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3,526,048

CELLULOSE FIBERS CROSS-LINKED AND ESTERIFIED WITH POLYCARBOXYLIC ACIDS

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No Drawing. Filed June 7, 1967, Ser. No. 645,097

Int. Cl. D06m 13/20, 13/32

U.S. Cl. 38—144

20 Claims

ABSTRACT OF THE DISCLOSURE

Crosslinked fibrous compositions comprising cellulose esterified with a polycarboxylic acid, which acid meets the following requirements: (1) contains no functional groups except carboxyl, (2) contains at least three free carboxylic groups, (3) each carboxyl group attached to a separate carbon atom, (4) at least two of the plurality of carboxyl groups separated by no more than one carbon atom, are prepared by treating fibrous cellulose with said carboxylic acid having varying amounts of the carboxylic acid function neutralized with an alkali metal hydroxide, ammonium hydroxide or an amine, and heating the treated cellulose to induce esterification and concurrent crosslinking. Fabrics composed of such fibers are capable of developing durable creases.

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 novel polycarboxylic acid derivatives of cellulose and to processes for producing the same. More particularly, the invention embodied herein relates to a process for imparting durable wrinkle resistance or so-called "wash-wear" properties to cellulose textiles and to articles fabricated therefrom. It provides a unique method for fixing ironed-in smoothness, ironed-in creases, gloss, or luster produced by calendaring and other mechanical effects, making these physical modifications durable through laundering operations.

An object of this invention is to provide modified celluloses which have superior properties when employed as fibers, yarns, fabrics, and films. Another object is to produce crosslinked cellulose compositions which develop no odors and which are chlorine-resistant. An additional object is to develop ester-crosslinked celluloses which withstand washes with built detergents in home washers. A further object is to provide chemically modified cotton fabrics having improved dye affinity for cationic dyes and greater retention of cationic finishes. A further object is to produce ester-crosslinked celluloses and cotton cellulose fabrics having improved wrinkle recovery properties and smooth-drying characteristics. A further object is to produce crosslinked cellulose fabrics which exhibit an ability to accept or release creases upon ironing creasing treatment at elevated temperatures. A further object is to provide a process for reacting the polycarboxylic acid directly with cellulose at elevated temperatures in an operation which approaches the conventional additive finishing process in simplicity and ease of operation.

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Cellulose esters of various types are known in the art [D. J. Stanonis, Encyclopedia of Polymer Science and Technology, vol. 3, p. 455, 1965; C. J. Malm, Svensk kemisk tidskrift 73, 523-530 (1961)]. A conventional procedure for preparing esters from mono- or dicarboxylic acids employs the acid chloride in an anhydrous system diluted with an amine and an organic solvent [D. J. Stanonis, Encyclopedia of Polymer Science and Technology, vol. 3, p. 455, 1965]. Cellulose may be esterified conveniently by employing agents such as trichloroacetic anhydride and trifluoroacetic anhydride in anhydrous organic media to impel the esterification of the free carboxylic acid with cellulose [D. J. Stanonis, Encyclopedia of Polymer Science and Technology, vol. 3, p. 455, 1965; M. D. Cruz-Lagrange, C. M. Hamalainen, and A. S. Cooper, Jr, Am. Dyestuff Repr. 51 (12) 40 (1962; H. J. Campbell and T. Francis, Textile Res. J. 35, 260 (1965)]. Cellulose esters containing free and reactive carboxyl groups in the acid or salt form have been prepared through the reaction of dibasic acid anhydrides with cellulose in the presence of a catalyst such as pyridine [C. J. Malm and C. R. Fordyce, Ind. Eng. Chem. 32, 405 (1940); F. Schulze to E. I. du Pont, U.S. 2,069,974, February 1937; F. C. McIntire to Abbott Laboratories, U.S. 2,505,561, April 1950], and through the impelling action of trifluoroacetic anhydride on tricarboxylic monoanhydrides [R. H. Wade to U.S.A., U.S. 3,097,051, July 1963]. Direct preparation of esters of cellulose from di- and tricarboxylic acids at elevated temperatures has been limited to a few organic acids [T. C. Allen, Textile Res. J. 34, 331, (1964); D. D. Gagliardi and F. B. Shippee, Am. Dyestuff Repr. 52, P300 (Apr 15, 1963)], and has been accompanied by considerable molecular degradation of the cellulose [D. D. Gagliardi and F. B. Shippee, Am. Dyestuff Repr. 52, P300 (Apr. 5, 1963)].

