and superpolyamide fibres without at the same time colouring the latter fibres. Most of the dyes which are available for colouring cellulose acetate fibres are also capable of colouring nylon 66 and other superpolyamide fibres. Thus the water-insoluble dyes which are so very largely used in the form of aqueous dispersions for the colouring of cellulose acetate fibres are very useful for colouring nylon 66 fibres, since they yield as a rule more uniform shades than can be obtained with the various acid dyes which have affinity for nylon 66. Again such acid dyes as colour cellulose acetate from aqueous baths colour nylon 66 even more readily. It would appear, therefore, to be a matter of some considerable difficulty to colour the cellulose acetate fibres of a mixed material of the kind in question without at the same time colouring the nylon 66 fibres. Such a method would, however, be very useful, since it would facilitate the production of two-colour effects on textile fabrics containing both cellulose acetate fibres and nylon 66 fibres. It would even be useful in the case of producing solid shades on these mixed materials, since it is not easy to find single dyes which dye cellulose acetate fibres to same shade as nylon 66 fibres from one and the same bath. Apart from questions of depth of shade the tone is often quite different on nylon 66 from what it is on cellulose acetate. Quite frequently, therefore, it is better to dye the cellulose acetate and nylon 66 in separate operations in spite of the fact that a solid shade is required.

It has been found that the aforesaid desirable results can be secured by applying to the mixed material dyes, for example those water-insoluble

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dyes capable of dyeing cellulose acetate in the form of aqueous dispersions, in solution in a liquid medium which swells the cellulose acetate without substantially swelling the nylon 66. The liquid medium is advantageously a mixture of water with a water-miscible organic liquid. It has been found that aqueous ethyl alcohol or other alcohol of the formula $C_nH_{2n+1}.OH$, particularly one containing up to 3 or 4 carbon atoms, is a very effective medium for forming the dye solution, particularly when containing a proportion of a thiocyanate.

As regards the concentration of this aqueous alcohol, it has been found that, when using methyl, ethyl, n-propyl or isopropyl alcohol, a concentration of 55%–75% by weight yields good results. The thiocyanate, when employed, may be for instance ammonium, sodium, potassium or zinc thiocyanate. The proportion of the latter may be of the order of 1% to 5% based on the water and alcohol together. A particularly effective mixture for the purposes of the invention is ethyl alcohol of 55%–75% strength by weight containing 1–5% e. g. about 2% or 3% of sodium or ammonium thiocyanate, the mixture being used at ordinary temperatures of around 20°–25° C.

A small proportion of an organic acid, for example formic, acetic or propionic acid, may be included in the dye liquid. The proportion should not be so high as to cause the mixture to swell the nylon 66. Thus, from 1% to 5% may be included in the dye liquid.

A very effective mixture for the purposes of the invention consists of 700 c. c. of methylated spirit, 240 c. c. of water, 30 c. c. of acetic acid and 20 gms. of sodium thiocyanate, together with the requisite dye. Using such a dye liquid containing a water-insoluble dye (at ordinary temperature) it is possible to colour the cellulose acetate of a fabric containing both cellulose acetate and nylon 66 while leaving the latter substantially uncoloured.

In place of the alcohol/water mixtures referred to above, other mixtures, particularly aqueous mixtures which have the requisite swelling action on cellulose acetate without undue swelling action on nylon 66, may be employed. Examples are mixtures of water with water-miscible ketones or esters, for example acetone, diacetone alcohol, glycol monoacetate or ethyl lactate. Concentrations of the order of 20% to 50% will usually give the requisite solvent power for the dye and swelling action on the cellulose acetate. Aqueous diacetone-alcohol of 30 to 45%

strength by weight may for instance be employed. Again there may be used a mixture of an alcohol, water, and a carboxylic ester which is not miscible in all proportions with water e. g. methyl, ethyl or propyl esters of formic, acetic, and propionic acids. An example of such a mixture is one of 40 parts of ethyl acetate, 60 parts of ethyl alcohol (92% strength by weight) and 20 parts of water. Non-aqueous liquids may also be used e. g. a mixture of a hydrocarbon with one of the above mentioned esters which are not miscible in all proportions with water, e. g. a mixture of ethyl acetate and xylene containing 70 or 80% of the former. The liquid medium is advantageously a good solvent for the particular dye or dyes employed.

