United States Patent Office 3,512,920 Patented May 19, 1970



3,512,920

# WRINKLE RESISTANT FABRIC

Robert Kirby Dunlap, Charlotte, N.C., assignor to Celanese Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Sept. 29, 1967, Ser. No. 671,605
Int. Cl. D06n 9/00
U.S. Cl. 8—115.7 4 Claims

## ABSTRACT OF THE DISCLOSURE

Wrinkle resistant, cellulosic-polyester fabrics having improved soiling resistance and hand are prepared by the application to the fabric of a resin treating bath comprising a textile resin, a solvent, a starch or cellulose derivative and a lower alkylene glycol/polyalkylene glycol terephthalate acid/polyester followed by heat curing the treated fabric.

This application is a continuation in part of co-pending Ser. No. 634,865, filed May 1, 1967, now abandoned.

The present invention relates to textiles and to a process for improving the properties thereof, and more specifically to the preparation of wrinkle resistant, cellulosic-polyester textiles having improved properties.

Recently, there has been an increased usage of cellulose-containing wrinkle resistant textiles, attributable primarily to the characteristics of such textiles to retain a fresh appearance during wearing and to require no ironing after laundering. In essence, wrinkle resistant textiles containing cellulosic fibers, either alone or in combination with other fibers, e.g., polyethylene terephthalate, are prepared by applying a textile resin to the fabric. Ordinarily, the textile resin is applied in the form of a resin treating bath, generally aqueous, comprising the textile resin, a catalyst, and optionally, a wetting agent. After application of the resin bath to the fabric, generally by padding, the fabric is heated briefly to a high temperature, e.g., 140°–200° C., to react the resin with the fabric, generally by cross-linking of hydroxyl groups of the cellulosic fibers. Optionally, the fabric may be dried of excess solvent prior to the higher temperature heating.

While the aforesaid resin treatment has imparted to the fabrics the property of wrinkle resistance, it has at the same time rendered the fabrics less desirable in other respects. To illustrate, the presence of a textile resin in the fabric generally increases the propensity of the fabric to soiling. Also, the presence of the resin tends to impart an undesirable hand to the fabric.

A method for reducing the aforesaid disadvantages is described in British Pat. No. 978,852. Briefly, the method proposed therein comprises the incorporation into the resin bath of a minor amount of a polyethylene softener and a minor amount of a derivative of starch or cellulose, e.g., carboxymethyl cellulose. While this method results in some reduction in the preceding disadvantages, it by no means eliminates them.

Therefore, is is an object of the present invention to provide an improved process for decreasing the soiling tendencies of wrinkle resistant fabrics.

It is a further object of the present invention to provide a process for improving the hand of wrinkle resistant fabrics.

Another object of the present invention is to provide an improved treating bath suitable for imparting desirable properties to fabrics.



It is yet another object of the present invention to provide a wrinkle resistant fabric having improved soiling properties and hand.

Other objects of the present invention, if not specifically set forth herein, will be readily apparent to one skilled in the art from a reading of the following detailed disclosure.

Surprisingly, it has been found that the treatment of cellulosic-polyester fabrics with a textile resin bath containing a minor amount of a low molecular weight, i.e., non-fiber forming, alkylene glycol/polyalkylene glycol terephthalic acid polyester in combination with a minor amount of a starch or cellulose derivative similar to those described in previously cited British Pat. No. 978,852, will yield a wrinkle resistant fabric having hand and heretofore unobtainable soiling resistance.

The application of low molecular weight alkylene glycol/polyalkylene glycol terephthalic acid polyesters to polyester fabrics by way of a resin treating bath has been previously disclosed in the art. However, there has been no suggestion of the application of such polyesters in conjunction with starch or cellulose derivatives to cellulosic-polyester fabrics, or of the advantages attendant therewith. As will be illustrated by later examples, application of the aforesaid combination in the herein described manner results in an apparent synergistic effect in that a degree of soiling resistance heretofore unobtainable with the utilization of any amount of a singular additive is obtained. Further, application of these materials in the described manner does not yield a fabric having an undesirable hand.