A method has been found whereby a new class of crosslinked, polycarboxylic acid esters of cellulose can be made; these constitute novel crosslinked cellulose compositions, especially valuable in the form of crosslinked cotton cellulose fabrics.

In the process of this invention, a native or regenerated fiber cellulose which may be in the form of free fibers, sliver, yarn, thread or fabric is contacted with a system comprising a suitable solvent or diluent, the polybasic acid, and an optional buffer and catalyst. The reaction between the polybasic acid and cellulose is caused to occur by elevating the temperature of the composition to the range of 100-250° C. for suitable curing.

When cellulose is reacted under the preferred conditions, the resulting partial esters retain the original color, appearance, and fibrous form of the cellulose. These products are insoluble in common solvents such as water, dilute bases, dilute acids, ethers, hydrocarbons, alcohols, ketones, and the like.

The reagent system can be deposited on the cotton from any solvent in which the components are soluble. It is preferred to dissolve the reagents and apply them to cellulose from an aqueous system. This assures intimate contact between the insoluble cellulose and the reactants. Other suitable solvents which may be applied together with or to the exclusion of water are dimethylformamide, dimethylsulfoxide, dioxane, pyridine, acetic acid, and the like solvents.

The concentration of reagents in the solution which is applied to cellulose may vary over a considerable range

depending on the solvent or diluent. In general, it is desirable that the polybasic acid be present to the extent of 1 to 25% of the total solution. This solution may be deposited on cellulose at any convenient level, but, most generally, to the extent of 50–150% of the weight of the cellulose. It is inefficient and uneconomical to use the highest proportions of the reagent solutions of highest concentrations. The ratios of reagent solution to cellulose and reagent to cellulose will depend upon the extent of reaction desired on the hydroxyl groups of the anhydroglucose units of the cellulose structure, and the particular properties desired in the final product. It is generally preferred to employ 5–10% solutions of polybasic acid and to deposit these on the cellulose to the extent of 80–120% of the weight of the cellulose. This will generally introduce 5–15% of carboxylic ester into the cellulose.

Polybasic acids which are suitable for this process are those which contain three, and preferably more, free carboxyl groups per molecule and which are free of olefinic unsaturation and hydroxyl groups. Each carboxyl group should be attached to a different carbon atom such that a malonic acid type of structure is not involved. Preferably, each carboxyl group should be located in the carbon skeleton of the molecule in such an arrangement that it is capable of forming a 5- or 6-membered anhydride ring with at least one adjacent carboxyl group. This requirement is met when the carboxyl groups are located on adjacent carbon atoms or separated by no more than one additional carbon atom. One carboxyl group in the polycarboxylic acid may be isolated from the other carboxyl groups and may be excepted from the foregoing requirement to form an anhydride structure with an adjacent carboxyl group.

Examples of specific polycarboxylic acids which fall within the scope of this invention are the following: propane-1,2,3-tricarboxylic acid, butane-1,2,3,4-tetracarboxylic acid, hexane-1,2,3,4,5,6-hexacarboxylic acid, cyclopentane-1,2,3-tricarboxylic acid (and the 1,2,4-isomer), cyclopentanetetracarboxylic acid, cyclohexane-1,2,3-tricarboxylic acid (and the 1,2,4-isomer), cyclohexane-1,2,3,4-tetracarboxylic acid (and 1,2,4,5-isomer and 1,2,3,5-isomer), benzene-1,2,3-tricarboxylic acid (and 1,2,4-isomer), pyromellitic acid, mellitic acid, naphthalene-1,4,5,8-tetracarboxylic acid, biphenyl-3,4,3',4'-tetracarboxylic acid, benzophenone-3,4,3',4'-tetracarboxylic acid and the like.

