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PROCESS FOR THE TREATMENT OF CYANOETHYLATED COTTON TEXTILES WITH AMINES

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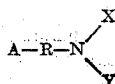
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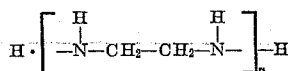
This invention relates to cotton products in the form of yarn or fabrics, and has for its object the provision of an improved process of increasing the tensile strength, elongation and abrasion resistance of such products. More particularly, the invention provides an improved process comprising the treatment of the cotton products with a water-soluble amine in liquid phase, advantageously in aqueous solution, to effect a surprising increase in the tensile strength, elongation, and abrasion resistance. The cotton product may be under tension or zero tension during the treatment. By "cotton products," we mean yarn, thread, cord, or fabrics formed of natural cotton or of partially cyanoethylated cotton.

The treatment of the cotton products under zero tension is also disclosed in our copending application Serial No. 388,054, filed October 23, 1953.

One of the important aspects of our invention is that we can treat the cotton product with a liquid amine at normal pressures and temperatures, or with a water solution of an amine in any suitable concentration, while under tension or zero tension, in a simple and practical operation in apparatus of the type commonly used to treat yarns and fabrics with liquids. The cotton product is treated with a water-soluble liquid amine having the general structure



wherein R is an aliphatic nucleus; X is a hydrogen atom, a hydrocarbon nucleus or a substituted hydrocarbon nucleus containing no substituents other than hydroxyl groups, mercapto groups or amino groups; Y is the same as X or OH; A is a radical including a characterizing atom that is either an oxygen atom, a sulfur atom or an amino nitrogen atom, the characterizing atom being attached directly to R, and having each of its remaining valences satisfied by a hydrogen atom or by a hydrocarbon nucleus. A more specific class of amines suitable for use in practicing the invention may be represented by the formula



in which n is an integer from 1 to 6.

The partially cyanoethylated cotton product treated according to the invention can be formed in any suitable way to a product containing from 0.1 to around 2.5 cyanoethyl cellulose units per anhydro-glucose unit. Cellulose which has been treated with an aqueous solution of alkali, such as sodium hydroxide, reacts with acrylonitrile to form the cyanoethyl cellulose ether. The degree of substitution depends upon the concentration of the alkali solution, the period, and the temperature of the treatment and concentration of the acrylonitrile. By controlling these variables a cotton product can be formed containing an effective amount of cyanoethyl cellulose.

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It is an object of the invention to combine only such an amount of acrylonitrile with the cotton as will impart the improved properties desired in the way of increased tensile strength, and also resistance to mold-causing microorganisms.

In accordance with our invention, we may treat the cotton in any suitable way with acrylonitrile to effect but a partial conversion to cyanoethyl cellulose, the major portion of the cotton preferably remaining in the form of cellulose. We aim to avoid such an amount of substitution that the cotton fibers lose their fibrous character and to this end prefer not to combine more than 2 to 2.5 cyanoethyl cellulose units per anhydro-glucose unit. We have found it advantageous and very practical to immerse the cotton in a sodium hydroxide solution varying, say, from 0.10% to 10% of sodium hydroxide, preferably around 0.25% to 2.5% for around twenty minutes, and then to squeeze out the excess caustic solution to about a 100% increase in weight. The cotton is then contacted with acrylonitrile, either as a vapor or as an aqueous solution until the required amount of conversion has been effected. This can be done by refluxing with acrylonitrile at 76° C. for about two minutes and then washing with water. In such an operation, the nitrogen content varies from 1.6% to 1.8%. The amount of conversion may also be expressed in terms of percent nitrogen and to this end we prefer to use cotton containing from 0.5% to 4.8% N. The following table gives the cyanoethylation expressed in percent N and cyanoethyl cellulose per glucose unit on native cotton:

TABLE A

Percent N	Cyanoethyl Cellulose per Glucose Unit
0.77	0.092
1.20	0.146
1.64	0.220
1.77	0.202
1.89	0.236
2.40	0.306
3.08	0.417
3.16	0.405
3.80	0.513
4.30	0.595
4.85	0.691
5.24	0.760
6.52	1.020
9.80	1.820
13.00	3.000

In using our preferred range of cyanoethylation, we not only produce a cotton product which is particularly amenable to the process of this invention but a product which is especially resistant to heat and the attack of such micro-organisms as the spores of *Chaetomium globosum* which cause mildew, as more fully described and claimed in the copending application of Jack Compton and Catesby P. Jones, Serial No. 201,063, filed December 15, 1950, now abandoned.

Any suitable kind of tensioning apparatus may be used, such as that used for stretching yarns or fabrics while immersed in liquid. A practical apparatus for laboratory purposes may consist of a beam balance arranged so that the weights needed for the desired tension can be attached to one arm while the skein to be treated is hung on the other arm. While we may use varying amounts of tension or zero tension while applying the amine in liquid phase as in aqueous solution, we prefer to use an appreciable tension, preferably just below that which would injure the yarn or fabric.