Ordinarily, the low molecular weight alkylene glycol/polyalkylene glycol terephthalic acid esters suitable in the present invention may be described as copolymers of terephthalic acid, a lower molecular weight alkylene glycol, and a polyalkylene glycol. Generally the copolymer will be a random copolymer, although a partial block copolymer may result under certain reaction conditions.

The low molecular weight terephthalate polymers may be prepared by esterification of appropriate glycols with free terephthalic acid or by ester interchange with lower molecular weight monoalkyl and dialkyl terephthalates. More specifically, the terephthalates which may be employed in preparing the polymers used in the present invention are those having a total of from about 1 to about 7 carbon atoms, and preferably from about 1 to about 4 carbon atoms, in the alkyl chain, or in the case of the diesters, in each alkyl chain. Examples of suitable esters are monoethyl terephthalate, dimethyl terephthalate, methyl ethyl terephthalate, and diethyl terephthalate.

Suitable alkylene glycols are the lower molecular weight alkylene glycols, e.g., alkylene glycols having a total of from about 1 to about 20 carbon atoms, and preferably from about 2 to about 6 carbon atoms. Illustrative alkylene glycols include ethylene glycol, 1,2-propane diol, 1,3-propane diol, butylene glycol, and mixtures thereof.

Similarly, the polyalkylene glycols employed in the present invention include the glycols having from about 2 to about 10 carbon atoms, and preferably from about 2 to about 4 carbon atoms per repeating unit. Such polyalkylene glycols include polyethylene glycol, polybutylene glycol, and copolymers and mixtures thereof. Desirably, the polyalkylene glycol employed will have an average molecular weight of from about 200 to about 20,000 and even more preferably from about 1,000 to about 5,000. From the standpoint of ease of preparation and commercial availability, those polyalkylene glycols are

preferred which are prepared from alkylene glycols having hydroxyl groups on adjacent carbon atoms.

Commonly, the lower molecular weight polyesters utilized in the present invention are prepared by heating a mixture of the aforesaid reactants in the presence of a catalyst such as antimony trioxide, and distilling off the volatile by-products to obtain the polymeric residue. The reaction should be stopped prior to the formation of a polymer which will be fiber-forming. Desirably, the relative viscosity of the polymer (the viscosity of a 1% solution in o-chloro-phenol at 25° C. divided by the viscosity of the solvent) will be from about 1.1 to about 2.0, and more preferably, will be from about 1.2 to about 1.5.

Preferably, the polyalkylene glycol and alkylene glycol are combined in a molar ratio of from about 1:1 to about 1:10, and even more preferably in the ratio of from about 1:2.5 to about 1:5. While ratios outside of the broader range given above will yield products which are still somewhat suitable in the present invention, it appears that the hydrophobic/hydrophilic balance obtained in products resulting from a combination in the above broader ratio is most desirable for the purposes of the present invention; the hydrophilic properties are imparted by the ether-oxygen atoms in the polyalkylene glycol chains.

In the above reaction, a stoichiometric amount of the dialkyl terephthalate, based on the total mols of alkylene glycol and polyalkylene glycol is employed.

Preferred lower molecular weight terephthalic acid polyesters are those prepared by reacting polyethylene glycol, ethylene glycol and dimethyl terephthalate utilizing the preferred molar ratios, molecular weights and relative viscosities given above.

While the foregoing method is commonly utilized in preparing the present non-fiber forming polyesters, it will be understood by one skilled in the art that other methods may be employed in preparing these materials for use in the present invention. Similarly, other equivalent polyesters containing hydrophilic groups may be employed, e.g., wherein the terephthalic moieties are replaced in whole or in part by adipic groups, and the like.

