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EFFECT THREADS, FIBROUS MATERIAL CONTAINING THE SAME AND PROCESS OF MAKING

Hans Helfenberger, Binningen, near Basel, and Werner Hagenbuch, Basel, Switzerland, assignors to Sandoz A. G., Basel, Switzerland, a Swiss firm

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The present invention relates to effect threads from natural or synthetic proteinic fibers such as wool, silk or Lanital and to fibrous material containing such effect threads, the latter being characterized by a reduced affinity for wool dyestuffs which draw from acid or neutral baths.

Processes are known according to which the affinity of wool and silk for dyes has been reduced by means of concentrated sulphuric acid or mixtures of acetic anhydride, acetic acid and sulphuric acid, or by treating the fibers with a solution of formaldehyde in aqueous sulphuric acid with or without the addition of aromatic sulphonation products, or also by means of tannic acid with the addition of tin, formaldehyde, $ZnCl_2$ or pyridine. It has also been proposed to treat wool or silk fibers with either synthetic resins or with aqueous solutions of glyoxal-bis-bisulphite or with alkaline hypobromite solutions in order to reduce their ability of being dyed with acid dyes.

The disadvantage of all these resist treatments resides in the fact that either the wool or silk fibers become damaged with regard to their physical properties, undergo discoloration or a change in handle, or the resist produced on the fiber is unsatisfactory. Some of these known processes have the disadvantage of being accompanied by unpleasant odors and in some of them special apparatus and solvent recovery plants are required. Most of these processes are also too expensive for technical application.

A primary object of the present invention is the embodiment of a method for the preparation of effect threads of the character described and of fibrous materials containing such effect threads with or without untreated, i. e. unreserved, threads which method is free of the aforedescribed disadvantage.

Briefly stated, the said disadvantages are avoided and effect threads, the tinctorial properties of which are so modified that they are excellently reserved with respect to wool dyes of the acid and neutral dyeing type are obtained when, according to the present invention, the natural or synthetic proteinic fibers, threads or yarns are treated with sulphamic acid, $NH_2.SO_2OH$.

According to the present invention, the natural or synthetic proteinic fibers are, for example, impregnated with a solution of sulphamic acid, freed from the excess of the impregnating solution by centrifuging or squeezing and dried as much as possible at temperatures below 100° C. The fibers are subsequently exposed to a heat treatment at temperatures of 120–175° C., preferably 140–150° C., rinsed and dried.

The impregnation can be carried out with an aqueous solution containing preferably from 16 to 25 per cent by weight of sulphamic acid at temperatures varying from 10 to 80° C., the preferred temperature range being 20 to 40° C. Alternatively it may be carried out with solutions of sulphamic acid in other solvents, such as for example formamide, or also in mixtures of these solvents, e. g. water and formamide.

In order to achieve uniform impregnation, acid-resistant wetting agents such as isooctylphenyl-nonaglycol ether or dodecylbenzol sulfonic acid can be added to these solutions. However these additions may be omitted without essentially altering the achieved results.

Furthermore, substances can be added to these aqueous solutions which have a swelling action on proteinic fibers and thus facilitate the chemical resist treatment of the latter. Such swelling agents are, for example, formic acid, acetic acid or urea as well as substances such as formamide, acetamide, thiourea, phenol, etc., listed in French Patent No. 794,750. If the impregnation is, for example, carried out with an aqueous solution of sulphamic acid to which has been added 0.2 to 1.0 mol of swelling agent, e. g. urea or acetamide, per mol of sulphamic acid present, then the heat treatment can be carried out within a shorter time and/or at lower temperatures, e. g. 100° C. Furthermore, the solubility of the sulphamic acid in the impregnating solution is thereby increased so that impregnation becomes possible at room temperature (e. g. about 20–40° C.) without undesirable crystal formation.

Addition of more than 1 mol of urea per mol of sulphamic acid present is of detrimental effect upon the fiber strength.

The process according to the present invention is thus substantially different from those already known, e. g. from the process described in British Patent No. 648,883, relating to the flame-proofing of cellulosic and proteinic materials where a high proportion of organic nitrogen-containing bases is required in order to achieve the desired effect.

