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PROCESS FOR PRODUCING CYANOETHYLATED NATIVE COTTON FIBERS BY REACTING CELLULOSE FIBERS WITH ACRYLONITRILE IN VAPOR PHASE

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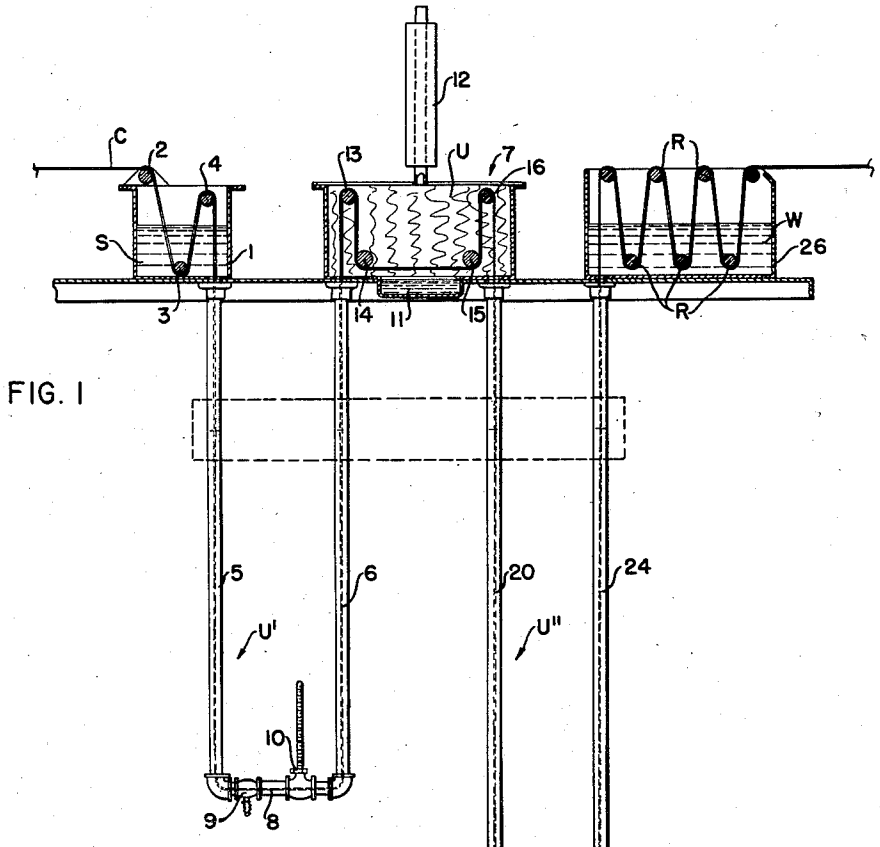


FIG. 1

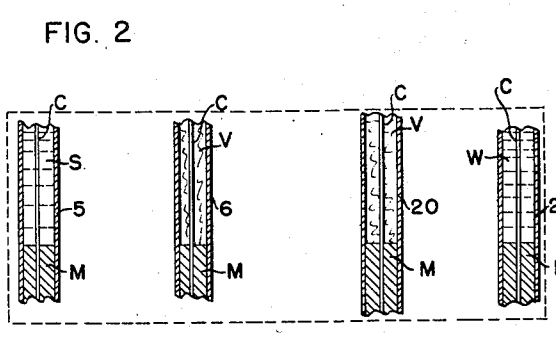
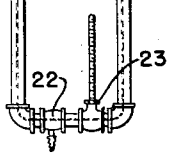


FIG. 2



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PROCESS FOR PRODUCING CYANOETHYLATED NATIVE COTTON FIBERS BY REACTING CELLULOSE FIBERS WITH ACRYLONITRILE IN VAPOR PHASE

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9 Claims. (Cl. 8—120)

This invention relates to the reaction of acrylonitrile with cotton and has for its object the provision of improved cotton products and a process of reacting acrylonitrile with cotton fibers in the form of bulk fibers, yarns, or fabrics to improve the properties of the cotton while maintaining the natural structure of the fiber and most of the properties of ordinary cotton. Our invention provides an economical and practical process of producing our improved cotton products with a minimum loss of chemicals through washing, neutralizing and undesirable by-product formation. The improved cotton products of our invention are a partially cyanoethylated cotton, but they have the important distinction of retaining the natural fibrous form of native cotton fibers, and their crystallinity in a substantially unaltered state.

