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PROCESS FOR TREATMENT OF CYANOETHYLATED COTTON FIBERS WITH AMINES TO IMPROVE THEIR PHYSICAL PROPERTIES

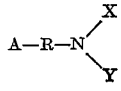
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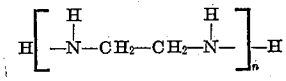
2 Claims. (Cl. 8—129)

This invention relates to cyanoethylated cotton products in the form of fibers, yarns 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 cyanoethylated 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. By "cyanoethylated cotton" as the term is used herein we mean cotton which is only partially cyanoethylated having, for example, from 0.1 to 2.5 cyanoethyl groups per anhydroglucose unit of the cellulose molecule. By "cyanoethylated cotton products," we mean products in the form of yarn, cord or fabrics formed of partially cyanoethylated cotton.

One of the important aspects of our invention is that we can treat the cyanoethylated cotton product with a liquid amine at normal pressures and temperatures, or with a water solution of an amine in any suitable concentration, in a simple and practical operation in apparatus of the type commonly used to treat yarns and fabrics with liquids. The cyanoethylated 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 groups per anhydro-glucose unit of the cellulose molecule. Cellulose which has been treated with an aqueous solution of alkali, such as sodium hydroxide, reacts with acrylo-nitrile 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 product derived from cotton can be formed containing an effective amount of cyanoethyl cellulose. 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 72–76° 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 groups per glucose unit of the cellulose in native cotton:

Table A

Percent N	Cyanoethyl Groups per Anhydro-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	0.515
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 cyanoethylated 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 spores of *Chaetomium globosum* which cause mildew.

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 attending decrease in crystallinity and the removal of such impurities as fats, waxes, and pectates resulting in an increase in inter-fiber friction, and a more perfect orientation of the fibril 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 polyalkylene poly-amines. Specific amines include: methylamine, ethylamine, dimethylamine, trimethylamine, triethylamine, triethanolamine, ethylenediamine, diethylenetriamine, 3-isopropoxypropylamine, 3-methoxypropylamine, 3,3'-iminobispropylamine, 3-dimethylaminepropylamine, 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. Thereafter, the amine is neutralized with dilute acid and the product rinsed in water, dried, and conditioned.

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 alkyl-amines, the yarns were impregnated with the primary alkylamines under normal conditions of pressure and temperature.

The effect of skein immersion time in trimethylamine on the single end breaking strength of cyanoethylated 40/2 cotton yarns containing 1.6% nitrogen is indicated in Table I. The strength increase was significantly less 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 I

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

Original breaking strength of cyanoethylated yarns=547 grams.

The effects of contacting skeins of partially cyanoethylated 40/2 cotton yarn for various periods, without tension, with ethylenediamine and diethylenetriamine on the breaking strength are shown in Table II.

Table II

Amine	Time	Single End Breaking Strength, gms.	Percent Increase in Strength
Ethylenediamine	12 hrs.	762	41.0
Do	10 min.	734	34.2
Do	5 min.	748	36.7
Diethylenetriamine	12 hrs.	780	42.4
Do	10 min.	778	42.2
Do	5 min.	742	35.6

The original breaking strength of the acrylonitrile treated yarn was 545 grams. As a result of this treatment, the strength increased from 35% to 40%. Table II indicates that after a 10 minute reaction time there is no increase in breaking strength even when the reaction time is increased to 18 hours.

The effects of diethylenetriamine skein treatment of partially cyanoethylated cotton yarns, under no tension, on the abrasion and tensile strength are shown in Table III. The cotton contained 1.7% nitrogen and the 22/1 yarns of various twist multipliers were treated with 70% diethylenetriamine. The Stoll flat abrasion resistance data is given in cycles required to break the yarns.

Table III

Yarn, T. M.	Single End Breaking Strength, Grams		Stoll Abrasion Resistance, Cycles		
	Native Cotton	Plus Amine	Native Cotton	AN [1]	Plus Amine
7.25	279	323	883	1,516	1,753
3.41	302	364	542	983	1,439
2.79	275	345	281	358	632
2.55	175	298	156	209	279

[1] AN-acrylonitrile treated cotton yarn.

The effects of varying the concentration of diethylenetriamine on the single end breaking strength of cyanoethylated 40/2 cotton yarns containing 1.6% nitrogen treated for ten minutes under zero tension are shown in Table IV:

Table IV

Concentration, Percent of Diethylenetriamine	Single End Breaking Strength, gms.
3.5	567
7.0	610
17.5	606
35.0	602
52.5	627
70.0	778

The original breaking strength of the cyanoethylated yarns was 545 grams.

The 3-substituted propylamines are especially effective amines for the purpose of the invention. The effects of skein treatment of 40/2 partially cyanoethylated cotton yarns containing 1.6% nitrogen with various 3-substituted propylamines for 10 minutes on the breaking strength and elongation are shown in Table V. These tests show a significant increase in breaking strength.

