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# CELLULOSIC FABRICS AND METHODS FOR MAKING THE SAME

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This invention relates to methods for treating cellulosic textile materials to improve certain characteristics thereof and to the fabrics thus obtained. This application is a continuation-in-part of my copending applications Serial Number 789,798, filed January 29, 1959, and Serial Number 677,204, filed August 9, 1957, now abandoned, and Serial Number 575,516, filed April 3, 1956, now U.S. Patent 2,985,501.

According to this invention, a cellulosic textile material containing free hydroxy groups is subjected to the combination of steps of first cross linking a sufficient portion of the free hydroxy groups while the cellulosic fibers are in an essentially dry, unswollen condition and the material is in an essentially wrinkle free configuration to impart drip dry flat drying properties to the material and then cross linking a sufficient portion of the free hydroxy groups while the cellulosic fibers are in an essentially wet, swollen condition and the material is in an essentially wrinkle free configuration to impart spin dry flat drying properties to the material.

It is now well known that cellulosic fabrics can be treated with a textile resin to impart certain minimum care characteristics, i.e., flat drying properties, thereto and many such fabrics have been marketed. It is a characteristic of such fabrics, however, that they must normally be "drip dried," i.e., hung to dry while dripping wet in order for them to have a semblance of a pressed appearance when dry and this characteristic has somewhat limited their commercial success. In other words, resin treated fabrics, while possessing improved dry crease recovery, do not possess good spin drying properties. Another disadvantage of the prior art resin treated minimum care fabrics is that they have either a harsh hand or insufficient wrinkle resistance as it has been found that in order to impart a relatively high degree of wrinkle resistance to a cellulosic fabric, it is normally necessary to employ such a large amount of the textile resin that that the hand of the treated fabric is rough. Further, even when these large amounts of the textile resin are applied, the fabric often does not have as high a degree of wrinkle resistance as is desired. Moreover, large amounts of textile resins reacted with cotton fabrics embrittle the fibers, i.e., lower their tear and tensile strength and/or flex abrasion resistance, and render them less serviceable in normal wear.

It is now known to modify cellulosic fibers by reacting them with wet cross linking agents, i.e., cross linking agents which will react with the fibers while the fibers are in a wet, swollen condition, including those which can be employed in the process of this invention. For example, divinyl sulfone, epichlorohydrin and glycerol dichlorohydrin have been found to be as suitable wet cross linking agents to produce fabrics having flat drying properties. See e.g., U.S. 2,985,501.

However, all of the known wet cross linking agents while giving various degrees of spin dry flat drying properties to cellulosic textile fabrics, i.e., wet crease recovery, do not give the dry crease recovery or wrinkle resistance that is obtainable with the resin treated fabrics. They therefore cannot be tumble dried with satisfactory results.



Thus, heretofore, it has not been possible to produce a commercial product having good flat drying properties under all conditions, e.g., spin dry followed by line or tumble drying, as well as good wrinkle resistance.

It has now been found that a resin treated, wet cross linked cellulosic textile material obtained according to the process of this invention has all of the aforesaid desirable properties and, surprisingly, in excess of those that one would expect from these two treatments. For example, as it is known that wet cross linking agents do not give improved dry crease recovery to a significant extent, it would be expected that a wet cross linked, resin treated fabric would have only that dry crease recovery that would have been obtained by a resin treatment alone. However, surprisingly it has been found that when employing the process of this invention, a fabric having dry crease recovery can be obtained that is greater than would be obtained employing the same amount of the textile resin alone and also that lesser amounts of textile resin are required to achieve a degree of dry crease recovery or drip dry flat drying properties the same as or better than that obtained when employing a resin treatment alone. The improved hand and appearance and the improved laundering characteristics of the finished fabric are of considerable importance.

As will be discussed more fully hereinafter, outstandingly desirable results are obtained when the textile material is resin treated first and then treated with the wet cross linking agent. This result is surprising in view of the fact that the wet cross linking agents employed in this invention are often and preferably catalyzed with relatively strong aqueous alkali and it is well known that many resin treated fabrics will lose their enhanced dry crease recovery in the presence of strong alkali. It would therefore be expected that the alkali employed in such a subsequent wet cross linking step would harm the resin treated textile material and reduce the dry crease recovery that would otherwise be obtained. However, quite the opposite effect is obtained, i.e., not only is dry crease recovery not reduced but it is often materially increased. Further, the durability of the resin treatment is materially enhanced when used in conjunction with a wet cross linking step, i.e., some resins lose their good dry crease recovery after repeated washings and the process of this invention prevents this rapid loss.