Several processes have been proposed heretofore for treating cellulose with aqueous solutions of sodium hydroxide and acrylonitrile to effect from a partial to a complete cyanoethylation, usually resulting in a soluble product, but, in any event, resulting in a product having a materially changed physical structure. Notwithstanding a considerable number of patents and other publications concerning the cyanoethylation of cotton and regenerated cellulose, namely rayon, there has not been any commercially successful process developed heretofore.

Our invention is based on several important discoveries we have made in an extensive investigation of the cyanoethylation of cotton through which me may control the conditions for reacting acrylonitrile, $CH_2=CH_2-CN$, with but a relatively small proportion of the cellulose giving cyanoethylcellulose which may be represented as

$$Cell—O—CH_2—CH_2—CN$$

We have found that very desirable cotton products can be formed by effecting but a partial etherification of the cellulose molecule, resulting in but from 0.06 to 1.0 cyanoethyl group per anhydro-glucose unit (equivalent to from 0.50 to 6.50% nitrogen based on the weight of cyanoethylated cotton). In the preferred and most advantageous embodiment of our invention, we control the conditions to combine but from 0.1 to 0.6 cyanoethyl groups per anhydro-glucose unit.

The following table shows the relationship between the cyanoethyl groups per anhydro-glucose unit and the nitrogen content of the cyanoethylated cotton:

TABLE A

Percent N	Cyanoethyl Groups per Anhydro-Glucose Unit
0.50	0.060
0.62	0.074
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

Our invention is specifically directed to the treatment of native cotton because we aim to produce an improved cotton fiber and cotton is peculiarly suited to our process. While cotton is a relatively pure form of cellulose, the fibers are considered to be formed of three distinct types of layers each having a different physical structure, consisting of amorphous and crystalline components. Mild reaction conditions, such as the preferred cyanoethylation procedure herein described, are required to maintain this desirable fiber structure. In particular the relationship between the amorphous and crystalline components should be maintained. One further characteristic of cotton is that the degree of polymerization varies from about 1500 to 4500 and in this respect it differs from viscose rayon which has a degree of polymerization of from about 150 to 450. In general, all regenerated cellulosic fiber materials have a greater proportion of the amorphous component than native cotton and the crystalline component is characterized by having the mercerized cellulose molecular arrangement. Cotton thus has a different structural arrangement and responds differently than regenerated cellulose when treated with such chemicals as sodium hydroxide and acrylonitrile. Because of its structure, cotton is a very important textile material and our process maintains its structural identity.

We have discovered a very important relationship involving the concentration of sodium hydroxide in the steeping solution for treating the cotton prior to cyanoethylation, the amount of sodium hydroxide fixed to or combined with the cellulose, and the time and temperature of the reaction of acrylonitrile with the steeped cotton to effect the amount of cyanoethylation necessary to produce the improved cotton products. We can carry out our process in producing our improved cotton products without excessive loss in sodium hydroxide and in by-product formation which results in a loss of acrylonitrile. Our invention can be carried out with a relatively small amount of sodium hydroxide, and this is important since this chemical is lost in the neutralizing and washing operations necessary in the process. Not only is the saving

in sodium hydroxide an appreciable item but the saving in the neutralizing acid required in the process is also an important item.

In addition to an important saving in chemicals, the fibers of cotton are reacted under controlled conditions of time and temperature to effect the desired reaction to fix a definite amount of acrylonitrile on the cotton and thus maintain its natural fibrous character and internal molecular arrangement with an improvement in its utility as a cotton-like fiber.

The manner in which we treat the cotton with sodium hydroxide is a very important part of our invention because the cyanoethylation cannot give satisfactory results unless there has been a relatively uniform application of sodium hydroxide to all the fibers thereby leaving on the fibers, whether combined or sorbed, a predetermined amount of sodium hydroxide, and to this end we prefer to use a dilute solution of sodium hydroxide, in no event more concentrated than 10%, preferably below 2% and most advantageously in the range of 0.10% to 1.75%. Objectively, the sodium hydroxide solution should be used to cause the cotton to acquire the minimum amount of sodium hydroxide required to effect the reaction to the desired extent with a saving of chemicals. This is most advantageous in the range of 1.5 to 22 milligrams of sodium hydroxide per gram of cotton.