Although our understanding of the chemistry of the reaction of these polycarboxylic acids, as such, in the partial alkali salt form and in the partial or in the complete amine salt form, is not complete, it appears that the requirement for 3 (preferably 4 or more- carboxyl groups, the location of these carboxyl groups on adjacent carbons (on immediately adjacent carbons or separated by no more than one more carbon atom), and the absence of other functional groups such as hydroxyl groups or reactive (olefinic) unsaturation are essential for adequate reaction with the cellulose, for effective crosslinking of the cellulose chains for development of high levels of wrinkle resistance, and for amenability to introduction and removal of creases at elevated temperatures.

Substantially any strong base capable of forming a soluble, partial salt of polybasic acid in an effective concentration in the reactant-containing liquid, can be used as the buffering agent. Illustrated examples of suitable strong bases include: alkali metal hydroxides, carbonates, bicarbonates, acetates, phosphates, borates, ammonia, secondary amines, tertiary amines, quaternary ammonium hydroxides.

The proportionate amount of catalysts or buffer contained in the reactant-containing liquid can be varied widely. Both the catalyst and the buffer can be incorporated into the reagent in the form of solutions, emulsions, or dispersions in a liquid in which they are appreciably soluble. The reactant-containing liquid can be modified to include any supplementary agents conventionally

employed for textile finishing operations (lubricants, dyes, and the like), provided of course that these agents are compatible with the other reactants. The proportion of buffer or catalyst is not highly critical and depends upon the specific polybasic acid being employed, the temperature of cure, and the desired rate of reaction. Buffer or catalyst to the extent of approximately 1–10% of the total solution may be employed effectively. It is generally desirable that the pH of an aqueous reagent system be in the range of 2.5–5.

The apparatus and handling techniques usually employed for the chemical treatment of textile fibers can be employed in the process of this invention. In general, the employment of fibers in the form of yarns or fabric is preferred. Examples of fibers which may be employed include cotton, flax, ramie, and the like natural vegetable textile fibers; mercerized, partly acetylated, partially cyanoethylated, partially benzylated, or the like chemically modified natural vegetable textile fibers which contain at least one cellulosic free hydroxyl group per anhydroglucose unit; and derived or regenerated cellulosic textile fibers such as the fibers regenerated from natural vegetable textile fibers by the cuprammonium and viscose processes. The natural vegetable textile fibers are particularly suitable for employment in this process.

At the time the cellulose fibers are wetted with the reagent, the reagent may be maintained at substantially any temperature above the freezing point and below the boiling point. In general, the reagent is preferred at about room temperature and the step of wetting the fibers may be carried out by any convenient method, including a textile paddler. In some cases it may be desirable to evaporate the solvent or diluent from the cellulose prior to cure at elevated temperature. This may be carried out conveniently at temperatures in the range of 50–100° C.

The temperature at which the reaction between polybasic acid and cellulose is conducted may be varied, depending, for example, upon the particular solvent and the reactants employed. The rate of the reaction and the particular performance properties desired in the product may be controlled, to some extent, by the temperature at which the impregnated cellulose is cured. It is preferred to carry out the reaction above 100° C. in order to obtain rates of reaction which are in a practical range. The duration of reaction is intimately dependent upon the temperature; a very short exposure to temperatures in the range of 200–250° C. is sufficient to react the polybasic acids with cellulose. On the other hand, an exposure of several minutes at 150° C. is essential for good reaction, and an exposure of several hours is required for temperatures close to 100° C.

The foregoing process is described by way of general illustration of the procedures for preparation of the compositions of this invention. However, it should be noted that the acid chloride method and the impeller methods have been generally unsatisfactory for preparing the desired polycarboxylic acid-modified celluloses.

The invention is set forth in the following paragraphs and examples by way of illustration and not as a limitation.

