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PROCESS FOR PRODUCING SHRINKAGE
EFFECTS IN TEXTILES

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The present invention relates to a process for producing shrinkage effects in textile materials.

It is an object of the invention to provide a process by which textile materials containing in part fibers of organic cellulose derivatives and at least one-hydrophile additional component may be easily and effectively shrunk. Further objects will be seen from the detailed specification following hereafter.

10 There have been many proposals for producing pattern effects in textiles by working-up together fibrous material having different capacities for swelling or shrinking and then subjecting the material to the action of a shrinking agent. For example, stretched and non-stretched acetate artificial silk have been used in alternation as a weft and then the fabric has been subjected to the usual wet processing whereby a crepon effect is produced because the non-contracting threads of the non-stretched artificial silk are pressed outwards. Also fabrics of mixed acetate artificial silk and viscose have been patterned by treating them with agents for strongly shrinking the acetate artificial silk, for instance alcohol of 50 per cent strength and a mixture of methylene chloride and alcohol. In this case the pattern of the viscose artificial silk is produced by the contraction of the acetate artificial silk.

This invention relates to a process whereby, already without stretching and without costly shrinking agents, such as alcohol or acetone, various effects of this kind are obtained by making a mixture which contains at least in part fibers of organic cellulose derivatives which, in addition to their main component, for example cellulose acetate or ethyl cellulose, have one or more components which from the first or, if desired, after additional treatment with, for instance, hydrolysing, alkylating or aminating agents, have a stronger hydrophile nature than the main components, and then, so far as may be necessary after imparting hydrophile properties to these additional components, subjecting the material to the action of an agent which causes these additional components to swell or loosen and the main components to soften. In this manner the fibres become thicker and at the same time shrink in length, which changes considerably the physical character of the treated yarn, warp or fabric.

In addition to the shrinkable fibres of hydrophobe material any other fibrous material may be added, for example ordinary acetate artificial fibres, viscose artificial fibres or natural silk. However, it is not necessary that the portion of

the fibrous mixture which does not shrink or shrinks only little in warps, yarns or fabrics, should differ in its original structure from the shrinking component. Those mixtures also come within the scope of the invention in which the pretreatment that makes the shrinking process possible or favours it has been applied only partially or mixtures in which one part of the fibres has been treated to produce hydrophile properties and another part has been treated to produce hydrophobe properties. In such cases it is possible to produce shrinking effects with mixtures of fibres which subsequently may still be dyed uniformly, especially if the substances which impart hydrophile properties or hydrophobe properties are removed or are neutralised in action before the dyeing process. Also, if the dyeing precedes the treatment for shrinking or the operation for increasing the hydrophile properties of the additional components, the advantage of uniform dyeing is in some cases retained.

As additional materials there may be selected those of neutral nature, for instance hydrophile polymerisates, like polyvinyl methylether or polyvinyl ethylether, polyvinyl chloracetate saponified from its pyridium compound on the fiber, cellulose nitrate, cellulose acetate nitrate, methylcellulose nitrate, each denitrated within the fibre, mixed polymerisates from vinyl alcoholether and vinyl formate, saponified in the fibre.

It is of particular advantage, however, to use materials which contain a pronounced salt-forming group of cationic or anionic nature or substances which are changed into products of this kind by an after-treatment on the fibre.

Anionic additions are, for example, the polymerisates and mixed polymerisates from or with α -unsaturated acids, such as acrylic acid, methylacrylic acid, maleic acid, itaconic acid, sorbic acid, as components, among which the anhydric mixed polymerisates from maleic anhydride and vinyl compounds, such as vinyl alkyl ether, vinyl halide, vinyl esters of carboxylic acids, such as vinyl formate, vinyl acetate or vinyl chloracetate, will take the form of the addition. There also come into question certain alkyd resins having many free acid groups and ester acids of highly polymeric hydroxyl compounds, for example the acid esterification products of methylcellulose, acetylcellulose, partially acetylated vinyl alcohols with dicarboxylic acids, for instance succinic acid, maleic acid, diglycolic acid, phenyl-pyro-tartaric acid.

Cationic additions suitable for the invention are, for example, aminated polymeric halides,

such as polyvinyl chloracetate or polyglycide chloracetate aminated on the fibre; also polyacrylic acid- ω -diethyl-amino-ethylamide, highly polymeric ethylene-imine, pyridine carboxylic acid ester of cellulose alkylated on the fiber. It is also possible to have anionic and cationic compounds together in the product which is to be treated, for example the above-named mixed polymerisate with maleic anhydride as a component and the polyvinyl chloracetate aminated with pyridine on the fibre.