While the invention is not predicated on any theory as to the improved properties imparted to the product, it may be explained as being due to the swelling action and decrease in crystallinity and the removal of such impurities as fats, waxes, and pectates resulting in an in-

crease in inter-fiber friction, and a more perfect orientation of the fibrile and other organized elements of the fiber structure.

Particular types of amines which have been used very effectively in the process of our invention include the following: the alkyl mono-, di-, tertiary-, 3-substituted propyl-, and polyalkylenepoly-amines. Specific amines include: methylamine, ethylamine, dimethylamine, tri-methylamine, triethylamine, triethanolamine, ethylenedi-amine, diethylenetriamine, 3-isopropoxypropylamine, 3-methoxypropylamine, 3,3'-iminobispropylamine, 3-di-methylaminepropylamine, 3-isopropylaminopropylamine.

In determining the tensile strength on yarns, single end breaking tests were carried out on all samples. The procedure employed involved treating two 17 yard skeins under the same conditions, testing 10 ends from each skein, the average of which (20 single ends) gave the breaking strength of the yarns treated. The percent increase in strength was based on the difference in the number of grams tension required to break the treated yarns in comparison with the original breaking strength of the yarns before the treatment. In some cases the breaking strength is expressed as grams/grex.

In treating the cotton products with an amine, the product is preferably immersed in the liquid amine to effect complete penetration and while wet with the amine the product may be subjected to tension. Thereafter, the product is rinsed in water and dried.

The amine treatment used in the following tests was carried out as follows: (a) the yarn skein was placed on the tensioning apparatus and tension applied, (b) a container was filled with the amine solution and by means of a crank the skeins were passed continuously through the amine solution and (c) after the required time in the amine solution, the amine was removed from container by means of suction, water was added and the skeins washed several times to remove the amine. After several washings, the skeins were placed in running water for neutralization.

Two skeins were treated under the same conditions. The physical testing on the yarn was carried out on an IP-2 Incline Tester. Ten single ends were tested from each skein. The average of the data obtained on the two skeins gave the breaking strength of the yarns. The two skein procedure was used to minimize experimental errors.

In a series of tests carried out using several primary alkylamines, the yarns were impregnated with the primary alkylamines under normal conditions of pressure and temperature. (Hereinafter, for convenience, "acrylonitrile" will sometimes be referred to simply as "AN.") The results of these experiments are shown in Table I.

TABLE I

Effect of the treatment of native and partially cyanoethylated 80/2 cotton yarns containing 1.8% nitrogen, under 2000 grams skein tension for 10 minutes at room temperature with various alkylamines on the single end breaking strength

Amines	Concentration	Single End Breaking Strength, Gms.	
		Native	AN Treated
Triethanolamine.....	Pract.....	373	388
Ethylamine.....	33%.....	416	422
Triethylamine.....	Pract.....	422	449
Choline.....	50%.....	451	451
Dimethylamine.....	25%.....	384	402

Original breaking strength of native yarns=341 gms.

Original breaking strength of An yarns=366 gms.

The effects of lowering the concentration of the amines to 50% in water solution and varying the tension are shown in Table II. The data indicates that as the tension increases the breaking strength increases.

TABLE II

Effects of various skein tensions on the single end breaking strength of cyanoethylated 80/2 cotton yarns containing 1.8% nitrogen treated with 50% alkylamines for 10 minutes

Tension, gms.	Single End Breaking Strength, Gms.		
	Triethanolamine	Ethylamine	Dimethylamine
0.....	363	344	374
2,000.....	380	384	402
3,000.....	394	430	402
4,200.....	411	416	402

Original breaking strength of cyanoethylated yarns=358 gms.

The effect of varying the skein tension during the treatment with trimethylamine on the single end breaking strength of the yarns is shown in Table III.

TABLE III

The effects of various skein tensions on the single end breaking strength of native and cyanoethylated 40/2 cotton yarns, containing 1.6% nitrogen treated for 10 minutes at room temperature with trimethylamine

Tension, gms.	Single End Breaking Strength, Grams	
	Native yarns	AN yarns
0.....	628.....	719
1,000.....	608.....	671
2,000.....	582.....	653
3,000.....	588.....	670
4,000.....	614.....	676
5,000.....	614.....	676
6,000.....	616.....	686
8,000.....	Skein broke.....	707

Original breaking strength of native yarns=595 grams.

Original breaking strength of AN yarns=547 grams.

In the case of the native yarns, there was no significant increase in strength, but there was a significant increase in breaking strength of the partially cyanoethylated yarns treated with trimethylamine.