EXAMPLE 1

A 10 g. sample of 80 x 80 desized, and bleached cotton print cloth was thoroughly wet with a solution of disodium cyclopentanetetracarboxylate in water; this disodium salt solution was prepared from the free acid by adding one mole of sodium carbonate for each mole of cyclopentanetetracarboxylic acid. The treating solution had a pH of 4.5–5.0. The cloth was wrung to a wet pick-up of 111–114%, and cured in a forced-draft oven at 160° C. for 10 min. The fabric was washed in hot running water, dried at 85° C. and allowed to equilibrate in air at the prevailing humidity. The weight gain shown by

the fabric depended on the concentration of disodium salt in the treating solution, as tabulated below:

	Concentration of disodium salt, percent	Weight gain, percent	Addition efficiency, ¹ percent	Elmendorf tear str. (warp) (g.)	Breaking str. (warp: 1 in. strip) (lbs.)	Monsanto wrinkle Rec. (W+F)	
						Wet (°)	Dry (°)
1-----	8.7	7.1	73	700	53	201	230
2-----	11.8	8.9	66	720	53	204	228
3-----	17.7	10.1	50	807	49	198	244
4-----	0.0	0.0	00	1,100	58	158	195

$$^1 \text{ Percent efficiency} = \frac{100 \times \text{weight gain}}{\text{concentration} \times \text{wet pick-up}}$$

The treated fabrics had enhanced wrinkle resistance in the wet and dry states, as indicated by the listed wrinkle

gain shown by the fabric depended on the number of carboxylic groups in the cyclopentanetetracarboxylic acid that

were neutralized in making up the treating solution, and are tabulated below.

	No. of COONa groups per molecule	Weight gain, percent	Addition efficiency, ¹ percent	Elmendorf Tear (warp) (g.)	Breaking Str. (warp: 1 in. strip) (lbs.)	Monsanto Wrinkle Rec. (W+F)	
						Wet (°)	Dry (°)
1-----	1.0	7.1	81	653	44	222	254
2-----	1.5	7.4	89	713	46	210	248
3-----	2.0	7.1	73	700	53	201	230
4-----	3.0	2.7	26				
5-----	Untreated	0.0	00	1,100	58	158	195

$$^1 \text{ Addition efficiency} = \frac{100 \times \text{weight gain}}{\text{salt concentration} \times \text{wet pick-up}}$$

² Data taken from run 1 of Example 1.

recovery values and by "crumpling" tests. The fabrics retained their original suppleness and were free of discoloration. Fibers of the treated fabrics were insoluble in 0.5 M cupriethylenediamine solution, showing that the cellulose had been crosslinked by the treatment.

Had the reaction proceeded by disproportionation of the disodium salt into tetrasodium salt and free tetracarboxylic acid, with only the free acid becoming bound to the cotton cellulose, the maximum efficiency possible would have been 42.5%. In all of the above experiments, the reaction efficiency was greater than this, showing that the disodium salt of cyclopentanetetracarboxylic acid reacted directly with the cotton cellulose. The breaking strength remained in the treated fabrics was 84-91% of that for the untreated fabric, and the tearing strength retention was 64-73%. The high retention of strength observed is the result of using the nearly neutral disodium salt, wherein the hydrogen ion concentration was only 1×10^{-5} to 3×10^{-5} molar, thus avoiding acid degradation of the cotton cellulose.

EXAMPLE 2

A 10 g. sample of 80 x 80 desized, scoured and bleached print cloth was thoroughly wet with a solution prepared by dissolving 7.4 parts by weight of cyclopentanetetracarboxylic acid in 90 parts of water; sufficient sodium carbonate was then added to neutralize the carboxylic acid to the extent indicated in the table below. The cloth was then wrung to a wet pick-up of 109-111%, and cured in a forced draft oven at 160° C. for 10 min. The fabric was washed in hot running water, dried at 85° and allowed to equilibrate in air at the prevailing humidity. The weight

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The treated fabrics had enhanced wrinkle resistance in the wet and dry states, as shown by the tabulated wrinkle recovery values and by resistance to manual crumpling. They retained their original suppleness. Fibers of the treated fabrics were insoluble in 0.5 M cupriethylenediamine solution, indicating that the cellulose had been crosslinked.