It is an object of this invention to provide a method for producing resin treated cellulosic fabrics having improved dry crease recovery.

It is another object to provide a method for producing resin treated cellulosic fabrics having good dry crease recovery while employing lesser amounts of textile resin than heretofore required.

Another object is to provide a method for preventing resin treated cellulosic fabrics from losing their dry crease recovery after repeated washings.

Another object is to provide a method for producing resin treated cellulosic fabrics having improved hand and/or spin dry properties.

Another object is to provide a method for producing wet cross linked cellulosic fabrics having improved dry crease recovery.

Another object is to provide a method for producing wet cross linked cellulosic fabrics having improved tumble dry properties.

Another object is to provide a method for producing wet cross linked cellulosic fabrics having both improved spin drying properties and dry crease recovery.

Still another object is to provide cellulosic fabrics having both increased spin drying properties and dry crease recovery, as well as other desirable properties, as compared with fabrics resin treated or wet cross linked alone.

Other objects will be apparent to those skilled in the art to which this invention pertains.

The objects of this invention can be achieved by cross linking the free hydroxy groups of cellulosic fibers of textile materials according to procedures described hereinafter.

The term "flat drying" means a fabric which when washed, tends to dry in an essentially wrinkle free condition. The degree of flat drying properties of a fabric can be determined by A.A.T.C.C. Test Designation T–88–1958. Commercial "wash and wear" fabrics usually have a flat dry rating by this test, after drip drying, of at least 3.5 and the term flat drying when used herein means a fabric having a rating of at least 3.5 by this test. It is also recognized in the art that fabrics having a rating of at least 4.0 by this test are preferred and the process of this invention, in its preferred ramifications, is directed to the production of fabrics having at least a 4.0 rating.

The term "drip dry flat drying properties" when used herein means the ability of a fabric to dry in an essentially flat, i.e., reasonably wrinkle free condition, when hung dripping wet to dry.

The term "spin dry flat drying properties" when used herein means the ability of a fabric to dry in an essentially flat, i.e., reasonably wrinkle free condition, when damp dried in the spin cycle of an automatic washer and then hung to dry on a line.

The term "resin treatment" is one commonly used in the textile art and refers generally to a process whereby a fabric is contacted with a reagent reactive to cellulose, and usually an acid acting catalyst, dried if moisture is present, e.g., from room temperature to 140° C., and then "cured," i.e., reacted with the fabric in its dry state, at a higher temperature, e.g., 140° C. to as high as 200° C. to produce a fabric having improved dry crease recovery. At this temperature, many of these reagents, even by themselves, will resinify in the presence of the appropriate catalyst, thus probably contributing to the use of the term "resin treatment."

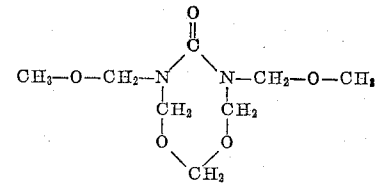
In other words, in the textile art "resin treatment" means a process in which a fabric in its dry state, i.e., the fibers are essentially dry and unswollen, is heated or "cured" at an elevated temperature while impregnated with the selected reagent and a catalyst for the reaction.

Along with the use of the term resin treatment, the textile art has also adopted the practice of using the term "resins" to define the reagents employed in this resin treatment and distinguish them from "sizes" which merely coat the fibers, although the term is a misnomer in that in contradistinction to the generally accepted meaning of the term resin, these textile reagents have relatively low molecular weights, are almost always water soluble and are often liquids. Therefore, in conformity with the generally accepted usage in the textile art, the term "resin" or "textile resin," when used herein, defines those classes of reagents commonly employed in the textile art for the "resin treatment" of fabrics as described above.