In carrying out our invention, precautions must be taken to direct the addition of the cyanoethyl groups —CH_2—CH_2—CN without or with no appreciable hydrolysis to form carboxyethyl groups

—CH_2—CH_2—COOH

It is accordingly necessary to avoid the use of strong caustic solutions (say over 10% NaOH) since the presence of such solutions tend to hydrolyze the nitrile —CN to carboxyl —COOH and significantly increase the proportion of the amorphous fiber component. It is particularly advantageous, therefore, to avoid the use of concentrations of sodium hydroxide which cause these changes in the cyanoethylated product and its precursor.

We have found that in order to preserve the fibrous character of the cotton and form only a small portion of cyanoethylcellulose that uniformity of sodium hydroxide treatment is necessary and we can best achieve the desired uniformity by treating the cotton with a large volume of dilute solution rather than with a small volume of strong solution objectively to treat all fibers alike. It is definitely advantageous to use a dilute solution of sodium hydroxide and to sorb on the cotton from 1.5 to 22 milligrams of sodium hydroxide per gram of cotton.

Our invention provides improved cotton products derived from native cotton characterized by having the amorphous portion of the fibers combined with acrylonitrile in the form of cyanoethylcellulose while substantially all of the crystalline structure of the cotton fiber is retained. The amorphous portion has such an amount of combined acrylonitrile that the nitrogen content of the entire fiber varies from 0.50 to 6.5%.

The partially cyanoethylated cotton fibers of our invention are similar in appearance, hand, and processing characteristics to cotton, but differ primarily and significantly in that they are permanently resistant to microorganism attack, such as cause mildew; more resistant to wet and dry heat degradation; more receptive to many dyes of all classes, including acid dyes; and more resistant to abrasion.

One of the features found in our investigations is that the amount of sodium hydroxide sorbed takes place in a very few minutes and that longer contact does not add appreciable amounts. Based on the amount of available sodium hydroxide in the solution, the actual sorption is a function of the sodium hydroxide in the liquor and there is about as much sodium hydroxide sorbed in fifteen minutes as in thirty minutes.

In our copending application, Serial No. 442,762, filed July 12, 1954, we describe and claim our improved fibrous cotton product, and a process for treating cotton fibers with aqueous solutions of sodium hydroxide, preferably in a steeping process, and under the conditions described herein, but in the process of that application the presteeped cotton fibers are treated with liquid acrylonitrile containing some water, whereas in this process the presteeped cotton fibers are treated with acrylonitrile in the vapor phase giving the advantage of simple and effective control of the reaction.

The cotton impregnated with sodium hydroxide solution in a presteeping treatment is treated to remove substantially all of the adhering solution as by centrifuging, for example, until the weight of the presteeped cotton is about double the weight of the untreated cotton. Acrylonitrile vapor is then applied to the cotton at a temperature of from about 46° C. to 85° C., and preferably at a temperature around the boiling point of the acrylonitrile which is about 76° C. under atmospheric pressure. At temperatures above the boiling point of acrylonitrile the treatment will be carried out under pressure. The extent of cyanoethylation increases with the amount of sodium hydroxide sorbed on the cotton. The rate of cyanoethylation also increases with an increase in temperature, other factors being equal. In producing our products the temperature of acrylonitrile and the time of treatment must be observed in relation to the sodium hydroxide content of the cotton to acquire the desired cyanoethylation. Our invention provides a process for controlling cyanoethylation to prevent an undue substitution of cyanoethyl groups with a material saving in chemicals, in a relatively short time, to selectively cyanoethylate the amorphous portion of the fibers, resulting in superior cotton-like fiber products.

In achieving the important resistance to degradation by mildew-causing organisms we do not appreciably change the physical properties of the fibers, and unlike the proposed practices published heretofore we avoid deterioration in strength resulting from the higher degrees of substitution and also impart heat resistance to the cotton. Moreover, we obtain products having superior resistance to mildew.

In carrying out a process of our invention, the cotton fibers with sorbed sodium hydroxide as previously described is then exposed to the vapor for but a few minutes, say, from 1.5 to 90 minutes, but not more than 4 hours, to cause the desired substitution of from 0.1 to 0.6 cyanoethyl groups per anhydro-glucose unit. The reaction may be carried out in any suitable equipment. One satisfactory arrangement comprises a chamber for the gas through which the cotton may be continuously passed having closure means whereby the cotton may enter and leave to minimize the loss of vapor, and means to supply vapor to the chamber continuously. This may be done by evaporating the liquid acrylonitrile and passing the vapor into the chamber. In carrying the operation out at atmospheric pressure, upright pipes may be attached to the chamber and provided with cooling means to condense the vapors therein and return the condensate to the body of liquid as in refluxing operations.