In effecting the desired colouring of the cellulose ester or ether portions of the materials, the materials are preferably left in contact with the dye solution for suitable periods which may range from a few minutes, say 5 to 10, up to an hour or more. On a large scale dyeing may be effected on a jig. Mechanical impregnation methods may be used though the best results are obtained as a rule by providing for a longer time of contact between dye solution and material than is usually convenient when employing such methods.

The dyes employed may be any of those water-insoluble dyes which, in the form of aqueous dispersions, are capable of colouring cellulose acetate fibres. These dyes may be of the nitrodiarylamine, azo, or amino-anthraquinone series. Examples are the azo dye obtained by coupling diazotised p-amino-acetanilide with o- or p-phenyl-phenol, the azo dye from diazotised p-nitroaniline and di-(beta-hydroxyethyl)-m-chlor-aniline, 1-phenylamino-anthraquinone, 1-amino-4-phenyl-amino-anthraquinone, and 1-amino-4-phenylamino-anthraquinone-2-carboxylic-hydroxyethyl-amide. Again, water-soluble dyes can be used and it is remarkable that good resist effects can be obtained on the nylon 66 when using acid dyes. Most acid dyes, in aqueous solution, have good affinity for nylon 66. Acid dyes which can be used are Xylene Milling Blue 6G, (Schultz, 7th edition, 1st supplement, p. 146), Crocein Scarlet 3BS, (Color Index No. 252), Azo Rubinol 3GP, (Schultz, 7th edition, 2nd supplement, p. 121), Neolan Orange R, (AATCC Year Book 1947-48, page 212), Coomassie Brown RS, Solway Ultra Blue BS, (1-amino-4-phenyl-amino-anthraquinone-2-sulphonic acid), and Supramine Green G, (Schultz, 7th edition, vol. 2, p. 203). The reference to Schultz is to the well known Schultz Farbstofftabellen, 7th edition. Any of the foregoing dyes may be used as solutions of say 1% strength in the methylated spirit/water/acetic acid/sodium thiocyanate mixture referred to above the proportions being 70/24/3/2 as indicated.

Following the application of the dye solutions to the textile material by immersion, printing, padding or other methods, the material is preferably washed off, for example first in cold water and then in warm water. This removes adhering dye liquor from the fabric, but removes little or no colour from the cellulose acetate portion. The material may then be dried in the usual way.

After colouring the cellulose acetate portion of the material, the latter may then have its nylon 66 content coloured in any suitable way. For this purpose acid colours, or direct cotton colours which have affinity for nylon 66 but little or no affinity for cellulose acetate, can be applied as aqueous baths. The dyeing may be, of course, carried out so as to obtain a contrast of shade between the cellulose acetate fibres and the nylon 66 fibres. Alternatively, the nylon 66 fibres may be dyed with acid or direct cotton dyes in the same shade as the cellulose acetate fibres. As already indicated, this may be a convenient method of obtaining a solid shade on the two fibres, since there are very few dyes, particularly among the yellows, oranges and reds, which dye nylon 66 in the same shade as they do cellulose acetate. If desired, the nylon 66 may be dyed before dyeing the cellulose acetate portion of the material.

The fibres of the textile material coloured in accordance with the invention may be in the form of continuous filaments or in the form of staple fibres, and both components of the material may be in the same form or the two may be in different forms. The textile materials containing the two kinds of fibres may be yarns or fabrics; yarns may be those spun from a mixture of cellulose acetate staple fibre and nylon 66 staple fibre, or those obtained by doubling together two or more yarns, at least one of which is of cellulose acetate fibres while another is of nylon 66 fibres; fabrics may be those formed from yarns containing both kinds of fibres, or those formed from cellulose acetate yarns on the one hand and nylon 66 yarns on the other. Such fabrics may be jacquard fabrics, for example jacquard fabrics woven from a nylon 66 warp and a cellulose acetate weft, so as to exhibit a satin-faced pattern of nylon 66 upon a ground showing both cellulose acetate yarns and nylon 66 yarns. Alternatively, the warp may consist of cellulose acetate yarns, and the resulting fabric exhibit a satin-faced pattern of cellulose acetate yarns on a ground of the two types of yarns.