Concerning the choice of the serviceable components, reference may be made to U. S. A. patent application Ser. No. 41,500 filed September 20, 1935, now U. S. Patent 2,142,007 dated December 27, 1938, and also British Patents 455,602 dated October 19, 1936 and 459,711 dated January 8, 1937.

In the case of the material which contains a polymeric addition compound of neutral non-salt-forming character, the shrinking process is comparatively independent of the pH-value of the liquor so far as the swelling or softening agent is not dependent upon this for its action. In the case of materials of salt-forming character, the amount of the shrinking can be widely affected by adjustment of the pH-value and by addition of certain ions. Thus, the shrinking in the case of materials having acid groups is increased by an alkaline treatment for activating the acid groups by salt-formation or by direct addition of an alkaline agent, especially a salt of alkaline reaction to the treating liquor. Such agents are, for example, amines, like triethanolamine, hydroxyethyl-cyclohexylamine, sodium oleate, sodium tetraborate, tetramethyl ammonium acetate, alkali acetate, alkali phosphate, alkali phenolate.

Also very feeble bases like urea are highly favourable in effect if they are used in sufficient concentration.

On the contrary, in the case of cationic additions an acid pretreatment or an addition of acid to the shrinking bath is of essential effect.

It is by no means immaterial what alkali or what acid is used. For increasing the shrinking it is necessary that the ions in question should enhance the hydrophile character of the added substance. In this case, therefore, additions which react with the reactive groups with formation of hydrophobe or sparingly soluble products are to be avoided. Correspondingly, in the case of substances having carboxyl-groups, amines of high molecular weight (especially when insoluble in water) and inorganic bases having polyvalent cations and also many complex cations are to be avoided.

In the case of cationic additions, those acids or their salts should be selected which in general form with organic bases freely soluble compounds, for example formic acid, acetic acid, glycolic acid, lactic acid, tartaric acid, glyceric acid, citric acid, gluconic acid, maleic acid, glycerophosphoric acid, hydrochloric acid, hydrosulphocyanic acid.

The specific behaviour of the various ions may with advantage be used for producing certain effects; for example, a mixed yarn may be produced which consists of one and the same fibrous material, for example an acetyl cellulose with an addition of 12.5 per cent of the mixed polymerisate from vinyl methylether and maleic anhydride in which, however, a part has been treated before the spinning in a liquor ratio of 1:50 with 6 grams of soap per litre for 2 hours at 75° C.

When this yarn is submerged in water at 95-100° C., the component which has been saturated with alkali in part shrinks considerably, while the other components not treated with alkali suffer hardly any change of length and, therefore, are pressed outwards. After acidifying the effect thread can be dyed uniformly with basic dyestuffs or even with dyestuff suspensions.

If, on the other hand, the shrinkage has been produced by an alkaline liquor, especially a soap liquor, similar results are obtained if the one component of the yarn is previously treated with a salt having hydrophobe cations, for example with dodecylamin-acetate, zinc-acetate, calcium acetate or cadmium acetate.

The structures having cationic components may be given similar effects by using for the production of hydrophobe properties acids or salts which yield with amines in normal manner sparingly soluble salts, for example trichloroacetic acid, perchloric acid, tetrahydro-naphthalene-sulphonic acid, naphthalene- and alkyl-naphthalene sulphonic acids, dodecyl sulphuric acid. A definite boundary between hydrophile and hydrophobe ions obviously cannot be determined, since the properties of the addition in question as regards their capacity for swelling and solubility in the form of the acid or base of the salts may be quite different. In both cases, however, by a simple preliminary experiment the behaviour can be quickly ascertained so that there is no difficulty for the expert in finding a suitable assistant.

Obviously there is no reason why the shrinkage should not be enhanced by the addition of swelling agents specific for the cellulose derivative. The use of such an agent is, however, generally unnecessary but may have importance if for some reason, for example in consideration of a dyeing, the treatment is to be carried out at a low temperature or if the cellulose derivative has a very low swelling capacity in water.

The following examples illustrate the invention:

Example 1

An acetate artificial silk warp of 100 deniers is woven in alternation with ordinary acetate artificial silk of 150 deniers and with an acetate silk having 10 per cent of the mixed polymerisate from vinyl methyl-formate and maleic anhydride also of 150 deniers in such a manner that over a breadth of about 4 mms. small alternating rectangles are produced. By treatment with a soap solution which contains 7 grams of soap per litre and has a temperature of 85° C. there is produced an embossed effect. The material is finally dyed in the usual manner with 3 per cent of Cellitone Fast Yellow G (Schultz, Farbstofftabellen, vol. II, page 45) and top-dyed cold with 1 per cent of Coelestin Blue B (Schultz, Farbstofftabellen, vol. I, page 439). There is obtained a yellow relief pattern on a green ground.