The resin treating bath utilized in the present invention is prepared by dissolving in a suitable solvent, generally water, from about 50–225 g./l. (based on the solids), and preferably, from about 75–150 g./l. of the desired textile resin; from about 1.5 to about 15 g./l. of the non-fiber forming polyester; at least 2 g./l., preferably up to about 25 g./l. of a starch or cellulose derivative; hereinafter defined more fully, a minor amount of a catalyst; and minor amounts of antioxidants, wetting agents and/or softening agents, if desired. Use of an amount of non-fiber forming polyester in excess of 15 g./l. is possible in the present invention although slight yellowing of the fabric may result.

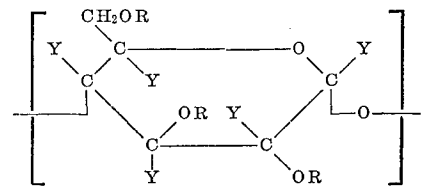
The term "textile resin" as it is used in the present disclosure is intended to encompass the class of materials commonly known in the textile art by that term, namely reagents which are capable of being fixed within the fibers of a fabric in order to impart crease resistance thereto, even though said reagents are not capable of resin formation. The terms "resin treatment" and "resin treating bath" are intended to have a like meaning.

Textile resins found to be preferable in the present invention are the cyclic ethylene urea formaldehyde resins, e.g., dimethylol ethylene urea, dimethylol propylene urea, and dimethylol dihydroxy ethylene urea. Additionally preferred textile resins are the carbamate-type resins, such as, methyl carbamate, ethyl carbamate, and hydroxy ethyl carbamate. Other aminoplast resins formed by reacting compounds such as urea and/or melamine with formaldehyde are also suitable in the present invention. Such additional resins include dimethylol urea, trimethylol urea, acrolein urea formaldehyde resins, trimethylol acetylene diurea, tetramethylol acetylene diurea, dimethylol melamine, tetramethylol melamine, penta-methoxymethyl melamine, and triazone resins, e.g., 1,3-dimethylol methyl-perhydrotriazone and dimethylol-ethyl triazone.

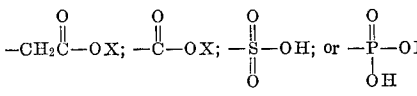


In addition to the above, other textile resins suitable in the practice of the present invention include epoxy compounds such as those taught in U.S. Patent. No. 2,752,269, and the polyglycol acetals such as those taught in U.S. Pat. No. 2,786,081. In addition, mixtures of the foregoing resins may be employed in the present invention.

The starch or cellulose additives employed in the present invention comprise recurring units of the following formula:



wherein, at least one R is an anionic radical, and the remaining R's are selected from the group consisting of hydrogen, lower alkyl radicals of preferably 1–4 carbon atoms, and lower hydroxyalkyl radicals of preferably 1–4 carbon atoms; and Y is selected from the group consisting of hydrogen and lower alkyl radicals of preferably from 1–4 carbon atoms. Preferably the anionic radical is selected from the group consisting of



wherein X is selected from the group consisting of hydrogen and alkali metals, preferably sodium or potassium. The preferred starch or cellulose additives are those in which the anionic radicals comprise from about 4 to about 30 percent of the weight of the additive. Mixtures of the foregoing additives may also be employed instead of a singular member of the group.

Of the foregoing starch and cellulose derivatives, carboxy methyl cellulose or the alkali metal salts thereof, are preferred from the standpoint of superior performance, economy and ready availability.

