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[54] **MODIFICATION OF COTTON TEXTILES AND COTTON/POLYESTER TEXTILE BLENDS BY PHOTO-INITIATED POLYMERIZATION OF VINYLIC MONOMERS**

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[58] **Field of Search** ..... 8/120, 189, 194, DIG. 12, 8/DIG. 18

[56] **References Cited**

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[57] **ABSTRACT**

Cotton and cotton/polyester blended fabrics are impregnated with aqueous solutions of certain water-soluble monomers and each treated fabric subsequently exposed to near-ultraviolet light thereby initiating polymerization of the monomer on and/or within the yarn and fiber structure. The resulting textiles have improved physical and chemical properties, among which are dye-receptivity, moisture-regain, and personal comfort.

8 Claims, No Drawings

MODIFICATION OF COTTON TEXTILES AND COTTON/POLYESTER TEXTILE BLENDS BY PHOTO-INITIATED POLYMERIZATION OF VINYLIC MONOMERS

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.

This invention relates to a method of modifying cotton and/or cotton-polyester fabric blends by durably depositing select polymers on and within the yarns and fibers of the textile substrate to change the physical properties of the cellulosic textiles. Specifically, this invention refers to a process for producing polymer-modified cellulosic textile products wherein (1) a cotton and/or cotton-polyester fabric blend is padded with an aqueous solution of a water-soluble vinyl monomer and then (2) the treated fabric is subsequently exposed to near-ultraviolet light (3000–4000 A) to yield cellulosic textile products modified with a durable polymer deposited on and/or within the yarns and fibers of the fabric.

The method of this invention has as its objective the permanent modification of the basic physical properties and characteristics of cellulosic textiles by photo-initiated deposition of durable polymer so that desired properties such as increased moisture regains and improved dye-receptivity are enhanced in one or more ways, depending on the particular monomeric material or mixture of monomers that is employed in the photo-polymerization process.

The instant invention represents a distinct improvement over the methods currently available for modifying and improving the properties of cellulosic textiles with polymers. Currently, polymer-modified cellulosic textile products are produced by the conventional technique of applying a preformed polymer coating to a fabric surface. The usual procedure is to dissolve or disperse the polymer that is desired for the intended coating in a suitable solvent, coating the resulting composition on the cloth, and then removing the excess solvent. This process gives a polymer-modified fabric in which the surface of the fabric is modified with little or no polymer deposition within the yarns or fibers of the coated material. Alternatively, polymer-modified cellulosic textiles may be produced from reactions of free radicals in the macromolecular chains of the cellulose molecule with vinyl monomers in a graft copolymerization process. The cellulosic free radicals which initiate the copolymerization reaction can be produced by a number of techniques such as exposure of the cellulosic substrate to high-energy radiation, or hydrogen abstraction from a cellulose molecule by reactive chemical intermediates which are produced either chemically or photochemically. However, the effect of high-energy radiation, as well as other methods for producing cellulosic free radicals, is to depolymerize the macromolecules of the cotton fiber resulting in measurable and undesirable changes in the textile properties of the fabric products. Since exposure of cotton to near-ultraviolet light has no adverse effect on the cellulose molecule, the original strength properties of the cotton fiber in cotton and/or in cotton-polyester blend fabrics are thereby conserved to a maximum extent by the method of this invention and new properties are imparted to the cellulosic textile fabric after photo-initiated polymer deposition. Practice of the present invention requires no chemical catalyst. The practice of this invention also obviates the problem of undesirable homopolymerization of the water-soluble monomer which is common to the other methods for modifying cellulosic textiles with polymers.

