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ESTERIFICATION OF CELLULOSIC TEXTILES WITH UNSATURATED LONG CHAIN FATTY ACIDS IN THE PRESENCE OF TRIFLUOROACETIC ANHYDRIDE USING CONTROLLED CELLULOSE-ACID-ANHYDRIDE RATIOS

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ABSTRACT OF THE DISCLOSURE

This invention relates to the production of partial cellulose esters with improved crease recovery. More particularly, this invention relates to the esterification of celluose with unsaturated fatty acids in the presence of trifluoroacetic anhydride (TfAA) in benzene solution with improved wet and dry crease recovery.

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

A primary object of this invention is to provide an improved esterification process for the esterification of hydroxy groups containing cellulosic textile fibers with unsaturated alkanoic acid without destroying the textile properties of the fibers. A further object is to provide a process for modifying properties of cellulosic textiles that contain hydroxyl groups to enhance such properties as wet and dry crease recovery. Another object is to provide unsaturated fatty acid esters of cellulose in textile fiber form wherein the esterification treatment is durable to home laundering.

Esterification of cotton with long-chain fatty acids and trifluoroacetic anhydride in benzene is known in the prior art. In these processes, the mole ratio of reactants employed is such that the treated fabrics possess only improved wet crease recovery.

We have discovered an improved esterification process for the production of long-chain fatty acid esters of cellulosic materials whereby the treated cellulosic material possesses both dry and wet crease recovery at relatively low D.S. (degree of substitution) and improved elongation-at-break which properties are endurable to at least ten home launderings. The new process uses more fatty acids to prevent competitive reaction between trifluoroacetic anhydride and cellulose from proceeding too rapidly. The mixed ester formed when trifluoroacetic anhydride reacts with cellulose rather than the fatty acid has lower dry crease recovery properties. The presence of short chain trifluoroester groups accounts for this reduced crease recovery. In addition, excess trifluoroacetic anhydride will cause the cellulose to swell excessively and will deter the attainment of dry crease recovery. The improved esterification process of the present invention does not alter significantly the strength, color, appearance, hand or fibrous form of the cellulosic material.

In general, in accordance with the present invention, a hydroxyl group containing cellulosic material is esterified by reacting it with an unsaturated fatty acid wherein the acyl radical contains from 10 to 17 carbon atoms. In carrying out the esterification process of this invention, the esterification is accomplished by a reaction between the cellulosic material and one or more of the unsaturated long-chain fatty acids in the presence of trifluoroacetic anhydride in benzene solution. The process of the present invention is characterized by a critical adjustment of the molar ratios of fatty acids to trifluoroacetic anhydride to anhydroglucose units (cellulose).

Substantially any cellulosic material containing hydroxyl groups can suitably be employed in the present process. Illustrative examples of such materials include cellulose derived from cotton, flax, ramie and the like vegetable materials, wood cellulose, regenerated cellulose such as viscose rayon and the like, partial esters of cellulose such as partially acetylated cellulose, beta-propiolactone-reacted cellulose, and the like, partial ethers of cellulose such as partially cyanoethylated, partially aminoethylated, partially carboxy methylated, and the like partially etherified cellulosic materials. In general, the celluosic textile fibers, in the form of free fibers, slivers, yarns, threads or fabrics, including the natural fibers and partial ethers or partial esters thereof which are produced by reactions in which the fibers retain their cellulosic textile properties are preferred starting materials. The cellulose textile fibers in the form of spun textiles, i.e., yarns, threads or cloths, are particularly suitable starting materials.

Any unsaturated long-chain fatty acid wherein the acyl radical contains from 11 to 18 carbon atoms can be used in the present process. Acids which can be employed include undecenoic, oleic and linoleic and the like acids. It is important to use only long-chain unsaturated acids as esterifying agents since the saturated fatty acids do not produce an improved dry crease recovery.

In reacting the cellulosic material with the esterifying agent and the impeller, trifluoroacetic anhydride, substantially any apparatus usually employed in the esterification of cellulose can be used. In carrying out the improved esterification process, the fabric employed must contain the normal amount of absorbed water. Predried fabric seriously curtails the rate of the reaction. The reaction solution is prepared by mixing the acid in excess benzene and then adding the trifluoroacetic anhydride. The cotton is rolled and immersed in the reaction media and allowed to react at room temperature for various times, up to 26 hours, with agitation. The preferred mole ratio of cellulose (anhydroglucose units) to fatty acids to trifluoroacetic anhydride is 1:1:2.

The extent of reaction, and thus the degree of substitution (i.e., the number of the three reactive hydroxyls per anhydroglucose unit which have been substituted by replacing a hydrogen atom with an unsaturated acyl radical, as indicated by the proportion of acyl groups per unit weight of cellulosic material and/or by titration using the Eberstadt Method), can be varied widely.

The degree of substitution can be varied primarily by (a) varying the proportion of fatty acid in contact with the cellulosic material, i.e., increasing the molar ratio of acid to cellulose (AGU) and (b) varying the time and temperature of the esterification reaction. In general, it is preferable to conduct the esterification reaction at a temperature about the freezing point of the solution used for esterification and below a temperature at which an undesirable amount of cellulose degradation takes place. Reaction temperatures from about 20° C. to about 50° C. are preferred.

