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(54) **Shrink-proof treatment of cellulosic fiber textile**

(57) A method for the shrink-proof treatment of a cellulosic fiber textile comprising the steps of treating a cellulosic fiber textile with liquid ammonia and subsequently treating it with steam.

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Description**BACKGROUND OF THE INVENTION**5 **Field of the Invention**

[0001] The present invention relates to a method for the shrink-proof treatment of a cellulosic fiber textile. More particularly, it relates to a method for imparting good durable shrink resistance to cellulosic fiber textile without special chemical treatment such as resin finishing.

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Prior Art

[0002] Heretofore, cellulosic fiber textiles have been widely used as clothing materials since they have the advantages of moderate moisture absorption, water absorption, good hand-and-feel textures, and ease of treatment. Such cellulosic fiber textiles, however, suffer from shrinkage after washing and hand-and-feel hardening after repetitive washing.

[0003] The cause of the shrinkage after washing is correlated to two phenomena. One phenomenon is the deformation of woven and knitted goods by various forces applied during their manufacture and treatment. More particularly, as washing causes woven and knitted goods to be tossed and turned in a free state without the application of force, they tend to resume their original stable state, inviting shrinkage. Such shrinkage can be prevented by mechanical methods such as is typified by sanforization. The method using a sanforizing machine of the rubber belt or felt blanket type is to impart shrink-proof by physically and continuously compressing the fabric for contraction to reduce the shrinkage potential of the fabric. However, the method cannot achieve a full reduction of the shrinkage potential of thick fabric pieces or hard finished fabrics.

[0004] The other phenomenon is the shrinkage of woven and knitted goods as a result of individual fibers absorbing water to swell and to increase their cross-sectional area. This shrinkage occurs upon the absorption of water. After the fabric is dried to remove the water, the fabric tissue cannot recover its original size prior to swelling by itself. The fabric remains shrunk.

[0005] Finishing with a resin such as a cellulose reactive resin is effective for preventing the shrinkage. This resin finish forms chemical crosslinking between cellulose molecules of fibers to prevent swelling and impart shrink resistance.

[0006] The resin treatment of a cellulosic fiber textile, however, has the tendency that as the amount of resin added increases, the shrink-proof property is improved, but the tensile strength is reduced and hand-and-feel hardening is increased. Moreover, if a formaldehyde-containing resin is used, there is a problem that formaldehyde would be left in a fiber textile.

35 **SUMMARY OF THE INVENTION**

[0007] It is an object of the present invention to provide a method for the shrink-proof treatment of a cellulosic fiber textile to be fully durable shrink-proof without a resin treatment using a cellulose reactive resin or the like.

[0008] In order to achieve the above-mentioned object, the present inventors carried out a series of researches, which led to the findings that it is possible to obtain cellulosic fiber textile having fully durable shrink-proof if a cellulosic fiber textile is treated with liquid ammonia and then the treated cellulosic fiber textile (which has the crystal structure of cellulose III) is treated further with steam.

[0009] It is known that the treatment of cellulosic fiber textile with liquid ammonia causes fiber swelling and transforms the crystalline structure of cellulose I or cellulose II into the crystalline structure of cellulose III, with the swollen structure remaining after the removal of liquid ammonia, and that the treatment with liquid ammonia lowers the crystallinity and the liquid ammonia-treated fabric exhibits high shrink resistance by resin finish, without appreciable decrease in strength. The present inventors found that if the cellulosic fiber textile having the crystalline structure of cellulose III (which has been obtained by ammonia treatment for fiber swelling, with its crystalline structure transformed) is treated with steam at 98°C to 150°C under tension or without tension, the resulting treated textile exhibits significant shrink resistance without requiring special resin finish using a cellulose reactive resin or the like. The treated textile also has little loss of strength and experiences minimal shrinkage after washing and minimal hand-and-feel hardening after repetitive washing. Even in the case of thick fabrics and hard-finished fabrics, fully durable shrink-proof can be obtained. The present invention is based on these findings.