Example 2

A sateen fabric which consists in the warp of alternating stripes above 6 mms. broad of an acetate artificial silk containing an addition of 12 per cent of a mixed polymerisate from vinyl methylether and maleic anhydride in the ratio of 1 mol:1 mol and of stripes of 3 mms. broad of ordinary artificial silk is treated at the boil with 5 grams of soap per litre for 10 minutes. In this manner there are obtained matt ribs on lustrous ground. On dyeing cold with Coelestin Blue B the ground is dyed clear blue while the ribs remain white.

Example 3

An acetate sateen of matt acetate artificial silk contains in the warp and weft a narrow rib of a lustrous artificial silk having 8 per cent of the mixed polymerisate from vinyl methyl-ether and maleic anhydride in the ratio of 1 mol:1 mol and 4 per cent of polyvinyl chloracetate. The fabric is first dressed in the usual manner, then brought into a soap bath of 95° C., whereby shrinking occurs. Finally, it is dyed by the nitrite process in the presence of 5 per cent of cyclohexyl-dimethyl-thiourea with 2 per cent of Indigo Sol Green JB (Schultz, Farbstoff-tabellen, 7th edition, page 133, vol. II). The undyed areas are raised in relief.

Example 4

A thread of 100 deniers from untwisted acetate artificial silk with a content of 1 per cent of titanium dioxide and 10 per cent of the mixed polymerisate from vinyl methylether and maleic anhydride in the ratio of 1 mol:1 mol is united with two threads of untwisted ordinary acetate artificial silk also having 1 per cent of titanium dioxide. The double threads are passed through a stretching device whereby they are partially torn. The roughed yarn is directly afterwards twisted on a ring spinning machine. By subsequently boiling for a short time in soap solution of 0.5 per cent strength containing 1 gram of borax per litre in the vat ratio of 1:50, there is obtained a very voluminous yarn in which the ordinary acetate artificial silk is pressed outwards. In producing such effect yarn it is advantageous to choose the material which is to shrink of higher individual titre, so that in the roughening the unshrinkable crimped component may preferably be torn.

Example 5

An acetate artificial silk produced by the dry spinning process and containing 10 per cent of monomethyl cellulose nitrate is denitrated by means of 25 grams of cyclohexylamine-hydro-sulphide per litre at 50° C. The denitrated yarn is then twisted with a thread of ordinary acetate silk. By treating the twisted thread at 40° C. with calcium sulphocyanide solution of 10 per cent strength, the denitrated silk shrinks more strongly than the ordinary acetate artificial silk, so that the latter is pressed to the surface. On dyeing with Naphthol AS components and developing with diazonium salts, the outer part remains nearly white while the core is intensely dyed.

Example 6

There are worked-up together to form a warp acetate artificial silk, which contains 10 per cent of the mixed polymerisate of vinyl methyl ether and maleic anhydride and has been pretreated for an hour with an aqueous liquor containing 10 per cent of zinc acetate, and a similar material, which has been immersed at 30° C. in a liquor ratio of 1:30 in an aqueous solution of 10 per cent of tri-ethanolamine calculated on the weight of the silk, and the finished goods are brought into a boiling soap bath containing 3 grams of soap per litre. After 10 minutes the goods are removed and soured. The portion which has been treated with tri-ethanolamine is shrunken, the other portion being practically unchanged in length. Correspondingly, the portion pretreated with zinc acetate is pressed into relief. If, instead of zinc acetate, cadmium acetate is used, the effect is practically the same. In this case,

if a fabric is immersed in a dilute ammonium-sulphide solution after the shrinking treatment, the part mordanted with cadmium is dyed yellow whereas the rest remains pure white.

Example 7

Strongly crimped acetate artificial wool is worked up in the proportion of 2:1 with an acetate artificial silk which contains 12 per cent of the mixed polymerisate from vinyl formate and maleic anhydride to produce a cord yarn and this is treated for 10 minutes with a boiling soap solution of 0.5 per cent strength. The volume of the yarn is increased by the contraction produced.

Example 8

A sateen ribbon of acetate artificial silk having an addition of 10 per cent of the mixed polymerisate from vinyl methylether and maleic anhydride in the ratio of 1 mol:1 mol, which in the breadth is woven 10 per cent more loosely than is normal for the desired quality of goods, is woven with the same material as in the warp but with the difference that the weft yarn has previously been treated for 4 hours at 40° C. in a liquor ratio of 1:30 with a solution containing per litre 2 grams of soap and 2 grams of borax. By treating the material with water of 95° C. shrinkage over the desired breadth is produced, while in the warp direction there is essentially no change of length. After souring, the product may be dyed with basic dyestuffs or suspension dyestuffs in uniform tints. In this way there is obtained a more uniformly covered product than that normally obtained; moreover, the quality of the dressing need not be so high.