In the case where three of the four carboxyl groups of the cyclopentanetetracarboxylic acid were neutralized prior to application to the cotton (run 4), the pH of the treating solution was 6. Appreciable reaction and crosslinking still occurred, again demonstrating that the esterification of cellulose can be conducted in essentially neutral media. The reaction efficiency remained essentially constant as the amount of sodium carbonate added ranged from 0.5 to 1.0 mole per mole of cyclopentanetetracarboxylic acid.

All of the treated fabrics were dyed a medium shade by methylene blue in aqueous solution, while the untreated cloth was but slightly colored after being washed. The enhanced affinity of the cationic dye for the treated fabrics indicates that these fabrics contained anionic groups. This established that not all of the carboxyl groups in each molecule of cyclopentanetetracarboxylic acid are esterified with cellulose.

EXAMPLE 3

Desized, scoured, and bleached cotton print cloth was padded in solutions containing 7.4% of polycarboxylic acid and varying amounts of sodium carbonate to adjust the pH of the solution. The wet pick-ups were adjusted to 100%; the samples were dried for 8 minutes at 80° and cured for 10 minutes at 160° C. in a forced draft oven. The cured samples of fabric were washed and then characterized for physical properties. The results are summarized in the accompanying table.

Polycarboxylic acid	pH of reagent	Monsanto wrinkle Rec. (W+F)		Elmendorf tear strength (warp)
		Wet	Dry	
1----- Cyclopentane-tetracarboxylic acid.	1.9	225	260	480
2----- Propane-1,2,3-tricarboxylic acid.	3.0	233	283	550
	1.9	233	240	440
	3.0	217	272	570
3----- Butane-1,2,3,4-tetracarboxylic acid.	6.1	165	185	850
	5.0	181	215	690
	6.7	170	184	880
4----- Citric acid	1.6	229	237	310
	3.1	206	247	590
	6.5	174	183	930
5----- Aconitic acid	1.5	219	216	390
	2.9	195	220	700
	6.9	175	184	920

¹ The acid was insoluble without substantial conversion to the sodium salt.

It will be noted from the above data that the maximum of dry wrinkle recovery is realized when the acids are applied as partial sodium salts, which is illustrated in this table for the system having a pH of 3. At the lowest pH (which is that characteristic of the free acid) and at the highest pH (which results from more complete neutralization of the acid with sodium carbonate), the wrinkle recovery values are significantly lower. In the cases illustrated, substantially less reaction occurs at the higher pH. While significant reaction of the carboxylic acid occurs with the cotton at the pH characteristic of the free acid, the reaction is accompanied by considerable degradation as indicated by the fact that these fabric are characterized by the lowest values of tear strength.

In certain cases, such as illustrated in run 3, the acid is insoluble in the aqueous system without partial salt formation and cannot be reacted with the cotton cellulose except in the latter form.

It will be noted that polycarboxylic acids containing functional groups other than carboxyl groups (see run 4 and run 5 above) performed poorly with respect to wrinkle recovery. Moreover, the presence of functional groups other than carboxyl in the polycarboxylic acid interferes markedly with crease removal, which property of the treated fabric is an important feature of our invention. Coloration also develops in these modified cottons.

EXAMPLE 4

A variety of carboxylic acids was applied to cotton print cloth by the general procedure described in Example 3. In these cases the polycarboxylic acids were applied in the form of partial sodium salts and partial triethylammonium salts. The results are summarized below.

Polycarboxylic acid	Fraction of sodium salt	Carboxyls in salt form triethylammonium salt	Weight gain from reaction of acid, percent
1. Nitrilotriacetic acid	0.67	0.67	0.0
2. Cyclopentane-tetracarboxylic acid	0.1	0.1	3.8
3. Mellitic trianhydride	0.67	0.67	7.2
4. Pyromellitic acid	0.45	0.45	8.8
5. Benzophenone-3,4,3',4'-tetracarboxylic acid	(¹)	(¹)	0.0
			11.6
			0.0
			5.0
			0.0
			4.3

¹ Excess base—an excess of 35% over the stoichiometric amount.