In the accompanying drawings:

Fig 1 illustrates more or less diagrammatically an arrangement of apparatus suitable for carrying out a process of the invention, and

Fig. 2 is an enlarged vertical sectional view taken within the area of the broken lines of Fig. 1.

The apparatus illustrated in the drawings utilizes some of the principles of the Standfast molten-metal machine which has been used for the dyeing of cotton. The apparatus comprises a vessel 1 for holding the steeping solution of sodium hydroxide and guide rolls 2, 3 and 4 to provide a long travel. The leg 5 of the U-shaped vessel U' connects to the vessel 1 while the leg 6 connects to the closed vessel 7. The bottom cross-connector 8 has a drain valve 9 and a well for the thermoregulator 10. The U-shaped vessel may be heated externally in any suitable

way as with an electrical resistance heater controlled by the thermoregulator and may be covered with thermal insulation.

The vessel 7 has a pan or pot 11 at the bottom for receiving liquid acrylonitrile with or without some water and it may be heated with any suitable means to boil the acrylonitrile and fill the chamber of vessel 7 with vapor. Preferably commercial acrylonitrile which contains some water is used, and this solution is boiled at the temperature of the azeotrope, or constant boiling mixture, which is about 71° to 72° C. The water-jacketed condenser 12 is open to the atmosphere and is positioned to return condensate to the pan 11. The chamber has direction guide rolls 13, 14, 15 and 16 to provide the required travel for the cotton, the roll 13 being directly over leg 6 and roll 16 being directly over leg 20 of U-shaped vessel U''. The cross connector 21 has a drain valve 22 and a well for the thermoregulator 23. This U-shaped vessel may be heated with an electrical resistor and the temperature controlled with the thermoregulator 23. The leg 24 connects to washer 26 in which are mounted several guide rolls R to provide a long travel through the acid sour or hot water W, as the case may be.

The apparatus illustrated had U-shaped vessels of circular cross-section formed of pipe for treating yarn or cord; however, these vessels may be rectangular in cross-section for treating fabrics. The legs of U-shaped vessel U' were 9 inches long and the legs of U-shaped vessel U'' were 12 inches long and both were filled to the level indicated with Wood's metal having a melting point of about 70° C. Any alloy having a suitable melting point that is non-reactive with caustic and acrylonitrile can be used in these vessels.

In carrying out a process of the invention, the cotton yarn or fabric C is run through the caustic, say, a 0.25% to 10% sodium hydroxide solution S at 45° to 50° C., which solution rests on the metal M in leg 5 which is maintained at about 75° C. As the cotton passes through the metal in U-shaped vessel U', it is both heated to effect the reaction and squeezed to remove much of the excess solution. The acrylonitrile vapor V in the vessel is at refluxing temperature, about 71° to 72° C., and this vapor is in contact with the metal M in leg 6. On the other side, the vapor V is in contact with the metal M in leg 20. The metal M in leg 24 is in contact with the sour solution or hot wash water W in washer 26. The cotton passes through vessel 7 and then through the molten metal in U-shaped vessel U'' in which a further extent of the reaction with acrylonitrile adhering to the cotton is carried out, and then the cotton passes through the washer 26 where it is neutralized, if desired, washed, and then dried as a finished article.

Example I

In this example of an operation carried out in the apparatus of Fig. 1, a cotton cord of 22/5/3 construction was run through the equipment at a speed of 1 yard per minute, using a 2% sodium hydroxide solution at 45° to 50° C. and an acrylonitrile vapor at 71° to 72° C. After the cord passed through the caustic steeping solution and the hot metal in legs 5 and 6, it passed through the vapor in chamber 7, the time being determined in part by the number of rolls and the length of travel they provide. In this example, the cotton was exposed to acrylonitrile vapor for about 1½ minutes.

The cord, after impregnation with acrylonitrile, passed through the molten metal in U-shaped vessel U'', the legs of which are of such length as to remove as much acrylonitrile as possible by pressure. At the same time, the temperature in this vessel can be regulated so that the residual acrylonitrile reacts with the cellulose. The process should drive the acrylonitrile into the fiber and yarn structure.