The monomer or mixture of monomers selected in the application of the method of this invention would determine the physical and performance properties of the polymer modified cellulosic textile fabrics produced therefrom. By the method of this invention polymer modified cotton textile fabrics having improved rot resistance, mildew resistance, weather resistance, water-proofing properties, flame-resistance, wrinkle-resistance, etc., can be prepared depending on the molecular constitution of the monomer or mixture of monomers selected. The fabrics in many instances have demonstrated improved moisture regain properties which is related to the personal comfort characteristics of textile garments and increased receptivity for dyes that are not commonly applicable to cotton (unmodified) textile products. The water-soluble monomer that is employed for polymer-modification of cellulosic textiles in the practice of this invention is selected from the group consisting of acrylamide, N-methylol acryiamide, methacrylamide, N,N-methylenebisacrylamide, diacetone acrylamide, acrylic acid, and vinyl lactam monomers (especially N-vinyl pyrrolidone).

Samples of cotton textile fabrics used were commercial grey printcloth, about 3.2 ounces per square yard, that had been enzymatically desized, alkali scoured, and peroxide bleached on a pilot plant scale. Samples of cotton (50 percent)/polyester (50 percent) textile fabrics used were commercial fabrics with about the same weight per square yard as cotton printcloth; the cotton/polyester fabrics were used as received from the commercial supplier. Samples of the textile fabrics were padded to a wet pick-up of about 160 percent with aqueous solutions of vinyl monomers, such as acrylic acid, acrylamide, diacetone acrylamide, methacrylamide, N-vinyl pyrrolidone, N,N-methylenebisacrylamide, containing 7 to 20 percent vinyl monomer. Water was usually used as the solvent for the monomers; however, aqueous solvent mixtures, such as water plus isopropanol, could be used. The amount of wet pick-up was not critical, but was a convenient amount for normal padding operations. The padded textile fabrics in an atmosphere of nitrogen were photolyzed by near-ultraviolet (3000–4000 A) light at ambient temperatures (about 48°C) for 3 to 90 minutes to initiate free radical formation on the cellulose molecules of the cotton and to graft copolymerize the vinyl monomer onto and within the fibrous structures to add-ons of polymer ranging from 1 to about 14 percent to yield polymer modified textile fabrics with moisture regains ranging from about 3.5 to 8.9 percent.

Near ultraviolet light generated a maximum number of free radical sites on the cellulose molecules of the cotton with little or no effect on the desirable natural physical properties of cotton. Monomer solutions exposed to near ultraviolet light in the absence of cotton did not polymerize. This indicated that the initiating free radical for polymerization of the monomer was formed on the cellulose molecule of cotton. When the padded textile fabrics were dried and then exposed to near ultraviolet light, cellulosic radicals were formed; however, graft polymerization of the vinyl monomer

was not initiated probably because the low mobility of the monomer molecules in the dried textile fabric minimized or inhibited a chain polymerization reaction. When the padded textile fabrics were exposed to near ultraviolet light in an atmosphere containing oxygen, graft polymerization of the vinyl monomer onto cellulose did not occur. Although reaction oxygen with the cellulosic radical did not terminate this radical, reaction of oxygen with the propagating poly(vinyl) radical did terminate this radical thereby terminating chain polymerization.

The following examples are provided to illustrate the invention and are not to be construed as limits to the invention in any manner whatsoever.

Example 1

A piece of cotton fabric (printcloth about 3.2 oz/yd^2 which had been desized, scoured, bleached) of about 4 by 8 inches and which weighed 2.154 grams was impregnated with an aqueous solution of about 10.0 grams of methacrylamide in 90 grams of water by padding to a wet add-on of about 16%. The treated fabric was then placed inside a glass (pyrex) tube with a 2-inch diameter so that both sides of the fabric were exposed to light. To remove oxygen, the system was evacuated twice to about 0.3 torr at about 25°C and flushed with nitrogen each time. The sample was then irradiated under nitrogen at about 48°C in a photochemical reactor equipped with sixteen 3500A lamps for 15 minutes. The piece of treated cotton fabric was then removed from the reaction tube and washed 50 minutes in running hot water, dried at 60°C for 20 minutes, and air-equilibrated at 25°C and about 50% RH for 24 hours. The modified fabric sample weighed 2.472 grams corresponding to a pickup of about 15%. The polymer-modified cotton fabric had a moisture regain of 8.89%; the unmodified cotton fabric had a moisture regain of 6.58%. The polymer-modified fabric had a breaking strength of 43.1 pounds and 14.1% elongation. The unmodified cotton fabric had a breaking strength of 44.5 pounds and 11.6% of elongation. Cotton printcloth that had been subjected to the same irradiation for 15 minutes after impregnating with plain water had a moisture regain of 7.35%, a breaking strength of 46.5 pounds, and 18.8% elongation.