Under the preferred esterification conditions, durable dry and wet crease resistant fabrics with high elongation-at-break can be produced using reaction times as low as about six hours at 25° C. The dry and wet crease resistance and high elongation-at-break is achieved at low degrees of substitution. It is generally preferred to esterify the cellulose to a degree of substitution between 0.1 and 0.2 to impart the aforementioned properties. If desired the cotton can be esterified to considerably higher degrees of substitution to impart improved wet and dry crease re-

covery and increased elongation-at-break without significant alteration of the strength, color, appearance, or fibrous form of the cellulosic material.

Following completion of the esterification reaction it is very important that the reacted cellulosic material be washed free of the reactant solution before washing the cellulosic material in water. In the preferred washing procedure, the treated material is segregated from the reaction mixture and is first quenched several times in cold benzene, then washed several times in absolute methanol, soaked once in 5% $NaHCO_3$ and finally washed in cold (20–25° C.) tap water for several hours. The fabrics are then rinsed in distilled water and ironed dry or dried by any conventional method employed for drying cellulosic materials. The drying temperature should be relatively low and should not exceed 160° C.

Example 1

An 80 x 80 printcloth weighing 5.1 g. (0.03 mole AGU) was immersed in a graduate cylinder (100 ml.) which contained a solution prepared by first mixing 9.5 ml. (0.03 mole) of oleic acid in 82 ml. of benzene, then adding 12.6 g. (0.06 mole) of trifluoroacetic anhydride. The mixture and the fabric were agitated in the stoppered graduate cylinder for 16 hours. The fabric was then removed and rinsed three times in cold benzene, three times in cold methanol, once in 5% sodium bicarbonate. The fabric was then rinsed in cold tap water for one hour and finally with distilled water. The fabric was then ironed dry and equilibrated. The treated fabric had a weight add-on of 25% (D.S.=0.14) and had a dry and wet crease recovery of 280− and 271− $(w+f)$ degrees with an elongation of 11.2%.

Example 2

An 80 x 80 fabric weighing 10.7 g. (0.06 mole AGU) was immersed in a graduate cylinder (250 ml.) which contained a solution prepared by first mixing 14.0 ml. (0.06 mole) of oleic acid and 164 ml. of benzene and then adding 25.2 g. (0.12 mole) of trifluoroacetic anhydride. The mixture and the fabric were agitated in the stoppered graduate cylinder for 24 hours. The fabric was then removed from the mixture and washed as in Example 1. The partially esterified fabric had a weight add-on of 35.7% (D.S.=0.21) and a dry and wet crease recovery of 284 and 269 $(w+f)$ degrees and an elongation of 16.6%.

Example 3

An 80 x 80 cotton fabric was treated as in Example 2 except in thic case phenylstearic acid was used in place of oleic acid. The partially esterified fabric had a weight add-on of 22.4% (D.S.=0.13) and a dry and wet crease recovery of 239 and 228 $(w+f)$ degrees and an elongation-at-break of 12.8%.

Example 4

The following samples were treated as in Example 1 and details are given in the following table:

Sample	Reaction time (hr.)	Percent add-on	D.S.	Dry	Wet	Percent Elongation
1	8	13.1	0.08	251	217	8.4
2	12	20.6	0.12	245	231	13.8
3	16	26.6	0.15	253	268	15.9
4	20	33.0	0.19	268	268	10.3
Control				190	150	6.6

Example 5

The following samples were treated as in Example 1 with the exception that linoleic acid was substituted for oleic acid. Thte treated fabric properties were as follows:

Sample	Reaction time (hrs.)	Percent add-on	D.S.	Dry	Wet
1	16	21.1	0.12	282	275
2	24	30.1	0.17	292	290

The following example is included to show that by decreasing the chain length of the esterifying agent (acid) to C_{11} (undecenoic acid) that the fabric properties are such that only minimal increases in dry crease recovery are obtained.

Example 6

Three 80 x 80 cotton fabrics were treated as in Example 1 except in this case undecenoic acid was used in place of oleic acid and details are given in the following table:

Sample	Reaction time (hrs.)	Percent add-on	D.S.	Dry	Wet
1					
2	4	22.8	0.20	205	225
3	5	24.4	0.21	190	219
	6	29.5	0.26	195	229
Control				188	142

We claim:

1. A process for converting a cellulosic textile fiber having free hydroxyl groups in the cellulose molecule to an esterified cellulose textile fiber containing unsaturated long-chain acyl radicals attached to oxygen atoms of cellulose molecules, comprising:
   (a) impregnating the cellulosic textile fiber having free hydroxyl groups in the cellulose molecule in the reaction mixture prepared by mixing an unsaturated, long-chain acid selected from the group consisting of oleic acid, phenylstearic acid, linoleic acid, and undecenoic acid in excess benzene and then adding trifluoroacetic anhydride, the mole ratio of fibrous cellulose (anhydroglucose units) to acid to trifluoroacetic anhydride being 1:1:2;
   (b) reacting the impregnated fiber with agitation at a temperature ranging from about 20° C. to 50° C. for a minimum of 6 hours;
   (c) washing the resulting fiber free of reagents, ironing it dry, and allowing it to equilibrate.
2. The process of claim 1 wherein the unsaturated long-chain acid is oleic acid.
3. The process of claim 1 wherein the unsaturated long-chain acid is phenylstearic acid.
4. The process of claim 1 wherein the unsaturated long-chain acid is linoleic acid.
5. The process of claim 1 wherein the unsaturated long-chain acid is undecenoic acid.

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