After reaction with acrylonitrile, the cord passed from leg 24 of U-shaped vessel U'', practically free of this material, into an acid sour containing 0.5% H_2SO_4 at 55° to 60° C. in vessel 26. The sour wash may be omitted and the cord merely washed in hot water washer at 80° to 90° C. The vapor from this hot water washer is carried to any suitable recovery tower to recover acrylonitrile. Upon analysis, the cord was found to contain 0.62% nitrogen.

The yarn or fabric, after souring and washing thoroughly, is dryed and packaged.

This operation may be modified by charging the vessel 7 with liquid acrylonitrile instead of the vapor, and the speed of treatment may be regulated by the speed of travel of the cotton yarn or fabric and the length of travel in the various vessels.

Example II

This is an example of another treatment of cotton fibers according to the invention in which the steeped cotton fabric was passed through a chamber containing acrylonitrile vapor.

Indian Head cotton fabric was steeped in a 2% solution sodium hydroxide for five minutes at room temperature and then centrifuged to a 100% increase in weight. The fabric was then rolled up and pulled through a chamber of hot acrylonitrile vapor at such a rate that all parts of the fabric were uniformly exposed for a period of 2½ minutes. The acrylonitrile vapor was obtained from a boiling solution contained in a vessel attached to the reaction chamber. Reflux condensing means were attached to the chamber to condense vapors that would otherwise escape. The temperature of the acrylonitrile vapor was maintained at the boiling point which, in the presence of some water, may vary from 71° to 76° C., since the reflux condensers returned the condensate to the vessel. The fabric was shielded from the cold acrylonitrile condensate by a baffle.

The partially cyanoethylated cotton fabric was then thoroughly washed with hot water to remove excess caustic and acrylonitrile, dried and subjected to mildew, heat resistance tests, and chemical analysis. It was found that the product had reacted to the extent of 0.37 cyanoethyl group per glucose unit, and was mildew and heat resistant. Thus, 10 days after inoculation with *Chaetomium globosum* in static culture there was no evidence of mildew growth, whereas the untreated control fabric supported a heavy growth. Also, after heating at a temperature of 320° F. for 20 hours, the untreated cotton fabric had suffered a tensile strength loss of 44.4%, whereas the partially cyanoethylated fabric had a tensile strength loss of only 25.4%.

The invention may also be carried out by treating yarn or fabrics on the dye tubes, for example, of a Gaston County package dyeing machine. In using a one-pound machine, for example, with 1⅝ inch dye tubes on which the cotton is wound, the tubes are placed in the machine which is then closed and the valves adjusted for the dyeing cycle, 5500 ml. of sodium hydroxide of the desired concentration was introduced through the expansion tank. When treating finished goods, such as kiered fabrics, it is advantageous to include in the steeping solution a suitable wetting agent, such as Tergitol P–28 (sodium di (2-ethylhexyl) phosphate) or Aerosol-OS (isopropyl naphthalene sodium sulfonate). This sodium hydroxide solution containing 0.1% Tergitol P–28 was circulated through the fabric for fifteen minutes, reversing the flow of the liquid every two minutes. Then the sodium hydroxide solution was drained, and the package removed from the dyeing machine. It was placed in the centrifuge specifically designed for a single dye package and centrifuged for two minutes to give a caustic pickup of 70–100%.

The fabric package was then returned to the dyeing machine and the machine was adjusted to the drying cycle in which air is forced through the cotton. In this variation of our process the vapors of acrylonitrile are circulated through the steeped cotton fibers in substantially

the same manner that air is circulated for drying, the principal difference being one of temperature to prevent undue condensation of the acrylonitrile. After the reaction has been carried to the desired extent, the circulation of acrylonitrile is stopped, a solution of acetic acid in water is circulated through the fibers to neutralize the sodium hydroxide and simultaneuosly cold water is circulated through the dye pot jacket to reduce the temperature. The fabric was then washed by circulating water through the fibers. The fabric was then removed from the machine and thoroughly washed and rinsed, but without using a detergent.

Cotton yarns may be similarly cyanoethylated and in practice this is the preferred form for the equipment employed, although it may also be used on bulk fibers with the proper machine adapter.