Example 9

A skein of acetate artificial silk containing 10 per cent of polyvinyl chloracetate is aminated for 10 hours at 70° C. with 3 equivalents of pyridine in the form of vapour. By immersing the skein in acetic acid of 20 per cent strength at 40° C. there is produced a shrinkage of about 11 per cent accompanied by considerable increase of volume and a strong crimping. If, instead of the uniform material, a mixed yarn of the usual acetate artificial silk and the acetate artificial silk having the addition is used, there is produced a still more voluminous character especially if the acetate silk in question has already been subjected to a crimping treatment before the spinning. An interesting effect is produced also when in similar manner acetate silk is worked-up together with an addition of polyvinyl chloracetate and cellulose tri-acetate silk or fibre which is stable to boiling. While the shrunken threads are matt, the tri-acetate silk remains highly lustrous.

What I claim is:

1. A process for producing shrinkage effects in a textile material consisting chiefly of an organic cellulose derivative having incorporated throughout the filaments and fixed therein at least one polymeric hydrophile component of the group consisting of—polymerized vinyl ethers, polymerizates and mixed polymerizates containing α - β -unsaturated acids, mixed polymerizates from maleic acid anhydride and vinyl compounds, alkyl-resins containing free acid groups, ester-acids of polymeric hydroxy-compounds, polymerizates of the polyvinyl-series containing basic nitrogen, basic amides of polymerized acrylic acids, polymeric ethylene imines, and mixtures of these substances—which process comprises heating said textile material in an aqueous liquid

capable of swelling said polymeric component and of softening said organic cellulose derivative, whereby said hydrophile component is swollen, distorting the organic cellulose derivative filament and causing the same to shrink.

2. A process for producing shrinkage effects in a textile material consisting chiefly of an organic cellulose derivative having incorporated throughout the filaments and fixed therein at least one polymerichydrophile component of the group consisting of—polymerized vinyl ethers, polymerizates and mixed polymerizates containing α - β -unsaturated acids, mixed polymerizates from maleic acid anhydride and vinyl compounds, alkyd-resins containing free acid groups, ester-acids of polymeric hydroxy-compounds, polymerizates of the polyvinyl-series containing basic nitrogen, basic amides of polymerized acrylic acids, polymeric ethylene amines, and mixtures of these substances—which process comprises heating said textile material in an aqueous liquid capable of swelling said polymeric component and of softening said organic cellulose derivative at a temperature of from about 40° C. to the boiling point of said aqueous liquid, whereby said hydrophile component is swollen, distorting the organic cellulose derivative filament and causing the same to shrink.

3. A process for producing shrinkage effects in a textile material consisting chiefly of an organic cellulose derivative having incorporated throughout the filaments and fixed therein at least one polymeric hydrophile component of the group consisting of—polymerized vinyl ethers, polymerizates and mixed polymerizates from maleic acid anhydride and vinyl compounds, alkyd-resins containing free acid groups, ester-acids of polymeric hydroxy-compounds, polymerizates of the polyvinyl-series containing basic nitrogen, basic amides of polymerized acrylic acids, polymeric ethylene amines, and mixtures of these substances—which process comprises treating said textile materials with the solution

of an ion which enhances the hydrophile character of the said additional-component and heating said textile material in an aqueous liquid capable of swelling said polymeric component and of softening said organic cellulose derivative at a temperature of from about 40° C. to the boiling point of said aqueous liquid, whereby said hydrophile component is swollen, distorting the organic cellulose derivative filament and causing the same to shrink.

4. A process for producing shrinkage effects in a textile material consisting chiefly of an organic cellulose derivative having incorporated throughout the filaments and fixed therein a mixed polymerizate of maleic acid anhydride with vinyl alkyl ethers treating said material with an aqueous solution of an alkaline reacting salt and heating said textile material in an aqueous liquid capable of swelling said polymeric component and of softening said organic cellulose derivative at a temperature of from about 40° C. to the boiling point of said aqueous liquid, whereby said hydrophile component is swollen, distorting the organic cellulose derivative filament and causing the same to shrink.

5. A process for producing shrinkage effects in a textile material consisting chiefly of an organic cellulose derivative having incorporated throughout the filaments and fixed therein an aminated polymerized vinyl ester treating said textile material with an aqueous solution of an organic acid, which yields soluble salts together with amines, and heating said textile material in an aqueous liquid containing an agent capable of swelling said polymeric component and of softening said organic cellulose derivative at a temperature of from about 40° C. to the boiling point of said aqueous liquid, whereby said hydrophile component is swollen, distorting the organic cellulose derivative filament and causing the same to shrink.

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