[0010] Accordingly, the present invention provides a method for the shrink-proof treatment of a cellulosic fiber textile comprising the steps of treating a cellulosic fiber textile with liquid ammonia and subsequently treating it with steam. According to the present invention, the steam treatment should preferably be carried out at 98°C to 150°C.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0011] The shrink-proof treatment method of the present invention comprises steps of treating a cellulosic fiber textile with liquid ammonia and subsequently treating it with steam under tension or without tension.

[0012] A cellulosic fiber textile which can be processed by the method of the invention is composed of cellulosic fibers including natural fibers and regenerated cellulose fibers, for example, cotton, hemp, rayon, polynosics, cuprammonium fibers, and high-strength regenerated cellulose fibers (available under the trade name of Tencel, for example). These natural fibers and regenerated cellulose fibers may take the form of composite fibrous materials obtained by blending with other fibers such as synthetic fibers, typically polyesters and polyamides. The composite fibrous materials should preferably have a greater content of cellulosic fibers, more preferably a cellulosic fiber content of at least 50% by weight.

[0013] The cellulosic fiber textile, which can be used herein, includes woven fabrics, knitted goods and non-woven fabrics. If desired, the textile may be subjected to pretreatment such as singeing, desizing, scouring, bleaching, and mercerizing. Also, the textile may have been dyed or printed.

[0014] First, the cellulosic fiber textile is treated with liquid ammonia, for example, by impregnating the textile with liquid ammonia kept at a temperature of -33°C or lower under atmospheric pressure. The said impregnating means include dipping in liquid ammonia, spraying of liquid ammonia, and coating of liquid ammonia. The said impregnating time may be properly selected in the range of about 5 to 40 seconds.

[0015] Liquid ammonia is most often used to induce a transition of cellulose I or II in the cellulosic fiber textile into cellulose III, although lower alkylamines such as methylamine or ethylamine may be used if desired. At the end of the process, the ammonia is removed from the liquid ammonia-treated cellulosic fiber textile by heating.

[0016] The steam treatment is carried out by contacting the liquid ammonia-treated textile with steam at 98°C to 150°C, preferably 105°C to 150°C. An apparatus for the steam treatment is any one capable of treating a cellulosic fiber textile with steam at normal pressure or high pressure. A continuous high-pressure high-temperature steamer may be used.

[0017] The time for steam treatment may vary depending on the steam treatment temperature. Preferably, the condition for the steam treatment is as follows.

(a)	temperature:	98°C to less than 105°C
	treating time:	1 hour or more, preferably 1 to 5 hours
(b)	temperature:	105°C to less than 115°C
	treating time:	40 minutes or more, preferably 40 minutes to 4 hours
(c)	temperature:	115°C to less than 125°C
	treating time:	25 minutes or more, preferably 25 minutes to 2.5 hours
(d)	temperature:	125°C to less than 135°C
	treating time:	15 minutes or more, preferably 15 minutes to 1.5 hours
(e)	temperature:	135°C to 150°C
	treating time:	5 minutes or more, preferably 5 minutes to 1 hour

[0018] The steam treatment should be carried out under tension or without tension, depending on the type and application of the textile. In the case of steam treatment by a continuous high-temperature high-pressure steamer, the textile is preferably kept flat by application of slight tension. In the case of steam treatment by a batch steamer, the fabric is preferably left free of tension.

[0019] When the steam treatment is carried out on the textile kept under no tension using a batch type steamer, the stresses in the textile material are released, resulting in improved shrink-proof. As additional advantages, the wet/dry

crease-proof properties are improved due to the setting effect of the steam treatment, crispness ("Hari") and resilience ("Koshi") are imparted, and the surface appearance is changed.

[0020] On the other hand, when the steam treatment is carried out on the textile under slight tension using a continuous type steamer, advantages are obtained in that no crease or irregularity is introduced into the textile and the selvage is not rolled since the textile is kept flat during the steam treatment. Treatment on a mass scale becomes possible.