During the heat treatment of the proteinic fibers, impregnated according to the present invention, part of the sulphamic acid combines with the fiber molecules to yield a chemically modified fiber of increased weight. Uncombined sulphamic acid and its decomposition products are subsequently removed by thorough rinsing with water. The heat treatment has to be carried out in such a way that the increase in weight of the fiber, due to combined sulphamic acid, is 6 to 7.5 per cent. The required heating time depends on the temperature, the form of the material and the amount of swelling agent added to the impregnation solution. Predyed fibers require shorter heating times at the same temperature than undyed fibers to achieve the desired gain in weight of 6 to 7.5 per cent. If, due to prolonged heat treatment, pre-dyed fibers incur an increase in weight of more than 7.5%, then the dyestuff tends to be stripped on subsequent cross-dyeing. Undyed wool fibers however may undergo an increase in weight up to about 10 per cent without any other disadvantages than a slight yellow discoloration. Appropriate heating times for undyed wool yarn in hank form, impregnated e. g. with a 20% aqueous solution of sulphamic acid are for example:

Temperature, °C.:	Time, min.
130	30
140	10
150	5
160	2

When impregnated as above, but with the addition of 5

per cent urea, then suitable heating treatments are for example:

Temperature, °C.:	Time, min.
115	60
120	40
130	15

For pre-dyed yarns, impregnated e. g. with 20% sulphamic acid and 5% urea in water, appropriate heating treatments are for example:

Temperature, °C.:	Time, min.
105	60
110	45
115	30

The solutions employed according to the present invention can be re-used without further processing for new impregnations. Drying and heat treatment can, if desired, be carried out together; a two-stage process is however preferable for better control of the heat treatment. Effect threads and fibrous materials containing these can be produced according to the present invention from natural or synthetic proteinic fibers, threads or yarns.

The resisted fibers or threads possess a strongly diminished affinity for acid wool dyes and a more or less strongly reduced affinity for direct and vat dyes; they are, however, dyed more strongly with basic dyes. Woven or knitted fabrics, hosiery goods or other fibrous materials made from natural or synthetic proteinic fibers and/or other textile fibers, which contain effect threads produced according to the present invention yield white effects when piece-dyed with those acid wool dyes and chrome dyes which are known to give white effects on acetylated wool. Representatives of this group are e. g. besides those mentioned in the working examples, the dyes listed in the Textile Journal of Australia, vol. 21, Number 1 (20.3.1946), page 55 ff, which are known to exhibit a much greater affinity for chlorinated wool than for normal wool. When the effect threads, prior to being immunized, have been pre-dyed, especially with vat or chrome dyes fast to carbonizing, then colored effects will be achieved.

The effect is even, and fast to fulling in an alkaline medium and also fast to carbonizing if special precautions are taken. Wool retains its tensile strength, its felting property as well as its handle and look, and in addition undergoes a 6 to 10% increase in weight. A further advantage of the process is that it can be carried out with apparatus conventionally employed in the textile finishing industry.

The following examples illustrate the invention without limiting it. The percentages are percentages by weight.

Example 1

Wool yarn is impregnated at 30° C. in an aqueous solution containing 20% of sulphamic acid

$$NH_2.SO_2OH$$

and 0.2 gram per liter of a water-soluble isooctylphenylpolyglycol ether, centrifuged to a content of impregnation liquor of 45% and then dried at 70 to 75° C. It is subsequently heated for 2 minutes at 160° C. in a yarn drying oven, then thoroughly rinsed and dried. The increase in weight amounts to 6% and the tensile strength is completely maintained. This yarn is woven in equal parts with untreated wool to yield a mixed material and the latter is dyed with acid wool dyes such as Xylene Acid Milling Blue BR, Azo Acid Red L (Schultz Farbstofftabellen No. 105, 1931 edition), Fast Sulphone Black F (Rowe Color Index No. 306, 1924 edition) or Alizarine Yellow G (afterchromed) (Schultz Farbstofftabellen No. 230, 1931 edition) or Alizarine Light Green BT (afterchromed). The yarn treated according to the present invention remains substantially undyed.

Example 2

Wool yarn is impregnated at 35° C. in an aqueous solution containing 20% of sulphamic acid, 12.4% of urea and 0.2 gram per liter of a water-soluble isooctylphenylpolyglycolether, freed from the excess of the solution by centrifuging, dried and heated for 5 minutes at 150° C. The yarn undergoes an increase in weight of 7% and is completely reserved to dyeing by Azorhodine 2G (Schultz Farbstofftabellen No. 40, 1931 edition).

Similar results are obtained if instead of urea there is added an equivalent amount of another base such as dicyandiamide or pyridine.