When the time of photochemical irradiation was 10 minutes, the polymer add-on on the fabric was 9.6%; after 30 minutes of irradiation, 18.0%; after 45 minutes of irradiation, 19.1%; and, after 60 minutes of irradiation 19.8%.

Example 2

The method of Example 1 was repeated with printcloth blended textile fabric (containing 50% cotton and 50% polyester). In each case a fabric sample of the blended textile was impregnated with separate aqueous solutions of each monomer containing 10 grams of monomer and 90 grams of water (10%) by padding to a wet add-on of about 160%. The monomers included acrylamide, methacrylamide, diacetone acrylamide, and N-methylol acrylamide. The results that were obtained are set forth and included in the following Table I which indicated the time of irradiation, the percent polymer add-on, moisture regains, and certain physical properties for each of the samples tested. The control sample (A 1) was not subjected to irradiation. The control sample (A 2) was impregnated with plain water and subsequently irradiated for 30 minutes.

TABLE 1

Photo-initiated Polymerization of Various Monomers Onto Cotton/Polyester (50/50) Blended Fabric

Irradiation Time (min)	% Polymer, add-on	Sample	Moisture Regain, %	Wrinkle Recovery Angle Wet	Dry
0	0	A 1	3.45	248	252
30	0	A 2	3.61	255	249
		Acrylamide			
5	3.4	A 3	4.03	274	229
10	7.5	A 4	4.53	291	181
15	9.9	A 5	4.84	—	—
30	10.0	A 6	—	—	—
60	13.4	A 7	5.01	267	173
		Diacetone Acrylamide			
3	2.9	A 8	3.60	253	251
5	5.9	A 9	3.88	253	245
8	9.7	A 10	4.06	255	236
10	11.0	A 11	4.14	256	219
60	13.5	A 12	4.13	239	240
		Methacrylamide			
5	1.1	A 13	3.73	260	267
10	1.7	A 14	3.86	249	256
20	4.5	A 15	4.28	230	249
30	6.5	A 16	4.51	219	255
60	8.4	A 17	4.82	208	234
90	11.3	A 18	5.40	203	231

Example 3

The method of Example 1 was repeated except that the cotton fabric sample was padded with an aqueous solution of 8.45 grams of diacetone acrylamide in 100 grams of water (7.8%), and subsequently irradiated with near-ultraviolet light for 7 minutes. The polymer-modified cotton product had a polymer add-on of 12%, a moisture regain of 7.27%, and dyed better than the unmodified cotton with disperse dyes. The maximum polymer add-on was achieved after 7 minutes irradiation time.

Example 4

The method of Example 1 was repeated with separate solutions of 10 grams of acrylamide in 90 grams of water (10%), 7.2 grams of N,N-methylenebisacrylamide in 75 grams of water and 18 grams of isopropanol (7%), and 10 grams of N-vinyl pyrrolidone in 90 grams of water (10%). The add-ons obtained after 30 minutes photochemical irradiation of cotton printcloth fabrics impregnated with the above solutions were 10.7%, 6.4%, and 2.8%, respectively. The polymer-modified fabric samples prepared from N,N-methylenebisacrylamide had better dye receptivity for disperse dyes than the unmodified cotton fabric. The polymer modified fabric samples prepared from N-vinyl pyrrolidone had increased absorption of optical brighteners relative to untreated cotton.