[0021] The steam treatment may be applied to dyed or printed textile after dyeing or printing. Since the steam treatment needs no alkaline or acidic auxiliaries such as sodium hydroxide and acetic acid, it can be applied to dyed or printed textile without adverse effect on their color and color fastness. The absence of resin finish offers the advantage that the strength is not lowered.

[0022] Since the ammonia treatment and its subsequent steam treatment use no resins at all, the treated fabric is free of formaldehyde originating from resins. Moreover, it has little loss of strength and experiences minimal shrinkage after washing and minimal hand-and-feel hardening after repetitive washing. In addition, these treatments impart good shrink resistance even in the case of thick fabric or hard-finished fabric.

[0023] The following is a probable reason why the shrink-proof treatment method of the present invention achieves high shrink resistance without appreciable decrease in strength. Natural cellulose usually takes on the crystalline structure of cellulose I, and it is transformed partly into cellulose II upon mercerization (or treatment with caustic alkali). Regenerated cellulose originally takes on the crystalline structure of cellulose II. Upon treatment with liquid ammonia, the cellulosic fiber textile, which is composed of celluloses having different crystalline structures, swells as a whole because liquid ammonia enters the amorphous region as well as the crystalline region of cellulose, thereby destroying the hydrogen bond of cellulose. The subsequent heat treatment to volatilize ammonia forms new hydrogen bonds, giving rise to the crystalline structure of cellulose III in the crystalline region, with the result that the crystals are fixed in their swollen state. The steam treatment that follows the ammonia treatment returns the crystalline structure of cellulose III to the stabler crystalline structure of cellulose I or cellulose II. In this step, the fully swollen state is set. As the result, the fiber is immune to swelling by water at the time of washing. This produces good durable shrink resistance without deteriorating fabric strength.

[0024] After the shrink-proof treatment of the present invention, the cellulosic fiber textile may undergo final finish such as tentering and hand-and-feel control, as needed.

EXAMPLES

[0025] The invention will be described in more detail with reference to the following examples and comparative examples, which are not intended to restrict the scope of the invention.

Example 1

[0026] A plain weave cotton 100% fabric of 50-count single yarn (warp density 148 yarns/inch, weft density 80 yarns/inch) was conventionally bleached, treated with liquid ammonia for 10 seconds, and heated to evaporate the ammonia. The fabric was then wound loosely onto a plastic cylinder and was treated with steam in a flat state at 130°C for 1 hour by means of a small high-temperature/high-pressure steamer (supplied by Somei Senki K.K.).

Comparative Example 1

[0027] The procedure of Example 1 was repeated except that both the liquid ammonia treatment and the steam treatment were omitted.

Comparative Example 2

[0028] The procedure of Example 1 was repeated except that the steam treatment was omitted.

Comparative Example 3

[0029] The procedure of Example 1 was repeated except that the liquid ammonia treatment was omitted.

Example 2

[0030] A plain weave cotton 100% fabric of 50-count single yarn (warp density 148 yarns/inch, weft density 80 yarns/inch) was bleached conventionally, mercerized, treated with liquid ammonia for 10 seconds, and heated to evaporate the ammonia. The fabric was then treated with steam in a flat state at 130°C for 1 hour by means of a small high-

temperature/high-pressure steamer in the same manner as in Example 1.

Comparative Example 4

- 5 [0031] The procedure of Example 2 was repeated except that both the liquid ammonia treatment and the steam treatment were omitted.

Comparative Example 5

- 10 [0032] The procedure of Example 2 was repeated except that the steam treatment was omitted.

Comparative Example 6

- 15 [0033] The procedure of Example 2 was repeated except that the liquid ammonia treatment was omitted.

Example 3

- 20 [0034] A plain weave cuprammonium rayon 100% fabric of 75-denier cuprammonium rayon filament yarn as the warp and 100-denier cuprammonium rayon filament yarn as the weft (warp density 103 yarns/inch, weft density 80 yarns/inch) was desized conventionally, treated with liquid ammonia for 10 seconds, and heated to evaporate the ammonia. The fabric was then treated with steam in a flat state at 130°C for 1 hour by means of a high-temperature/high-pressure steamer in the same manner as in Example 1.