As previously mentioned, a catalyst is commonly employed in textile treating baths in order to obtain the desired fixation of the resin into the fabric. Catalysts suitable for this purpose are well known in the art. In the case of urea formaldehyde and melamine formaldehyde resins, catalysts commonly employed are hydrochloride or nitric salts of hydroxy alkyl amines such as monoethanol amine hydrochloride or 2-amino-2-methyl-propyl hydrochloride or nitrate. Cyclic ethylene urea formaldehyde resins, acetylene diurea formaldehyde and uron resins are preferably catalyzed by zinc nitrate, zinc fluoroborate, or magnesium chloride. Magnesium chloride and magnesium fluoroborate are suitable catalysts for the carbamate-type resins. Acid fluoride salts are preferably used to catalyze the epoxy resins. Ammonium chloride, magnesium chloride or pyridine hydrochloride are examples of catalysts used with the aldehyde and aldehyde derivative resins. Preferably the catalyst is employed in an amount of from about 0.5 percent to about 10 percent by weight of the resin, and may be used in amounts up to 20 percent by weight of the resin.

As previously mentioned, it may be found desirable to incorporate a minor amount of an antioxidant into the treating bath. Generally, the antioxidant will be quite useful in the prevention of polymer degradation and discoloration during the heat setting treatment. From about 0.02 to about 2.0 percent of the antioxidant based upon the weight of the resin is usually employed, with from about 0.05 to about 0.2 percent being preferred. Suitable antioxidants are, for example, the O-tertiary butyl phenols.

The cellulosic-polyester textiles to which the present invention is directed comprise fibers of natural or re-

generated cellulose or cellulose derivatives, e.g., cotton, linen, jute, flax, viscose rayon, and acetylated cellulose, wherein the cellulosic material contains at least 1.8 free hydroxy groups per unit, in combination with fibers formed from polyesters, such as polyethylene terephthalate, polymethylene terephthalate and poly(1,4 - bismethylenecyclohexane terephthalate).

While the present invention is applicable to the treatment of fabrics prepared from any combination of cellulosic and polyester fibers, the cellulosic and polyester fibers are preferably present in a percent ratio of from about 35:65 to about 65:35.

In imparting wrinkle resistance to cellulosic-polyester fabrics with the resin treating bath previously described, the fabric is first contacted with said bath, preferably by padding. However, said contacting may be by way of other techniques, such as, spraying or rolling. After contacting, the treated fabric is cured by heating or steaming at a temperature of generally from about 275 to about 390° F. for from about 8 seconds to about 20 minutes. Preferably, the curing treatment is at a temperature from about 330 to about 350° F. from about 1.5 to about 15 minutes. Optionally, the excess solvent may be removed from the fabric by evaporation prior to the heat curing step.

Normally, the fabric treating conditions will be sufficient to yield a pickup of 60–75% O.W.F. The percentage pickup is determined by measuring the grams of retained solids on 100 grams of fabric. To illustrate, a fabric treated to a 60% pickup will contain 60 grams of solids on 100 grams of fabric.

According to the accepted theory, the textile resin will react with the hydroxyl groups of the cellulosic fibers during curing. Further, the starch or cellulose derivative is believed to react with the textile resin. Additional additives, including the non-fiber forming polyester additive, are felt to be merely physically present in the fabric. The term "retained solids" is intended to encompass both the reacted and non-reacted additives. Subsequent curing, it is believed, results in interaction between the polyester fibers and the non-fiber forming polyester additive.

From the foregoing, it will be apparent that the improved fabric of the present invention will be a cellulosic-polyester fabric having a retained solids content of 60–75% O.W.F. of the solids of the hereinbefore defined treating bath.

The following examples are presented for the purpose of illustrating the practice of the present invention and for the purpose of showing the improved results obtained thereby, and are not to be construed as limiting the scope of the invention.

## EXAMPLES

In the following examples, a 50/50 polyethylene terephthalate/cotton blend fabric was padded to a 60 percent pickup with an aqueous resin treating bath containing, per liter, 115 grams of dimethylol dihydroxy ethylene urea, 25 grams of $MgCl_2$ catalyst, and the specified additives set forth below. After padding, the fabric was dried, and then oven cured at 345° F. for 10 minutes.