We have determined during our extensive investigations that as the nitrogen content of the cyanoethylated fabric increases, the percentage loss in strength during soil burial decreases. This relationship seems to hold regardless of the reaction conditions required to obtain a given nitrogen content when dilute sodium hydroxide is employed in the presteep. It has been found, however, that the minimum nitrogen content for immunity to attack varies with the construction and weight of the fabric. The reaction conditions in our process which make use of 0.25% to 2% sodium hydroxide solution as the presteep, and the reaction conditions with acrylonitrile such as will give a nitrogen content of 2.5% to 4.5% or greater yield a satisfactory product. Some data obtained indicates that for a given nitrogen content the fabric presteeped with a sodium hydroxide solution of a concentration less than 1% has the greatest resistance to microorganism attack. For example, when cotton fabric was treated with solutions of 0.25%, 2.0% and 10% sodium hydroxide and cyanoethylated to fix 2.5% of nitrogen, and the samples given identical soil burial tests at 28° C. for two weeks the loss in tensile strength for the three samples was 7%, 10% and 16%, respectively.

Cyanoethylated cotton fabric with nitrogen contents greater than 3% give satisfactory abrasion resistance as determined on the Stoll abrader. In the case of the flat abrasion test, abrasion resistance progressively increases with increasing nitrogen content. On the other hand, flex abrasion resistance progressively decreases until a nitrogen content of 2.5% to 3.0% is reached, after which the decrease becomes progressively smaller. At about 4.5% to 6.0% nitrogen the flex abrasion resistance of the cyanoethylated fabric is only about 10% to 20% less than that of the untreated cotton fabric.

The resistance of cyanoethylated cotton fabric to degradation by heat progressively increases with increasing nitrogen content. At equal nitrogen contents, cyanoethylated cotton fabric presteeped with sodium hydroxide solutions of less than 1% concentration and cyanoethylated at high reaction temperatures have the greatest resistance to degradation by heat. By way of example, cotton fabric presteeped with 0.1% sodium hydroxide and cyanoethylated to a nitrogen content of 2.0% gave a strength loss of 31% after heating for 15 hours at 160° C. When cotton fabric which was presteeped in a sodium hydroxide solution of 1.25% and cyanoethylated to a nitrogen content of 2.0% it lost 60% in strength in a similar test.

Cyanoethylated cotton fabrics with nitrogen contents in the range of 2.0% to 2.5% have the greatest affinity for many direct and vat dyes. The affinity for acid and acetate dyes increases with increasing nitrogen contents. The dye affinity of cyanoethylated cotton fabric thus depends upon the class of dye and perhaps on other dye characteristics which have not been identified. For many dyes, the rate of dyeing is increased, the extent of dye bath exhaustion is increased and the color yield is increased (by this is meant, a darker shade is obtained with the cyanoethylated cotton for the same dye pickup than with untreated cotton).

From published work on cyanoethylated cotton, it would be anticipated that the affinity of cyanoethylated cotton for acetate dyes would increase with increasing nitrogen content. Likewise, it would be expected that the affinity for acid dyes would improve as the nitrogen content increased. On the other hand, it would not be anticipated that the affinity of cyanoethylated cotton for direct, vat, napthol and developed dyes would be increased as the nitrogen content increased.

The most economical, and hence practical, conditions for cyanoethylation of cotton include: (*a*) presteep with low sodium hydroxide concentration in aqueous solution, (*b*) comparatively high temperatures, and (*c*) the shortest time permissible for treatment with acrylonitrile to obtain a given nitrogen content. Since the rate of cyanoethylation decreases with the time of reaction while the by-product formation increases, long reaction times are not economical. In general, a two to three-minute reaction time is preferable, and periods of time longer than thirty minutes appear to be undesirable. By using acrylonitrile in vapor phase, one can effect a precisely controlled reaction at a comparatively high temperature.

We have determined that the extent and rate of reaction of the presteeped cotton fabric with acrylonitrile at a given sodium hydroxide pickup increases with temperature. This is an effect that would not have been anticipated. In cellulose chemistry the extent of swelling of cotton with sodium hydroxide increases with sodium hydroxide concentration and also increases as the temperature is lowered. The conversion of crystalline cellulose to amorphous cellulose follows the swelling behaviour pattern. The extent of cyanoethylation should thus increase when the sodium hydroxide presteep conditions favoring the conversion of crystalline to amorphous cellulose are used. In the present instance the reverse of this is found; that is, increasing the temperature, which would be expected to decrease the extent of swelling, causes an increase in the rate and extent of reaction with acrylonitrile. Thus, at temperatures below 46° C., it is impossible to get a nitrogen content above about 2.2%, which is insufficient for good mildew and heat resistance. By raising the temperature the nitrogen content leveling off point of the reaction is increased. This dependence on temperature to achieve the desired products is an important and surprising feature of the invention.

This application is a continuation-in-part of our copending application Serial No. 201,063, filed December 15, 1950, now abandoned.

We claim:

1. The process of treating native cotton fibers to effect but a partial cyanoethylation of the cellulose and retain the natural physical structure of the fibers which comprises immersing said cotton fibers in an aqueous solution containing from 0.10 to 10% of sodium hydroxide to sorb on the cellulose from 1.5 to 22 milligrams of sodium hydroxide per gram of cotton, removing from the cotton substantially all the adhering liquid solution, and reacting the cotton while containing the said sorbed amount of sodium hydroxide with acrylonitrile in the vapor phase at a temperature of from 46° C. to 85° C. and for a period not to exceed 4 hours until there is such an amount of cyanoethylation that the cotton contains from 0.50% to 6.5% of nitrogen based on the weight of the cyanoethylated cotton, and retaining the crystalline structure of the cotton fibers substantially unaltered.

2. The process of claim 1 wherein the sodium hydroxide solution contains from 0.10% to 1.75% of sodium hydroxide.

3. The process of claim 1 wherein the extent of cyanoethylation is such that the cotton contains from 0.50% to 4.30% nitrogen based on the weight of the cyanoethylated cotton.

4. The process of claim 1 wherein the aqueous solu-

tion of sodium hydroxide in which the cotton is immersed contains from 0.1% to 1.75% sodium hydroxide at a temperature of from about 45° C. to 50° C. and the reaction with acrylonitrile is from about 1.5 to 90 minutes to cyanoethylate only the amorphous portion of the cotton.

5. The process of treating native cotton fibers to effect but a partial cyanoethylation of the cellulose and retain the natural physical structure of the fibers and produce a product having exceptional resistance to micro-organism degradation, which comprises presteeping native cotton fibers in an aqueous solution containing from 0.25% to 1.75% of sodium hydroxide to sorb on the cellulose from 1.5 to 22 milligrams of sodium hydroxide per gram of cotton, removing from the cotton substantially all of the adhering liquid solution, reacting the presteeped cotton while containing said sorbed amount of sodium hydroxide with acrylonitrile in vapor phase at a temperature of from 71° C. to 76° C. until the amorphous portion of the cotton fibers form cyanoethyl-cellulose in such amount that the nitrogen content varies from 2.5% to about 6.5% based on the weight of the cyanoethylated cotton, and retaining the crystalline structure of the cotton fibers substantially unaltered.

6. The process of claim 5 wherein commercial acrylonitrile which contains some water is used for reaction with the presteeped cotton and the vapor is at a temperature near the boiling point of the azeotrope which is about 71° C. to 72° C.

7. The process of treating native cotton fibers to effect but a partial cyanoethylation of the cellulose and retain the natural physical structure of the fibers which comprises impregnating the native cotton fibers with an aqueous solution containing from 0.10% to 10% of sodium hydroxide for a period of time sufficient to sorb on the cotton from 1.5 to 22 milligrams of sodium hydroxide per gram of cotton, removing from the cotton substantially all of the adhering liquid solution, and reacting the cotton while containing said sorbed amount of sodium hydroxide with acrylonitrile in vapor phase at a temperature of from 46° C. to 85° C. in a chamber to effect cyanoethylation with but the amorphous portion of the cotton, removing the cotton from the chamber, and maintaining the cotton at said temperature range to react the residual acrylonitrile vapor with the cotton, said cotton containing from 0.50% to 6.5% nitrogen based on the weight of the cyanoethylated cotton and having the crystalline structure of the cotton fibers substantially unaltered, whereby said cotton has the hand and appearance of natural cotton but is highly resistant to microorganism degradation.

8. The process of claim 7 wherein the cotton treated is an article in the form of yarn, cord, and fabric, and is passed continuously through the process, first through the sodium hydroxide solution, then while the cotton is at a temperature of about 75° C. removing excess solution and furthering the reaction with the cotton, then through the acrylonitrile vapor, and then washing and drying the article.

9. The process of claim 7 wherein the native cotton fibers are passed through the sodium hydroxide solution and then the cotton is passed through a chamber containing acrylonitrile vapors until there is such an amount of cyanoethylation that the cotton fibers contain from 0.77% to 4.30% of nitrogen based on the weight of the cyanoethylated cotton.

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