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[56] **References Cited**  
**UNITED STATES PATENTS**  
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[54] **ESTERIFICATION OF CELLULOSIC TEXTILES**  
**WITH SORBIC ACID IN THE PRESENCE OF**  
**TRIFLUOROACETIC ANHYDRIDE USING**  
**CONTROLLED CELLULOSE-ACID-ANHYDRIDE**  
**RATIOS**  
**1 Claim, No Drawings**

**ABSTRACT:** This invention relates to the production of partial cellulose esters with improved crease recovery through esterification of cellulose with unsaturated fatty acids in the presence of trifluoroacetic anhydride (TFAA) in benzene solution.

**ESTERIFICATION OF CELLULOSIC TEXTILES WITH  
SORBIC ACID IN THE PRESENCE OF  
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This is a continuation-in-part of Ser. No. 643,300 filed May 26, 1967, now U.S. Pat. No. 3,493,319.

A nonexclusive, 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 hydroxyl groups containing cellulosic textile fibers with unsaturated alkanolic 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 possess both dry and wet crease recovery at relatively low D.S. (degree of substitution) and improved elongation-at-break which properties are durable to at least 10 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 six 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 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 amino-ethylated, partially carboxy methylated, and the like partially etherified cellulosic materials. In general, the cellulosic 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 fatty acid wherein the acyl radical contains from six to 18 carbon atoms can be used in the present

process. Acids which can be employed include sorbic, undecenoic, oleic, and linoleic and the like acids. It is important to use only 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 process can be used. 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 6 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 recovery 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 percent NaHCO<sub>3</sub> 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 80×80 printcloth weighing 10.0 g. (0.06-moles AGU) was immersed in a graduate cylinder (100 ml.) which contained a solution prepared by mixing 6.8 g. Sorbic Acid (0.06 moles) in 80 ml. of benzene, then adding 16.8 ml. (0.12 moles) of trifluoroacetic anhydride. The mixture and the fabric were agitated for 120 minutes at room temperature. The fabric was then removed and rinsed three times in cold benzene, three times in cold methanol, once in 5 percent sodium bicarbonate. The fabric was then rinsed in cold tap water for 1 hour and finally with distilled water. The fabric was then ironed dry and equilibrated. The treated fabric had a weight add-on of 25 percent (D.S. =0.20) and had a dry and wet

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crease recovery of 300° and 278° (W+F) degrees with an elongation of 10 percent.

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 acyl radicals attached to oxygen atoms of cellulose molecules comprising:

- a. immersing the cellulosic textile fiber in a benzene solution containing an amount of sorbic acid at least the molecular weight equivalent of the cellulosic textile fiber as measured by anhydroglucose units and trifluoroacetic

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anhydride in 2:1 molecular weight ratio relative the weight of sorbic acid,

- b. reacting the immersed cellulosic textile fiber with agitation at a temperature of about from 20° C. to 50° C. for at least about 2 hours,
- c. washing the reacted cellulosic textile fiber from step (b) free of reagent and with cold benzene, then with cold methanol and finally with 5 percent aqueous sodium bicarbonate, and with water,
- d. drying and equilibrating the washed fabric.

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