The term "polyester" employed in the following description is intended to define a non-fiber forming polyester having a relative viscosity of 1.25, prepared by the reaction of polyethylene glycol of 1540 molecular weight and ethylene glycol in a molar ratio of 1:2.5 with a stoichiometric amount of dimethyl terephthalate.

Sludge soil ratings were obtained by treating a fabric in the aforesaid manner with a given treating bath; washing the fabric for the specified number of times; agitating the fabric for 15 minutes in an aqueous sludge mixture of oil and clay; rinsing off excess sludge mixture with cold water, drying the fabric; and visually observing the degree of soiling. The soiling of the fabric was rated on a numerical scale of from about 1 to 5( 1 designating severely soiled and 5 designating no soiling. The average sludge soil ratings are set forth in the following table.

TABLE

| Treating bath: | Polyester, q./liter | Carboxymethyl cellulose, q./liter | Sludge soil rating after 1 wash, then soil | Sludge soil rating after 10 washings, then soil |
|---|---|---|---|---|
| a | 0 | 0 | 1 | 1 |
| b | 15 | 0 | 2½ | 2⅜ |
| c | 0 | 20 | 2⅞ | 3⅛ |
| d | 15 | 20 | 3 | 3½ |
| e | 25.6 | 0 | 2⅝ | 2⅞ |
| f | 25.6 | 16 | 3½ | 3½ |
| g | 45 | 0 | 3 | 2⅞ |
| h | 45 | 20 | 3⅞ | 4 |

Consideration of the foregoing results will reveal that the present combination of a non-fiber forming hydrophilic polyester and a cellulose or starch derivative yields results superior to those which could be obtained when using either of the additives alone. Thus, the highest rating attainable after one washing with only one additive was 3 even when 45 grams were employed (Example (g)) while a rating of 3½ was realized with only 41.6 grams of additives (Example (f)); after ten washings the highest rating with but one additive was 3⅛ (Example (c)) but all the examples with two additives (Examples (d), (f), (h)) gave significantly higher ratings.

This latter factor is significant in that the described low molecular weight polyalkylene glycol polyesters, when used in substantial amounts, have a detrimental effect upon dye fastness. To the contrary, the present invention permits utilization of these materials in lower amounts which do not affect dye fastness, but which still produce the desired resistance to soiling. Further, the present combination may be used to treat dyed or undyed fabrics.

Prior utilization of starch and cellulose derivatives similar to those described herein have produced fabrics having an undesirable, harsh hand. However, a highly desirable, soft hand is obtained when fabrics are treated in accordance with the present technique. This improved hand is the result of two factors. First, a lesser amount of starch or cellulose derivative is required. In addition, the low molecular weight polyesters herein described tend to impart a softer hand to the fabrics.

Thus, it will be seen from the foregoing, that the combination of additives taught in the present invention permit the attainment of results heretofore unobtainable, and at the same time, allow for utilization of the additives for their desirable characteristics without experiencing the attendant undesirable properties heretofore associated with such materials.

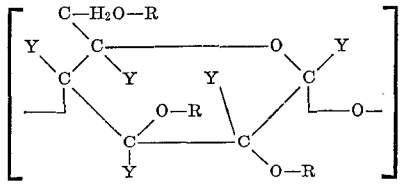
Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In a process for incorporating a textile resin into a cellulosic-polyester fabric wherein the cellulosic component of said fabric contains at least 1.8 free hydroxyl groups per unit and cellulosic and polyester fibers are in said fabric in a percent ratio of from about 35/65 to about 65/35, the improvement comprising the steps of sequentially:

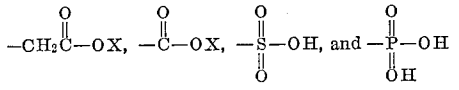
(a) applying to said fabric an aqueous solution consisting essentially of from about 50 to about 220 parts (by weight) of a textile resin capable of imparting crease resistance to said fabric, from about 0.5 to about 20 percent (by weight of said textile resin) of a catalyst to fix the resin into the fabric, from about 2 to about 25 parts (by weight) of a cellulose derivative, and from about 1.5 to about 15 parts (by weight) of a non-fiber forming polyester, wherein:

(1) said cellulose derivative is comprised of recurring units of the formula



wherein:

(a) at least one R is an anionic radical selected from the group consisting of



wherein X is selected from the group consisting of hydrogen, sodium, and potassium, said anionic radical comprising from about 4 to about 30 percent of the weight of the cellulose derivative;

(b) the remaining R's are selected from the group consisting of hydrogen, lower alkyl of 1 to 4 carbon atoms, and lower hydroxyalkyl of 1 to 4 carbon atoms; and

(c) Y is selected from the group consisting of hydrogen and lower alkyl of 1 to 4 carbon atoms;

(2) said non-fiber forming polyester is produced by copolymerizing a mixture of a terephthalate, an alkylene glycol, and a polyalkylene glycol, wherein:

(a) said terephthalate is selected from the group consisting of terephthalic acid and the mono- and dialkyl esters of terephthalic acid wherein said esters have from 1 to about 7 carbon atoms in each alkyl group;

(b) said alkylene glycol has from 2 to about 6 carbon atoms;

(c) said polyalkylene glycol has from 2 to about 10 carbon atoms per repeating unit and an average molecular weight of from about 200 to about 20,000;

(d) from about 1 to about 10 parts (by weight) of said alkylene glycol are present in said mixture for every part of polyalkylene glycol; and

(e) said mixture is copolymerized by heating it in the presence of a catalyst, distilling off the volatile by-produces, and stopping the copolymerization reaction when a polymer with a relative viscosity of from about 1.1 to about 2.0 is produced; and



(b) curing said treated fabric at a temperature of from about 275 to about 390 degrees Fahrenheit for from about 8 seconds to about 20 minutes.

**2.** The process of claim **1**, wherein said cellulose derivative is selected from the group consisting of carboxymethyl cellulose, the sodium salt thereof, and the potassium salt thereof.

**3.** The process of claim **2**, wherein:

(a) said fabric is treated with from about 75 to about 150 parts of said textile resin;

(b) said cellulose derivative is carboxymethyl cellulose;

(c) said terephthalate is a dialkyl ester of terephthalic acid having from 1 to about 4 carbon atoms in each alkyl chain, and a stoichiometric amount of said dialkyl ester (based on the total moles of alkylene glycol and polyalkylene glycol) is present in said mixture;

(d) said polyalkylene glycol has from 2 to about 4 carbon atoms per repeating unit and an average molecular weight of from about 1000 to about 5000;

(e) from about 2.5 to about 5 parts (by weight) of said alkylene glycol are present in said mixture for every part of polyalkylene glycol in said mixture; and

(f) said treated fabric is cured at a temperature of from about 330 to about 350 degrees Fahrenheit for from about 1.5 to about 15 minutes.

**4.** The process of claim **3**, wherein:

(a) said terephthalate is dimethyl terephthalate, said alkylene glycol is ethylene glycol, and said polyalkylene glycol is polyethylene glycol; and

(b) said copolymerization reaction is stopped when a polymer with a relative viscosity of from about 1.2 to about 1.5 is produced.


**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 3,416,952 | 12/1968 | McIntyre | 117—118 |
| 3,416,880 | 12/1968 | Kullman | 8—116.3 |

FOREIGN PATENTS

| | | | |
|---|---|---|---|
| 978,852 | 12/1964 | Great Britain. | |



GEORGE F. LESMES, Primary Examiner

B. BETTIS, Assistant Examiner

U.S. Cl. X.R.

8—116.2; 117—118; 260—9, 15, 16, 17.3, 75

# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,512,920 May 19, 1970

Robert Kjrby Dunlap

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 15, "having hand" should read -- having improved hand --. Column 6, line 67, "220" should read -- 225 --.

Signed and sealed this 2nd day of March 1971.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents