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TREATMENT OF CELLULOSIC FIBERS

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This invention relates to a method of altering the properties of cellulosic fibers, yarns, and fabrics. An object of this invention is to increase the water-receptivity or water-absorbing properties of fibers in the raw state. A further object is to increase the tendency of the fibers to swell when brought into contact with water, especially in the woven form. Still other objects are to increase the tensile strength of cellulosic yarns and to impart thereto a linen-like appearance.

These objects are achieved by treating the cellulosic fibers, as such or made up in yarns or fabrics, separately with acrylonitrile and caustic solution.

Treatment of cellulosic yarns with a strong caustic alone is known to increase the strength of the yarns to a limited extent. Treatment with acrylonitrile alone does not result in increased strength. Therefore, it is surprising that the treatment of cellulosic yarns with both acrylonitrile and caustic increases the strength far beyond that resulting from causticization alone. Furthermore, as a result of this treatment, yarns and fabrics become more linen-like in appearance, feel, and increased luster. Also, cellulose fibers treated as here disclosed acquire an affinity for dyes which is far greater than that imparted by the customary causticization or mercerization. Cellulosic fibers as such or in yarns or fabrics after treatment according to this invention swell on contact with water more rapidly and to a greater extent than untreated fibers and are thus much more water-receptive. Raw stock thus treated is capable of imbibing large amounts of aqueous media and, as a result, is ideally suited for the preparation of absorbent pads and sponges such as are used in surgery. The value of increased water-receptivity of fabric is best illustrated by a treated woven cotton fire-hose which, after treatment, becomes practically impervious to water and does not leak when the water in the hose is under high pressure, whereas the cotton hose in untreated form allows the water to diffuse through the fabric rapidly at relatively low water pressure. The use of acrylonitrile and strong hydroxides in the treatment of fire-hose is the subject of application Serial No. 468,662, filed of even date.

In the practice of this invention by the preferred method, the cellulosic fibers in the form of raw stock, batting, yarn, or fabric, are saturated with acrylonitrile by soaking, dipping, etc. The excess acrylonitrile may be removed for convenience, and the wet fibers are then subjected to the action of a strong hydroxide in solution. A strong hydroxide is one which dissolves in water and dissociates therein to yield a high concentration of hydroxyl ions. Such a solution is also identified herein as a "caustic solution." It has been found that the final properties of the fibers depend largely on the extent of causticization. The concentration of the caustic solution, the length of time during which the fibers are in contact with the caustic, and the temperature of the caustic solution are all factors which determine the results. After being subjected to the effect of the caustic, the fibers are freed of caustic by squeezing, hydro-extracting, or equivalent operation followed by thorough washing with water alone or with an acidified solution capable of neutralizing the caustic. The fibers are then dried and conditioned as desired.

While the preferred method has been described in detail, it is also possible to saturate the fibers first with caustic solution and subsequently with acrylonitrile. In such a case, the results will depend on the time and temperature of treatment with the acrylonitrile. In any event, the cellulosic fibers are treated in separate steps with acrylonitrile and caustic solution.

While the process is adaptable for the treatment of all cellulosic fibers, including regenerated cellulose, in all forms, it is especially advantageous when applied to the treatment of natural cellulosic fibers such as cotton, jute, ramie, linen, etc. It is also preferred to treat the cellulosic fibers, especially cotton fibers, in the form of raw stock or as yarn, although the woven fibers in the form of fabric respond very satisfactorily to the process and are improved greatly thereby. Likewise, regenerated cellulose may be treated and altered by the method of this invention. In general, regenerated cellulose is affected more rapidly than natural fibers and, accordingly, milder conditions and concentrations of caustic are ordinarily employed in order to avoid dissolving the regenerated cellulose.

The three chief effects of treating cellulosic fibers with acrylonitrile and caustic are, first, the increase in tensile strength of the fibrous yarn; second, the increase in receptivity to water which causes a swelling of the fibers, and, third, the acquisition of a linen-like appearance. When the fibrous yarns are treated while in a relaxed state, they become more water-receptive and have a greater tendency to swell thereafter than when they are treated under tension. On the other hand, when treated under tension, the yarns acquire more tensile strength than when treated in the relaxed state. Thus, by varying the condition of the fibers and yarns at the time of treatment, it is possible to effect various improvements in the tensile strength and the water-receptivity or "swellability" of the fibers.

As has been indicated, the extent of the causticization treatment in the preferred procedure affects the final properties of the treated fibers. At room temperature, a concentration of caustic

solution as low as 2% has been found to be effective. However, the effect is more marked as the concentration of caustic is raised to an optimal range, after which an increase in concentration appears to have no additional practical advantage. The maximum effect appears to be obtained at a concentration of between about 10% and about 20% caustic at room temperature.

Like chemical reactions in general, this one, involving acrylonitrile, cellulose, and caustic, takes place over a period of time, and, if other factors, such as concentration and temperature, are held constant, the effect of time of reaction becomes evident. Thus, at room temperature, the effect of causticizing the fibers, in alkali of a concentration of about 10% to 20%, increases with time up to a maximum, after which there is no increase of practical significance.

Increased temperatures of causticization cause an increase in the speed at which higher tensile strength of the treated fibers, yarns, or fabrics is acquired. Not only is the dry strength of the yarns increased by the causticization at higher temperatures, but the wet strength is likewise increased markedly.

It is unnecessary to raise the temperature of the acrylonitrile above room temperature. Due to the relatively high vapor pressure of the nitrile, it is preferred to maintain the material at room temperature and to vary the temperature of causticization.

While sodium hydroxide is the preferred strong hydroxide, in view of its low cost and general availability, other strong hydroxides, particularly of the alkali metals, such as potassium hydroxide, and quaternary ammonium hydroxides may be used. Examples of such quaternary ammonium hydroxides include tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, benzyl trimethyl ammonium hydroxide, dibenzyl dimethyl ammonium hydroxide, tetraethanol ammonium hydroxide, and butyl benzyl dimethyl ammonium hydroxide. It has been found that smaller amounts of quaternary ammonium hydroxides than of the inorganic hydroxides are required in order to effect the same change in the fibers. Also, quaternary ammonium hydroxides have a greater tendency to act on cellulose than inorganic hydroxides, even to the point of dissolving cellulose at sufficiently high concentrations if allowed to react over long times or at high temperatures.

It must be emphasized that the process of this invention is not the conventional one of sizing fibers and fabrics with polymerizable materials and subsequently causing polymerization of the latter. It appears that the changes in strength and water-receptivity of fibers, yarns, and fabrics treated according to the present process may result from the chemical combination of the nitrile and cellulose under the influence of the caustic. Such a reaction would produce β-cyanoethyl derivatives at least on the surface of the cellulose, which would in turn be capable of being hydrolyzed to the corresponding carboxylic derivatives. Whatever may be the chemistry involved, the facts remain that the strength, water-receptivity, and appearance are altered advantageously by the separate saturation with acrylonitrile and causticization, and as such the facts are independent of the theory. By varying the conditions employed in this invention, it is possible to alter the physical properties of the cellulosic fibers over a wide range.

The following examples will serve to illustrate the nature of this invention:

Example 1

Cotton yarn in skein form was thoroughly impregnated by soaking in acrylonitrile. The excess liquid was removed by padding the yarn. Portions of the impregnated yarn were soaked for one hour in caustic solutions of various concentrations, after which the yarn was freed of caustic by washing with large volumes of water. The swelling of the yarn was manifested by a shrinkage in length. A measurement of the extent of shrinking served, therefore, as an indication of the degree of swelling. The tensile strength of the treated yarns in this and the following examples was measured on a Scott inclined plane tester after the yarn had been dried and then conditioned for 12 hours at 70° F. and at a relative humidity of 65%. The percentage change in strength as listed in the following tables has been calculated against the strength of the dry control sample. The results, showing the effect of the concentration of caustic, indicate the degree of improvement obtained by treating first with acrylonitrile and then with caustic solutions.

Table 1

Percent concentration of NaOH	Shrinkage		Dry strength	
	Inches	Percent	Grams	Percent
Control			460	
2%	6	11	536	+16.5
10%	6	11	504	+9.6
20%	14	26	551	+19.7
30%	22	40	488	+6.1

Example 2

Example 1 was repeated with one change in procedure, namely, that the yarns were placed under tension by being wound around glass cylinders. The increase in tensile strength is here recorded:

Table 2

Percent concentration of NaOH	Dry strength	
	Grams	Percent
Control	460	
2%	527	+14.4
5%	561	+22.1
10%	700	+52.2
20%	724	+57.4
30%	720	+56.5

Example 3

The following data show the effect of treating yarn with caustic alone while under tension.

Table 3

Per cent concentration of NaOH	Dry strength	
	Grams	Per cent
Control	460	
5%	489	+6.4
10%	538	+16.9
20%	592	+28.6
30%	602	+30.7

A comparison of the data in Tables 2 and 3 serves to show the advantage of treating fibers by this process over customary causticization alone.

Example 4

The effect of varying the time of causticization of the acrylonitrile-impregnated fibers is shown in the following table. The tests were conducted as described in Example 1 at room temperature, and the caustic solution was maintained at 15%.

Table 4

Minutes in NaOH	Dry strength in grams
4	570
16	620
24	713
28	715

Example 5

The effect of temperature on the process is illustrated by the data in the following table. It will be noted that the tensile strength of the yarns treated with acrylonitrile and subsequently with sodium hydroxide at 160° F. is much greater than the strength of the fibers treated with hot caustic solution alone.

Table 5

Time in NaOH at 160° F.	Dry tensile strength	
	Acrylonitrile+NaOH	NaOH alone
	Grams	*Grams*
2 minutes	742	561
12 minutes	828	564
18 minutes	845	526

Example 6

A sample of surgical cotton was thoroughly soaked in acrylonitrile and hydroextracted. It was then immersed in a 15% solution of sodium hydroxide for one hour at room temperature, after which it was completely freed of caustic by washing with water. A second sample of batting was simultaneously subjected to the causticization rinsing operation. Both specimens were hydroextracted and dried.

When both samples were subsequently treated with water, it was found that the acrylonitrile-NaOH-treated sample was far more water-receptive, imbibed water faster and to a much greater extent than the specimen which had been treated with caustic alone.

Example 7

Identical samples of bleached and boiled cotton sheeting were placed on mercerizing frames and treated as follows:

Specimen A was immersed in acrylonitrile and then soaked in a 15% NaOH solution for one hour at room temperature and was then neutralized with acetic acid, washed and dried.

Specimen B was immersed in the caustic solution alone for one hour at room temperature and was then neutralized with acetic acid, washed and dried in the same manner as was specimen A.

There was considerably more swelling of the fibers of specimen A than of specimen B. Specimen B showed moderate mercerization effects and slight luster, while specimen A had high luster and a permanent linen-like hand. Samples each of A and B were dyed in the same bath with a dye known as "Brilliant Blue 6BA" (Color Index 406) and specimen A was much deeper in shade than specimen B.

Example 8

This example serves to show the degree of swelling imparted to regenerated cellulose fibers by treatment according to the method of this invention and by causticization alone. Skeins weighing 3.5 grams were wound from 1100 denier/480 filament rayon. Some skeins (set A) were saturated with acrylonitrile and then immersed in caustic solutions of varying concentrations for a period of seventeen hours. Others (set B) were not treated with acrylonitrile but were immersed for the same length of time as set A in the same caustic solutions. The amount of solution imbibed by the skeins serves as a measure of swelling, and tests were made by removing the skeins from the solutions by means of wire hooks and allowing each skein to drain for two minutes, at which point the weight was measured. As a control or standard of comparison, a skein was immersed in water, allowed to drain for two minutes, and weighed. The following data afford a comparison of the effect of caustic alone and the acrylonitrile-caustic treatment. It also serves to show that acrylonitrile-treated regenerated cellulose tends to dissolve in a relatively low concentration of caustic.

Table 8

Percent concentration of NaOH	Weight in grams of set A	Weight in grams of set B
Control	14.0	14.0
2	16.4	16.1
5	21.2	18.9
8	44.2	27.2
9	(1)	33.3

[1] Dissolved.

Thus, in accordance with this invention, the tensile strength of cellulosic yarns is increased, the fibers become more water-receptive, and the properties of the yarns and fabric become more linen-like when the fibers as raw stock, yarns, or fabrics are treated separately with acrylonitrile and a solution of strong caustic. This is of particular importance in applications where increased rate of water absorption and greater capacity for water absorption are required.

I claim:

1. A process for increasing the luster and water-receptivity of cellulosic yarns and fabrics which comprises treating the material in separate operations with acrylonitrile and a 2% to 30% aqueous solution of a strong hydroxide, washing the treated material until substantially free of the hydroxide, and drying the material.

2. A process for increasing the luster and water-receptivity of cellulosic yarns and fabrics which comprises saturating the material with acrylonitrile, treating the saturated material with a 2% to 30% aqueous solution of a strong hydroxide for from about two to about sixty minutes, washing the treated material until substantially free of the hydroxide, and drying the material.

3. A process for increasing the luster and water-receptivity of cotton yarns and fabrics which comprises treating the material in separate operations with acrylonitrile and a 2% to 30% aqueous solution of a strong hydroxide, washing the treated material until substantially free of the hydroxide, and drying the material.

4. A process for increasing the luster and water-receptivity of cotton yarns and fabrics

which comprises saturating the material with acrylonitrile, treating the saturated material with a 2% to 30% aqueous solution of a strong hydroxide for from about two to about sixty minutes, washing the treated material until substantially free of the hydroxide, and drying the material.

5. A process for increasing the tensile strength and water-receptivity of cellulosic yarns and fabrics which comprises subjecting the material to tension, treating the material while under tension in separate operations with acrylonitrile and a 2% to 30% aqueous solution of a strong hydroxide, washing the treated material until substantially free of the hydroxide, and drying the material.

6. A process for increasing the tensile strength and water-receptivity of cellulosic yarns and fabrics which comprises subjecting the material to tension, saturating the material while under tension with acrylonitrile, treating the saturated material under tension with a 2% to 30% aqueous solution of a strong hydroxide for from about two to about sixty minutes, washing the treated material until substantially free of the hydroxide, and drying the material.

7. A process for increasing the tensile strength and water-receptivity of cotton yarns and fabrics which comprises subjecting the material to tension, treating the material while under tension in separate operations with acrylonitrile and a 2% to 30% aqueous solution of a strong hydroxide, washing the treated material until substantially free of the hydroxide, and drying the material.

8. A process for increasing the tensile strength and water-receptivity of cotton yarns and fabrics which comprises subjecting the material to tension, saturating the material while under tension with acrylonitrile, treating the saturated material under tension with a 2% to 30% aqueous solution of a strong hydroxide for from about two to about sixty minutes, washing the treated material until substantially free of the hydroxide, and drying the material.

9. The process of claim 1 in which the strong hydroxide is sodium hydroxide.

10. The process of claim 5 in which the strong hydroxide is sodium hydroxide.

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