Table V

Amine	Single End Breaking Strength, gms.	Elongation, percent
3-isopropoxypropylamine	806	8
3-methoxypropylamine	710	7
3,3'-iminobispropylamine	796	11
3-dimethylaminopropylamine	798	8
3-isopropylaminopropylamine	788	8

Original breaking strength of yarns=545 gms.; elongation=5.10%.

These 3-substituted propylamines not only are very effective when used alone, but they are very effective when used with certain 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 fibers. It can be seen that the cyanoethylated yarns treated with the 3-substituted propylamines have a greater tensile strength than the cyanoethylated cotton yarn.

Cotton fibers in one-half pound lots were placed in the adapter of the Gaston County single package treating machine and a 2% sodium hydroxide solution circulated through it for 15 minutes at room temperature. The fibers were then removed and centrifuged to a weight increase of 75% and replaced in the package treating unit. The machine was then charged with acrylonitrile and this circulated for one hour at 135° F. At the end of this time, the temperature was lowered and the acrylonitrile flushed out of the system. The residual acrylonitrile and sodium hydroxide was then washed out of the fiber mass with a dilute acetic acid solution and with water.

The fiber was then centrifuged and allowed to air dry. The nitrogen content of four such batches was found to be within the range of 2.0 to 2.2%.

Four such batches were blended on the United States Department of Agriculture fiber blender and made into laps weighing about one pound each. These laps were then carded and the resulting sliver after two processes of drawing were processed into roving. The roving was then double creeled on the spinning frame to produce 40/1 yarn. The single yarn was then plied on a twister to make 40/2 yarn.

Part of the acrylonitrile treated fiber prepared as above described was then treated with ethylene diamine in a manner similar to that described for treating yarns. A five-minute treatment was found to be satisfactory in the present instance. At the end of this time the ethylene diamine was removed and the fibers washed free of the amine with 5% sulfuric acid solution, then thoroughly washed with water and air dried. The resulting fiber was then processed into 40/1 and 40/2 yarns as described above.

Table VI shows the physical properties of nominal 40/1 and 40/2 yarns prepared from cotton fibers treated with acrylonitrile before and after treatment with ethylene diamine.

Table VI

Actual Yarn Count		Single End Breaking Strength				Elongation, percent		Twist, T. P. I.	
		gms.		g./grex.					
40/1	40/2	40/1	40/2	40/1	40/2	40/1	40/2	40/1	40/2
[1] 39.3/1	40.2/2	200	370	1.33	1.26	4.4	4.3	--	10.7
[2] 40.0/1	39.6/2	228	412	1.54	1.38	5.8	5.3	--	12.2

[1] Fibers treated with acrylonitrile.
[2] Fibers treated with acrylonitrile and amine.

Upon treating the acrylonitrile fiber with ethylene diamine, the strength of the 40/1 was greater than that of the untreated yarns of about equivalent yarn number. It will be noted that the yarns prepared from amine treated acrylonitrile fiber are appreciably stronger than the yarns prepared from acrylonitrile fiber. The beneficial effect of the amine treatment on cyanoethylation fiber is thus clearly demonstrated.

In another experiment, cotton fibers were presteeped in 2% sodium hydroxide solution for 20 minutes, and the wet pick-up reduced to 100% by passing through squeeze rolls. The caustic impregnated fibers were then placed in acrylonitrile saturated with water at the boiling point of 71°–72° F. for two minutes. After neutralizing the residual caustic with acetic acid and thorough washing with water, the cyanoethylated cotton fibers were allowed to dry. The nitrogen content was found to be 1.5%.

Part of the cyanoethylated cotton fiber was treated with ethylene diamine in the manner previously described. The single fiber breaking strengths of the original cotton fiber, cyanoethylated cotton fiber, and cyanoethylated and ethylene diamine treated cotton fiber are shown in Table VII.

Table VII

Cotton Fiber	Breaking Strength, gms.	Elongation, Percent
Untreated	5.25	6.9
Cyanoethylated (AN)	5.14	6.7
AN+ethylene diamine	6.78	8.5

It will be noted that the single fiber strength and elongation of the cyanoethylated cotton fiber were the same as that of the original untreated cotton. After treatment with ethylene diamine, both the strength and elongation of the cyanoethylated cotton fiber were increased, the former by 32%, the latter by 26%.

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 improving the tensile strength, elongation and abrasion resistance of cyanoethylated cotton fibers products which comprises subjecting cyanoethylated cotton fibers having from 0.1 to 2.5 cyanoethyl groups per anhydro glucose unit to treatment with an amine in liquid phase of the group consisting of methylamine, ethylamine, dimethylamine, trimethylamine, triethylamine, triethanolamine, ethylenediamine, diethylenetriamine, 3-isopropoxypropylamine, 3-methoxypropylamine, 3,3′-iminobispropylamine, 3-dimethylaminepropylamine, 3-isopropylaminopropylamine until the tensile strength, elongation and abrasion resistance of the cyanoethylated cotton fibers are improved, said treatment resulting in an impregnation of the cotton with the amine, and washing the impregnated product to remove unreacted amine.

2. In the process of claim 1 impregnating the cyanoethylated product with the amine while in aqueous solution.

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