Example 3

Wool yarn, which has been dyed with 1% of Omega Chrome Yellow ME (Schultz Farbstofftabellen, Ergänzungsband II, page 221, 1939 edition) and afterchromed, is impregnated according to the method described in Example 1, freed from the excess of the impregnating solution and dried. It is then heated for 5 minutes at 150° C., rinsed in the cold and dried; the increase in weight amounts to 6%. The shade of the dyeing remains unchanged and does not change on cross-dyeing with Xylene Acid Milling Blue BR or Sulfonine Blue R (Schultz Farbstofftabellen, Ergänzungsband II, page 261, 1939 edition).

Example 4

Wool yarn, pre-dyed with 1% of Thianthrene Orange R (Rowe Color Index No. 1217, 1924 edition), is treated according to the method described in Example 3. The increase in weight amounts to 7.8%, the shade of the yarn remains unchanged, and the yarn is fast towards cross-dyeing with Xylene Acid Milling Blue BR or Sulfonine Blue R.

Example 5

Unloaded silk is impregnated according to the method described in Example 1, mangled to a content of impregnation liquor of 51%, then dried and heated for 2 minutes at 150° C. The silk, which remains white, increases in weight by 7% and is completely resistant to Azorhodine 2G.

Example 6

Lanital wool is impregnated at 20° C. in an aqueous solution containing 18% by weight of sulphamic acid and 0.2 gram per liter of a water-soluble isooctylphenylpolyglycol ether, hydro-extracted to a content of impregnation liquor of 48% and dried at 50° C. It is then heated for 5 minutes at 130° C., rinsed with water and dried. The Lanital wool thus treated has increased in weight by 6% and shows a strongly reduced affinity for Azorhodine 2G.

Example 7

Wool muslin material whose warp consists of colored threads which have been subjected to a resist treatment according to the method described in Example 3 and of untreated woolen threads in the proportion of 1:4 respectively, is dyed with the blue dyestuff described in Example 2 of the British Patent No. 512,618. A textile material with yellow stripes on blue ground is thus obtained.

Example 8

A wool yarn is impregnated at 30° C. in an aqueous solution containing 19% of sulphamic acid, 5% of glacial acetic acid and 0.1% of a water-soluble isooctylphenylpolyglycol ether, freed from the excess of the solution, dried at 70° C. and subsequently heated for 1 hour at 115° C. The yarn shows an increase in weight of 6.7% after rinsing and drying and remains practically unstained when cross-dyed with 0.5% Azorhodine 2G in the presence of an equal amount of untreated wool.

Example 9

Wool yarn is treated exactly according to the method described in Example 8, except that the impregnating solution contains 5% of acetamide instead of 5% of glacial acetic acid. The yarn undergoes an increase in weight of 7.9% and likewise remains practically white during cross-dyeing.

Example 10

Wool yarn is impregnated at 20° C. in a solution of 20% of sulphamic acid and 10% of urea in water, and after removing the excess of solution by centrifuging is dried at 70° C. and then heated for 1 hour at 110° C. After washing and drying the yarn exhibits the same properties as those described for yarn treated according to Example 8.

Example 11

A wool yarn, pre-dyed with 0.5% of Alizarine Light Grey BS (after-chromed) (Schultz Farbstofftabellen No. 1195, 1931 edition), is impregnated with an aqueous solution containing 20% of sulphamic acid, 10% of urea and 1 gram per liter of a water-soluble isooctylphenylpolyglycol ether. The yarn, after being freed from the excess of the solution, is dried at 70° C. and then heated for 10 minutes at 110° C.; it possesses after the rinsing and drying a good resistance towards acid and chrome dyes. The increase in weight amounts to 7.4%.

Example 12

Wool yarn, which has been pre-dyed with 0.5% of Alizarine Light Grey BS (afterchromed), is impregnated according to the method described in Example 1, dried and then heated for 1 hour at 120° C. The increase in weight amounts to 6.8% and the yarn exhibits a good reservation when cross-dyed with chrome dyes.

Example 13

A wool yarn, pre-dyed with 0.5% of Alizarine Light Grey BS (Rowe Color Index No. 1085, 1924 edition) (afterchromed), is impregnated at 20° C. with a solution consisting of 19% sulphamic acid, 5% urea and 76% water, and, after drying, heated for 1 hour at 105° C. The washed and dried yarn which is 6.4% heavier than the starting material is woven together with an equal amount of untreated undyed wool and this mixed material is cross-dyed with 0.5% of Azorhodine 2G. A colored article with pure grey and red threads is obtained.

Having thus disclosed the invention, what is claimed is:

1. A process for modifying the tinctorial properties of proteinic fibres, which comprises impregnating the said fibres with an acid solution containing sulphamic acid as effective resist-producing agent and having a pH which is lower than 6, and then subjecting the impregnated fibres to a heat treatment at 105 to 175° C. until there is an increase in weight of the fibres of about 6 to about 10 per cent, whereby the resultant fibres are reserved with respect to wool dyes of the acid and neutral dyeing type.