The textile resins which can be employed in the process of this invention include the low molecular weight, e.g., usually less than 1,000, water soluble acid or acid salt catalyzed materials which are thermosetting in the presence of cellulosic materials as defined hereinafter. There are many textile resins commercially available. The



largest class of known textile resins are the aminoplast resins formed by reacting compounds such as urea and melamine with formaldehyde. Specific examples of textile resins within this class include urea formaldehyde textile resins such as the resin commercially available from Rohm & Haas under the trade name of "Rhonite 610"; methyl ethers of urea formaldehydes such as the resin sold by Rohm & Haas under the trade name of "R–2 Resin"; acrolein urea formaldehyde resins; cyclic ethylene urea formaldehyde resins such as the resin sold by E. I. du Pont under the trade name of "Zeset" and the textile resin sold by Rohm & Haas under the name of "R–1 Resin"; trimethylol acetylene diurea; tetramethylol acetylene diurea; melamine formaldehyde textile resins, such as the resins sold by Monsanto under the trade names of "Resloom H.P." and "Resloom L.C.," including the methylated melamine formaldehyde textile resins such as the resin sold by American Cyanamid under the trade name of "M–3 Resin"; or the textile resin sold by Monsanto under the trade name of "M–75 Resin"; copolymers such as a copolymer of melamine formaldehyde and ethylene urea formaldehyde; and the textile resins known to the trade as urons, one of which has the formula:



In addition to textile resins of the above type, one can suitably employ polyepoxy resins which come within the general group set forth above. Examples of suitable resins of this class include the triglycidyl ether of glycerol, and the diglycidyl ether of glycerol, sold by Shell Chemical Company under the name of "Eponite 100." Still another class of textile resins which can suitably be employed are the triazone resins. Still another resin which can be employed is the tris-(1-azirindinyl) phosphine oxide which is prepared by reacting three moles of ethyleneimine with one mole of $POCl_3$ and which is known to the trade as "APO Resin" or "Imine I.P. Resin." One need not employ a single textile resin but can employ mixtures of the above type resins or copolymers thereof. Likewise, it is not necessary that the resins be entirely free from water-insoluble components since it has been found that dispersed particles of water-insoluble materials in the resin solution are not deleterious even though any portion of the resin that is water-insoluble probably does not contribute to the beneficial results obtainable according to this invention. Some of the commercially available resins mentioned above contain small percentages of water-insoluble polymeric materials and while an aqueous mixture of such resins can be filtered if desired, equally satisfactory results are generally obtained by employing the unfiltered material.

As stated above, some textile resins can be catalyzed by an "acid acting" catalyst, i.e., acidic in character and others by an alkaline catalyst although most of the textile resins employed today are catalyzed by acid acting catalysts.

Suitable acid acting catalysts for resins of the above types are well known in the art. Urea formaldehyde and melamine formaldehyde resins are best catalyzed by hydrochloric or nitrate salts of hydroxyalkyl amines such as monethanol amine hydrochloride or 2-amino-2-methyl-propanol nitrate. Cyclic ethylene urea formaldehyde resins, acetylene diurea formaldehyde and uron resins are preferably catalyzed by zinc nitrate or by magnesium chloride. The epoxy resins are preferably catalyzed by

acid fluoride salts, such as the catalyst compositions available from Shell Development Company under the trade names of "Curing Agent 48" and "Curing Agent 20."

The amounts of catalyst desirable to be employed are well known in the art. Generally any amount of catalyst up to about 20% by weight of the resin mixture will give satisfactory results with the preferred range being from about 0.5% to about 10% of the resin solids employed.

The term "wet cross linking agent" is used in this specification to distinguish compounds employed to cross link the cellulose under aqueous conditions from the "textile resins" described hereinbefore. They are characterized by the ability to react, or to be converted in situ to compounds which will react, with the free hydroxy groups of the cellulosic fibers of the fabric being treated according to the process of this invention, while the fibers are in a wet, swollen condition. Textile resins, on the other hand, do not properly react with the cellulosic fibers while they are in a wet, swollen condition, probably because the textile resin has a greater inclination to react with water at the elevated temperature employed in resin treatment, than with the free hydroxy groups of the cellulosic fiber.