Example 5

The method of Example 1 was repeated with aqueous solution of 10 grams of acrylic acid in 90 grams of water (10%). The cotton fabric sample was photochemically irradiated in the near-ultraviolet for 30 minutes to yield a polymer modified cotton product with a polymer add-on of 9.8%. The cotton fabric modified with the photo polymer of acrylic acid had greatly increased dye receptivity for basic dyestuffs and a moisture regain of 8.50%. The moisture regain for untreated cotton was 6.84%. When the photochemical irradiation time was 5 minutes, the percent polymer add-on was 3.7%; after 10 minutes, 6.0%; after 15

minutes, 8.6%; and after 45 minutes, 9.6%. When the cotton fabric was padded with a solution of 20 grams of acrylic acid in 80 grams of water (20%) and the time of photo irradiation was 30 minutes, the percent polymer add-on was 27%.

Example 6

Cotton fabric was padded with an aqueous solution of 10 grams N-methylol acrylamide in 90 grams of water (10%) and irradiated in the near-ultraviolet as described in Example 1 for 15 minutes to yield a polymer modified cotton product with a polymer add-on of 8.0%. When the time of photochemical irradiation was 5 minutes, the percent polymer add-on was 3.8%; after 40 minutes 12%; and after 60 minutes 14%. A sample modified with the photo polymer of N-mathylol acrylamide to a 10.8% polymer add-on had 1.39% nitrogen, 1.40% formaldehyde, a moisture regain of 7.77%, and wet and conditioned (warp and fill) wrinkle recovery angles of 230° and 167°, respectively. The untreated cotton fabric had a moisture regain of 6.84% and wet and dry wrinkle recovery angles of 165°and 194°, respectively. A cotton fabric sample impregnated with plain water and subsequently photoirradiated for 15 minutes had wet and dry wrinkle recovery angles of 168° and 193°, respectively.

Example 7

Several samples of polymer modified cotton textile fabric prepared as described in Example 1 in accordance with the present invention were extracted with various solvents, including water, ethanol, pyridine, and N,N-dimethylformamide (DMF), by allowing the polymer modified cotton sample to stand in a large excess of the solvent at 60°C for 24 hours before determining the loss in weight due to solvent extraction. The results are set forth in the following Table II wherein the percent polymer add-on before and after extraction with these solvents is indicated.

TABLE 11

Sample	Extraction Solvent	Polymer Add-on, % Before Extraction	After Extraction
	Cotton-Poly(diacetone acrylamide)		
B1	water	12.8	11.2
B2	ethanol	13.3	12.4
B3	pyridine	12.8	12.2
B4	dimethyl formamide	13.0	12.8
	Cotton-Poly(acrylamide)		
B5	water	8.2	7.6
B6	ethanol	9.2	8.9
B7	pyridine	9.5	8.7
B8	dimethyl formamide	9.2	8.5

We claim:

1. A method of imparting improved physical properties to cellulosic textiles, the method comprising:
   a. impregnating a cellulosic textile with an aqueous 7 to 20% by weight vinyl monomer solution, and
   b. irradiating with near-ultraviolet light of a wavelength of about from 3000 to 4000 Angstroms for about from 3 to 90 minutes.

2. A method of imparting improved physical properties to cellulosic textiles, the method comprising:
   a. impregnating a cellulosic textile with an aqueous solution containing about from 7 to 20% by weight of a monomer selected from the group consisting of diacetone acrylamide, acrylamide, N,N-methylenebisacrylamide, N-vinyl pyrrolidone, acrylic acid, and methacrylamide to a wet add-on of about 160% by weight.
   b. placing the wet-impregnated cellulosic textile in a nitrogen atmosphere, and
   c. irradiating the wet-impregnated textile with near-ultraviolet light (3000–4000 Angstrom) for about from 3 minutes to 90 minutes at ambient temperature of about 48°C thereby obtaining grafted polymer add-on of about 1% to 14% by weight.

3. The method of claim 2 wherein the monomer is diacetone acrylamide.

4. The method of claim 2 wherein the monomer is acrylamide.

5. The method of claim 2 wherein the monomer is N,N-methylenebisacrylamide.

6. The method of claim 2 wherein the monomer is N-vinyl pyrrolidone.

7. The method of claim 2 wherein the monomer is acrylic acid.

8. The method of claim 2 wherein the monomer is methacrylamide.

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