An examination of the above data shows that the greater degree of reaction of the polycarboxylic acid with cotton cellulose was realized when the acid was applied in the form of the partial triethylammonium salt. It is evident from run 5 and from other experiments that polycarboxylic acids may be reacted with cellulose when the acids are completely neutralized with triethylamine. By virtue of this surprising result, it is possible to apply to cotton a variety of carboxylic acids which are insoluble in aqueous systems as the free acids or partial sodium salts (i.e., up to a 1 Na per 2COOH), and which are insufficiently reactive with cellulose when neutralized to higher levels with sodium (i.e., even though solubilized at levels of Na above 1 per 2COOH, polycarboxylic acids show relatively poor reaction with cellulose). The acids illustrated in runs 4 and 5 are insoluble both as free acids and as half sodium salts; although solubilized at higher levels of neutralization with sodium, they are not reactive with cellulose in this form. The basis for the beneficial

effects (i.e., improved reaction) illustrated with the acids of runs 2 and 3 is less apparent. In both cases a higher extent of reaction is obtained from the application of the amine salt than is realized with the corresponding sodium salt (or any level of sodium salt).

Very similar results were obtained when trimethylamine or ammonia were employed in place of triethylamine. The latter is particularly attractive since it may be employed in almost any ratio with the carboxylic acid and since ammonia is available at low cost.

In addition to generating a higher extent of reaction of polycarboxylic acid with cellulose, the ammonium or alkylammonium salt of the acid develops a higher degree of wet wrinkle recovery; e.g., for propane-1,2,3-tricarboxylic acid, 244° vs. 217° applied from amine salt vs. sodium salt; and for butane-1,2,3,4-tetracarboxylic acid, 250° vs. 204° applied from amine salt vs. sodium salt.

EXAMPLE 5

Samples of cellulose were dissolved in cuprammonium hydroxide, cupriethylenediamine hydroxide, and benzyl-trimethylammonium hydroxide to produce solutions containing 1–5% of cellulose by weight. Mellitic acid and cyclopentanetetracarboxylic acid were introduced to the extent of 8–11% of the weight of cellulose and the cellulose was regenerated from this solution by coagulation with 9% solution of sulfuric acid containing 0.5% of zinc sulfate. The fibrous regenerated cellulose was dried at room temperature and was found to be completely soluble in the original solvents; however, insolubility in these solvents was developed when the regenerated cellulose was heated for a period of 10 minutes at 150° C.

EXAMPLE 6

Five percent of tetrasodium butane-1,2,3,4-tetracarboxylate was introduced into a cellulose xanthate solution on the basis of the cellulose content of the solution. The cellulose was regenerated by extrusion into a dilute solution of sulfuric acid containing zinc sulfate (see Example 5) and the fibers were washed thoroughly with water and dried in air. The product was soluble in cupriethylenediamine hydroxide but following a 5-minute treatment at 170° C., the fibers were completely insoluble in this solvent.

EXAMPLE 7

Cellulose modified by polycarboxylic acids as illustrated in the preceding examples is characterized by the unique ability to resist wrinkling, crumpling, and creasing under ordinary conditions to which a fabric is subjected during wear; however, these modified celluloses are amenable to introduction of new creases or removal of old creases at elevated temperatures. The temperatures normally required for the introduction or removal of a crease into this wrinkle resistant cellulose are in the range of 150–225° C. for periods ranging from hours at the lower end of the range to several seconds at the upper end of the range. A sample of cotton print cloth was modified with cyclopentanetetracarboxylic acid by the process described in Example 3. The modified fabric containing 6.3% of the acid residue as measured by weight gain was rinsed in 1 N hydrochloric acid; one half of the sample was rinsed with dilute sodium carbonate solution. Each half was rinsed with distilled water. The acid-rinsed sample, designated H⁺ form, had carboxyl groups in the free acid form, and the sodium carbonate-rinsed sample, designated Na⁺ form, had the unesterified carboxyl groups in sodium salt form. The samples of fabric were subjected to creasing tests; the durabilities of the creases were tested by subjecting the creased samples to 5 laundering cycles in an automatic washer with conventional detergent. The creases were rated by the visual AATCC method, which gives the best crease a rating of 5

and the absence of a crease a rating of 1. The results are tabulated.

dehyde, dimethylolethyleneurea, dimethyloldihydroxyethyleneurea).