*Example I*

A fabric having a warp of nylon 66 and a weft of cellulose acetate is immersed for five minutes at 25° C. in a solution of the following composition:

2100 cc. methylated spirit
720 cc. water
90 cc. acetic acid
60 g. sodium thiocyanate
3 g. 1-phenylamino-anthraquinone
0.2 g. 2-nitro-4-chlor-diphenylamine

which colours the cellulose acetate a deep rose pink but leaves the nylon 66 unstained. After rinsing thoroughly, first in cold and then in warm water, the fabric is dried, and entered into a bath at 40:1 volume ratio containing:

0.2% Naphthalene F Red BNS
0.1% Lissamine F Yellow 2GS, (Schultz, 7th edition, No. 736)
3% formic acid (80%)

calculated on the weight of the material. Dyeing is continued for one hour at 80° C., and the pattern well rinsed and dried. An "Old Rose" shade, having good fastness properties, is produced on both fibres.

*Example II*

A fabric composed of cellulose acetate yarns and nylon 66 yarns is immersed for 5 mins. at 25° C. in a mixture of the following composition:

700 ccs. methylated spirit
240 ccs. water
30 ccs. acetic acid
20 grs. sodium thiocyanate
10 grs. Croceine Scarlet 3BS

and thoroughly rinsed, first in cold, then in warm water and dried. The cellulose acetate is coloured a bright scarlet shade, while the nylon 66 is unstained, and if desired, may be dyed in self shade or contrasting shade with acid dye-stuffs as described in Example I.

*Example III*

A fabric composed of cellulose acetate and nylon 66 yarns is immersed for five minutes at 25° C. in a mixture of the following composition:

700 ccs. methylated spirit
240 ccs. water
30 ccs. acetic acid
20 grs. sodium thiocyanate
10 grs. Solacet Fast Blue 2BS, (identical with Solway Ultra-Blue BS)

and thoroughly rinsed, first in cold water, then in warm water, and dried. The cellulose acetate yarn is dyed a deep brilliant blue shade, while the nylon 66 is only very slightly tinted, and may be dyed in self or contrasting shades with acid dyestuffs as described in Example I.

*Example IV*

A fabric composed of equal parts of cellulose acetate and nylon 66 yarns is immersed for 1 hour at 25° C. in a dyebath of the following composition:

400 ccs. diacetone alcohol
600 ccs. water
20 grs. ammonium thiocyanate
2.5 grs. Artol Blue B, (corresponding with Wool Blue BL, Schultz, 7th edition, No. 974).

It is then thoroughly rinsed, first in cold, then in warm water, and dried. The cellulose acetate is dyed a medium shade of blue, whilst the nylon 66 is only slightly tinted.

The Artol Blue B may be replaced by Croceine Scarlet 3BS which gives a scarlet shade on the cellulose acetate leaving the nylon 66 white, or by 1-amino - 4 - phenylamine - anthraquinone-2-carboxylic-hydroxyethyl-amide, which gives a full blue on the cellulose acetate, the nylon 66 being only tinted.



Similar methods may be used for colouring analogous materials in which the cellulose acetate fibres are replaced by fibres of other cellulose esters or ethers, for example cellulose butyrate, propionate, acetobutyrate or acetopropionate, or in which the nylon 66 fibres are replaced by fibres of other superpolyamides.

Having described our invention, what we desire to secure by Letters Patent is:

Process for the coloration of textile material comprising both cellulose acetate fibers and fibers of a superpolyamide so as to color the former but leave the latter substantially uncolored, which comprises subjecting the material at ordinary temperatures to the action of a solution of an acid dye in aqueous ethyl alcohol of 55–75% strength by weight, said aqueous alcohol containing from 1–5% of acetic acid and from 1–5% of a compound selected from the group consisting of sodium and ammonium thiocyanates.

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