Comparative Example 7

- 25 [0035] The procedure of Example 3 was repeated except that both the liquid ammonia treatment and the steam treatment were omitted.

Comparative Example 8

- 30 [0036] The procedure of Example 3 was repeated except that the steam treatment was omitted.

Comparative Example 9

- 35 [0037] The procedure of Example 3 was repeated except that the liquid ammonia treatment was omitted.

Example 4

- 40 [0038] A plain weave rayon 100% fabric of 120-denier rayon filament yarn as the warp and 30-count single rayon staple fibers yarn as the weft (warp density 102 yarns/inch, weft density 57 yarns/inch) was desized conventionally, treated with liquid ammonia for 10 seconds, and heated to evaporate the ammonia. Then the fabric was treated with steam in a flat state at 130°C for 1 hour by means of a high-temperature/high-pressure steamer in the same manner as in Example 1.

45 Comparative Example 10

- [0039] The procedure of Example 4 was repeated except that both the liquid ammonia treatment and the steam treatment were omitted.

50 Comparative Example 11

- [0040] The procedure of Example 4 was repeated except that the steam treatment was omitted.

Comparative Example 12

- 55 [0041] The procedure of Example 4 was repeated except that the liquid ammonia treatment was omitted.
[0042] The results for washing endurance of the above woven fabrics according to tumble drying by JIS L-0217 103 method are shown in Table 1.

Table 1

		E1	CE1	CE2	CE3
Warp shrinkage	1 cycle of washing	0.3	7.4	4.2	4.1
	5 cycles of washing	0.6	8.9	4.8	5.4
	10 cycles of washing	0.9	9.6	5.1	6.1
		E2	CE4	CE5	CE6
	1 cycle of washing	1.8	6.8	4.8	3.3
	5 cycles of washing	2.5	8.1	5.9	4.4
	10 cycles of washing	3.1	8.6	6.3	5.2
		E3	CE7	CE8	CE9
	1 cycle of washing	1.2	6.5	3.1	1.6
	5 cycles of washing	1.2	8.7	3.3	1.7
	10 cycles of washing	1.3	8.9	3.5	2.0
		E4	CE10	CE11	CE12
	1 cycle of washing	2.5	13.6	9.0	3.5
	5 cycles of washing	2.8	15.8	9.7	3.8
	10 cycles of washing	3.2	16.2	10.2	4.3

Example 5

[0043] A 40-count two folded yarn cotton 100% tuck ("KANOKO") was treated with liquid ammonia for 10 seconds after mercerizing treatment, and heated to evaporate the ammonia. After bleaching, the knit was wound loosely onto a plastic cylinder, and was treated with steam in a flat state at 130°C for 1 hour by means of a high-temperature/high-pressure steamer, followed by tentering with pins for hand-and-feel adjustment as finishing treatment.

Comparative Example 13

[0044] The procedure of Example 5 was repeated except that both the liquid ammonia treatment and the steam treatment were omitted.

Comparative Example 14

[0045] The procedure of Example 5 was repeated except that the steam treatment was omitted.

Comparative Example 15

[0046] The procedure of Example 5 was repeated except that the liquid ammonia treatment was omitted.

[0047] The physical properties of the resulting knits ("KANOKO") are shown in Table 2.

Table 2

	E5	CE13	CE14	CE15
Warp + weft shrinkage(%) (103 method-tumble)	12.3	14.8	15.8	20.0
Wash-and-wear rating	2.5	2.3	2.2	2.0
Burst strength (kg/cm ²)	9.5	9.7	9.7	9.6

[0048] The shrink-proof treatment of the present invention imparts good durable shrink resistance to cellulosic fiber

textile without resin finish. The resulting textile has minimal shrinkage and minimal hand-and-feel hardening after repetitive washing.

Claims

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1. A method for the shrink-proof treatment of a cellulosic fiber textile comprising the steps of treating a cellulosic fiber textile with liquid ammonia and subsequently treating it with steam.

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2. The method of Claim 1, wherein the steam treatment is carried out at a temperature of 98°C to 150°C.

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