Fabric sample	Monsanto wrinkle Rec. (W+F)		Wash-wear rating	Rating of crease durability ¹	
	Wet	Dry		Ironing #1	Ironing #2
H ⁺ form.....	226	272	4.7	4.7	4.7
Na ⁺ form.....	195	248	4.7	4.7	4.8
Dimethylolethylene urea.....	-----	-----	5.0	1.0	1.0
Unmodified cotton.....	172	183	1.0	3.7	3.5

¹ Conditions of ironing to introduce the creases into these samples was as follows: Ironing #1: Samples were wet and creased for 30 seconds with an iron set at the "cotton-linen" setting; this procedure was repeated a second time and the samples were heated in the creased state for 10 minutes at 160° C. Ironing #2: samples were wet, creased for 60 seconds at the "linen" setting; the operation was repeated for a second time.

It is apparent in the table above that the cotton fabric modified with cyclopentanetetracarboxylic acid exhibits enhanced wrinkle recovery values in both wet and dry conditions, that the wash-wear rating is good (5 is maximum), and that the ironing operations introduce good creases into this sample of fabric. By comparison, unmodified cotton shows presence of a moderate crease and the cotton crosslinked with a conventional reagent (i.e., dimethylolethyleneurea) shows complete resistance to introduction of a crease.

By subjecting the creased portion of the cyclopentanetetracarboxylic acid-modified cottons to ironing as above in the flat condition, it was possible to remove the crease to essentially the same extent as for unmodified cotton.

EXAMPLE 8

Cotton print cloth modified with mellitic acid to the extent of 5.4% weight gain was rinsed with 1 N hydrochloric acid and subsequently with distilled water. The samples of fabric were ironed under the conditions defined in Example 7 and the creased swatches were laundered to delineate durability of the creases. One portion of the creased sample (prior to durability tests) was ironed flat and then put through the laundering cycles to measure the extent to which the crease could be removed. The results are tabulated hereafter.

Creasing conditions	Measurements of crease durability on the samples			
	After 5 wet laundry cycles		After 5 wet & dry laundry cycles	
	Crease ironed in ¹	Crease ironed in and out ¹	Crease ironed in ¹	Crease ironed in, ² degree
Ironing #1:				
Mellitic cotton.....	5.0	2.2	5.0	100
Cotton control.....	4.0	2.7	2.5	109
Ironing #2:				
Mellitic cotton.....	5.0	-----	4.2	100
Cotton control.....	3.8	-----	1.8	120

¹ Creases were rated by the AATCC method.

² Crease angles were measured by an adaptation of the Monsanto wrinkle recovery instrument. The smaller angles indicate the better crease. A sample of fabric which was crosslinked with dimethylolethyleneurea in the creased state exhibited a crease with an angle of 75°.

It is apparent from the data in the above table that the cotton modified with mellitic acid is amenable to reversible creasing, that the crease is substantially superior to that of unmodified cotton, and that the latter difference becomes more pronounced as the test for durability of the crease becomes more strenuous.

EXAMPLE 9

A variety of wrinkle-resistant crosslinked cottons was tested for amenability to introduction of a crease under the general conditions described in Example 7.

Cotton modified with polycarboxylic acids (e.g., those mentioned in preceding examples and specifications) showed pronounced development of durable creases while cotton crosslinked with dibasic acids (i.e., adipic acid) exhibited resistance to creasing as did also cottons crosslinked with conventioned crosslinking agents (i.e., formal-

We claim:

1. A process for preparing a polycarboxylic acid-modified cellulose in fibrous form comprising the following steps:

- (a) impregnating fibrous cellulose with an aqueous solution of a carboxylic acid selected from the group consisting of cyclopentanetetracarboxylic acid, nitrilotriacetic acid, mellitic trianhydride, pyromellitic acid, benzophenone-3,4,3',4'-tetracarboxylic acid, said aqueous solution having had substantially all carboxylic acid function neutralized with a strong base selected from the group consisting of ammonia, secondary amines, and tertiary amines, and
- (b) heating the impregnated cellulose to produce the cellulose esters and to induce concurrent crosslinking of the cellulose.