2. A process for modifying the tinctorial properties of proteinic fibres, which comprises impregnating the said fibres with an acid solution containing sulphamic acid as effective resist-producing agent and having a pH which is lower than 6, and then subjecting the impregnated fibres to a heat treatment at 120 to 175° C. until there is an increase in weight of the fibres of about 6 to about 7.5 per cent, whereby the resultant fibres are reserved with respect to wool dyes of the acid and neutral dyeing type.

3. A process for modifying the tinctorial properties of proteinic fibres, which comprises impregnating the said fibres with an acid solution containing sulphamic acid as effective resist-producing agent and having a pH which is lower than 6, the said solution containing from about 16 to about 25 per cent by weight of sulphamic acid, and then subjecting the impregnated fibres to a heat treatment at 120 to 175° C. until there is an increase in weight of the fibres of about 6 to about 7.5 per cent, whereby the resultant fibres are reserved with respect to wool dyes of the acid and neutral dyeing type.

4. A process for modifying the tinctorial properties of wool fibres, which comprises impregnating the said fibres with an aqueous acid solution containing sulphamic acid as effective resist-producing agent and having a pH which is lower than 6, the said solution containing from about 16 to about 25 per cent by weight of sulphamic acid, and then, after drying the same at a temperature below 100° C., subjecting the impregnated fibres to a heat treatment at 120 to 175° C. until there is an increase in weight of the fibres of about 6 to about 7.5 per cent, whereby the resultant fibres are reserved with respect to wool dyes of the acid and neutral dyeing type.

5. A process for modifying the tinctorial properties of wool fibres, which comprises pretreating the said fibres with a dyestuff which is fast to carbonization, impregnating the said fibres with an aqueous acid solution containing sulphamic acid as effective resist-producing agent and having a pH which is lower than 6, the said solution containing from about 16 to about 25 per cent by weight of sulphamic acid, and then, after drying the same at a temperature below 100° C., subjecting the impregnated fibres to a heat treatment at 120 to 175° C. until there is an increase in weight of the fibres of about 6 to about 7.5 per cent, whereby the resultant fibres are reserved with respect to wool dyes of the acid and neutral dyeing type.

6. A process for modifying the tinctorial properties of proteinic fibres, which comprises impregnating the said fibres with an acid solution containing sulphamic acid as effective resist-producing agent and having a pH which is lower than 6, the said solution containing from about 16 to about 25 per cent by weight of sulphamic acid, and also containing a water-soluble swelling agent for said fibres, and then subjecting the impregnated fibres to a heat treatment at 120 to 175° C. until there is an increase in weight of the fibres of about 6 to about 7.5 per cent, whereby the resultant fibres are reserved with respect to wool dyes of the acid and neutral dyeing type.

7. A process for modifying the tinctorial properties of wool fibres, which comprises impregnating the said fibres with an aqueous acid solution containing sulphamic acid as effective resist-producing agent and having a pH which is lower than 6, the said solution containing from about 16 to about 25 per cent by weight of sulphamic acid and also containing a water-soluble swelling agent for said fibres, and then, after drying the same at a temperature below 100° C., subjecting the impregnated fibres to a heat treatment at 120 to 175° C. until there is an increase in weight of the fibres of about 6 to about 7.5 per cent, whereby the resultant fibres are reserved with respect to wool dyes of the acid and neutral dyeing type.

8. A process according to claim 7, wherein said swelling agent is urea in an amount not exceeding about 1 mol per mol of sulphamic acid.

9. Heat-treated proteinic fibres having reduced affinity for wool dyes of the acid and neutral dyeing type, said fibres being obtained by a process according to claim 1.

10. Heat-treated wool fibres having reduced affinity for wool dyes of the acid and neutral dyeing type, said fibres being obtained by a process according to claim 4.

11. Heat-treated pre-dyed wool fibres having reduced affinity for wool dyes of the acid and neutral dyeing type, said fibres being obtained by a process according to claim 5.

12. Textile material comprising effect threads consisting at least in part of heat-treated proteinic fibres having reduced affinity for wool dyes of the acid and neutral dyeing type, said fibres being obtained by a process according to claim 1.

13. Textile material comprising effect threads consisting at least in part of heat-treated wool fibres having reduced affinity for wool dyes of the acid and neutral dye-

ing type, said fibres being obtained by a process according to claim 4.

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