The effect of skein immersion time in trimethylamine on the single end breaking strength of cyanoethylated yarn is indicated in Table IV. There was a significant decrease in strength upon increasing the time from 5 minutes to 40 minutes which is presumably due to a decrease in crystallinity as the time of contact increases.

TABLE IV

The effects of skein immersion time on the single end breaking strength of cyanoethylated 40/2 cotton yarns containing 1.6% nitrogen treated with trimethylamine, under zero tension

Time, Min.	Single End Breaking Strength, Grams—Cyanoethylated (AN) Yarns
5.....	712
10.....	709
15.....	694
20.....	688
30.....	682
40.....	666

Original breaking strength of cyanoethylated yarns=547 grams.

The 3-substituted propylamines are especially effective amines for the purpose of the invention. The effects of 3-propylamines on the breaking strength of partially cyanoethylated yarns are shown in Table V, and particularly by a significant increase in breaking strength.

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TABLE V

The effect of skein treatment of 40/2 native and partially cyanoethylated cotton yarns containing 1.6% nitrogen with various 3-substituted propylamines under zero tension for 10 minutes on the breaking strength and elongation

Amine	Single End Breaking Strength, Grams		Elongation	
	Native	AN	Native	AN
3-isopropoxypropylamine.....	760	806	7	8
3-methoxypropylamine.....	644	710	7	7
3,3'-iminobispropylamine.....	632	796	7	11
3-dimethylaminopropylamine....	815	798	7.5	8
3-isopropylaminopropylamine....	802	738	7.5	8

Original breaking strength of native yarns=595 gms.; elongation=5.0%.
Original breaking strength of AN yarns=545 gms.; elongation=5.10%.

TABLE VI

The effect of skein treatment of 40/2 native and partially cyanoethylated cotton yarns containing 1.6% nitrogen with 3-isopropoxypropylamine under various tensions for 5-minutes on the breaking strength and elongation

Tension, gms.	Single End Breaking Strength, gms.		Elongation, Percent	
	Native	AN	Native	AN
0.....	760	806	7.0	8.0
4,000.....	628	749	6.86	4.78
7,000.....	668	700	6.76	5.51

Original breaking strength of native yarns=595 gms.; elongation=5.0%.
Original breaking strength of AN yarns=545 gms.; elongation=5.10%.

In these tests the designated tensions were applied to the yarns in the presence of the amine for 5 minutes after which the elongation was held constant for 5 additional minutes. At zero tension the time of treatment was 10 minutes. It will be noted that the increase in strength of both native and AN yarns resulting from treatment with 3-isopropoxypropylamine under tension is less than when no tension was employed. However, the elongation of the yarn in the case of the AN yarn was materially decreased while considerable increases in strength over the control was effected. AN yarns thus lend themselves to engineering for specific end uses more readily than native yarns.

These 3-substituted propylamines not only are very effective when used alone but they are very effective when used with other amines. The 3-substituted propylamines possess comparatively high swelling power for cellulose and are good solvents for fats and waxes found on the surface of the cotton fibers. It can be seen that the cyanoethylated yarns treated with the 3-substituted propylamines result in a greater increase in tensile strength than the increase in strength imparted to native cotton given the same treatment.

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Many of the amines as described herein are available in liquid form as commercial products, i. e., they are liquid at normal room temperatures. However, such liquid amines may also be dissolved in water. Other amines are preferably dissolved in water. While the amount of water is not critical, we prefer to use less than 50% by volume of water.

We claim:

1. The process for the treatment of a cyanoethylated cotton textile product containing from 0.1 to 2.5 cyanoethyl cellulose units per anhydroglucose unit which comprises impregnating said product with an amine of the group consisting of methylamine, ethylamine, dimethylamine, trimethylamine, triethylamine, triethanolamine, ethylenediamine, diethylenetriamine, choline, 3-isopropoxypropylamine, 3-methoxypropylamine, 3,3'-iminobispropylamine, 3-dimethylaminopropylamine and 3-isopropylaminopropylamine, said amine being in liquid phase containing less than 50% by volume of water, said product being impregnated with the amine at normal room temperatures and pressures and maintained in contact with the amine for at least five minutes and until the tensile strength and elongation has been materially increased, washing and drying the product.

2. The process of claim 1 wherein the cyanoethylated cotton textile product, while being impregnated with the amine, is under tension.

3. The process of claim 1 wherein the amine is a 3-substituted propylamine.

4. The process according to claim 1 wherein the amine is 3-isopropoxypropylamine.

5. The process of claim 1 wherein the amine is 3-methoxypropylamine.

6. The process of claim 1 wherein the amine is 3,3'-iminobispropylamine.

7. The process of claim 1 wherein the amine is 3-dimethylaminopropylamine.

8. The process of claim 1 wherein the amine is 3-isopropylaminopropylamine.

9. The process of claim 1 wherein the cyanoethylated cotton textile product is impregnated with an amine in aqueous solution.

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