2. The process of claim 1 wherein the polycarboxylic acid is cyclopentanetetracarboxylic acid.

3. The process of claim 1 wherein the polycarboxylic acid is nitrilotriacetic acid.

4. The process of claim 1 wherein the polycarboxylic acid is mellitic trianhydride.

5. The process of claim 1 wherein the polycarboxylic acid is pyromellitic acid.

6. The process of claim 1 wherein the polycarboxylic acid is benzophenone-3,4,3',4'-tetracarboxylic acid.

7. A process comprising the following sequential steps:

- (a) forming crosslinked cellulose esters of fibrous cellulose, which cellulose is in the form of a textile fabric according to the process of claim 1,
- (b) forming a textile article from the esterified and crosslinked fabric of step (a), and
- (c) selectively installing or removing creases from the textile article of step (b) via the simultaneous application of heat and pressure.

8. A process for preparing a polycarboxylic acid-modified cellulose in fibrous form comprising the following steps:

- (a) impregnating fibrous cellulose with an aqueous solution of a carboxylic acid selected from the group consisting of cyclopentanetetracarboxylic acid, nitrilotriacetic acid, mellitic trianhydride, pyromellitic acid, benzophenone-3,4,3',4'-tetracarboxylic acid, said aqueous solution having had from approximately 0.01 to 1/2 of all carboxylic acid function neutralized with a strong base selected from the group consisting of alkali metal hydroxides, alkali metal carbonates, alkali metal bicarbonates, alkali metal acetates, alkali metal phosphates, and alkali metal borates, and
- (b) heating the impregnated cellulose to produce the cellulose esters and to induce concurrent crosslinking of the cellulose.

9. The process of claim 8 wherein the polycarboxylic acid is cyclopentanetetracarboxylic acid.

10. The process of claim 8 wherein the polycarboxylic acid is nitrilotriacetic acid.

11. The process of claim 8 wherein the polycarboxylic acid is mellitic trianhydride.

12. The process of claim 8 wherein the polycarboxylic acid is pyromellitic acid.

13. The process of claim 8 wherein the polycarboxylic acid is benzophenone-3,4,3',4'-tetracarboxylic acid.

14. The ester of fibrous cellulose and a polycarboxylic acid selected from the group consisting of cyclopentanetetracarboxylic acid, nitrilotriacetic acid, mellitic trianhydride, pyromellitic acid, benzophenone-3,4,3',4'-tetracarboxylic acid, said esters being characterized by a free carboxylic content in the range of 25-80% of the total carboxyl groups in the initial polycarboxylic acid, and which esters are characterized by insolubility in water, aqueous alkali, and organic solvents.

15. The fabric form of a fibrous cellulose acid polycarboxylate selected from the group consisting of cellulose cyclopentanetetracarboxylate, cellulose nitrilotriacetate, cellulose mellitate, cellulose pyromellitate and cellulose benzophenone - 3,4,3',4'-tetracarboxylate which cellulose acid polycarboxylate is characterized by enhanced wrinkle resistance and the ability to develop or alternatively release creases upon being brought into a new physical conformation at a temperature within the range of about from 100° C. to 250° C.

16. The fabric form of fibrous cellulose cyclopentanetetracarboxylate.

17. The fabric form of fibrous cellulose nitrilotriacetate.

18. The fabric form of fibrous cellulose mellitate.

19. The fabric form of fibrous cellulose pyromellitate.

20. The fabric form of fibrous cellulose benzophenone-3,4,3',4'-tetracarboxylate.

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U.S. Cl. X.R.

8-120; 2-243; 260-224