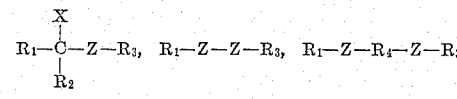
There are numerous reagents known in the art which can be characterized as "wet cross linking agents." They are generally characterized by being bifunctional, i.e., having at least two groups which will react, or are converted in situ to groups which will react, with the free hydroxy groups of the cellulosic fibers.

A catalyst is ordinarily required to produce the desired wet cross linking reaction. These can be either alkaline catalysts or acidic catalysts, depending upon the character of the wet cross linking agent. The dihalohydrins, i.e., those having either a pair of halohydroxy-ethylene groups or an alpha halogen atom on each side of the hydroxy group, the diepoxides, the epoxyhalohydrins and the α-haloepoxides are examples of the alkaline catalyzed wet cross linking agents. Examples of acid catalyzed wet cross linking agents are formaldehyde, glyoxal, α-hydroxy adipaldehyde, phenylglyoxal, α-keto-acetaldehyde and diacetyl.

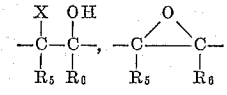
The preferred wet cross linking agents and those which ordinarily give best results are the alkaline catalyzed compounds. Preferred among this group are those containing from 3 to 15 carbon atoms, inclusive, e.g., those which produce cellulosic cross linkages of from 3 to 6 carbon atoms in length. The bridging chain formed by the cross linking agent can contain, depending on the choice of wet cross linking agent, elements other than carbon and, in fact, in all instances the cross linkage will contain oxygen as the cross linkage as a result of etherification of hydroxy groups of the cellulose. In addition to oxygen and carbon, the linkage may also contain nitrogen, phosphorus, sulfur, silicon, or other polyvalent elements known to form stable organic linkages. Likewise, the cross linkage may contain substituent groups or side chains. Examples of substituent groups which may be present include keto groups, hydroxy groups, halogen atoms, and methyl groups, although the presence of such substituent groups ordinarily is not preferred and the number and size of these substituent groups should be such that the molecular weight of the divalent radical connecting the cellulose-reactive groups of the cross linking agent is not in excess of about 260. It should also be emphasized that the preferred alkaline catalyzed wet cross linking agents, while spoken of as having two or more reactive groups, need not possess groups, as it is initially employed in the process of this invention, which are capable of reacting directly with hydroxy groups. The reactive groups can suitably be transformed in situ as a result of the action of the basic catalyst to give connective groups capable of reacting with cellulose, as in the case of the halohydrins.

Alkaline catalyzed, wet cross linking agents within the above general classification can be divided into three general classes. A first class comprises the polyepoxy cross linking agents including diepoxybutane; the diglycidyl ether of ethylene glycol, propylene glycol, or diethylene glycol; the triglycidyl ether of glycerol; and the diglycidyl ether of bisphenol A; and compounds having an α-halohydrin group, e.g., chlorohydrin or bromohydrin, in place of one or more of the epoxy groups and compounds having a halogen atom, e.g., chlorine or bromine, on a carbon atom adjacent either an epoxy group or a halohydrin group. Examples of such latter compounds are epichlorohydrin, 1,3-dichloropropanol-2, 1,3-dibromopropanol-2, and bis-(1-chloro-2-hydroxy-n-propoxy)ethane. A second class of preferred alkaline catalyzed wet cross linking agents include the sulfone activated divinyl compounds. Examples of this class of compounds are divinyl sulfone, bis-(vinyl sulfonyl) methane, and 1,4-bis-(vinyl sulfonyl)butane. A third class of alkaline catalyzed wet cross linking agents are the carbonyl activated divinyl compounds, e.g., divinyl ketone, and octa-1,7-diene-3,6-dione. A fourth class are the carbonyl and sulfonyl activated sulfuric acid and phosphoric acid esters and their alkali metal salts, e.g., disodium bissulfatoethyl sulfone.

The above-described first class of compounds are, generally speaking, the preferred class of alkaline catalyzed wet cross linking agents. A considerable number of known compounds fall within this class. These compounds can be represented by one of the formulae:



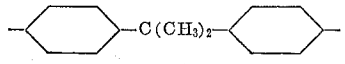
wherein X represents halogen, preferably chlorine or bromine, $R_1$, $R_2$, and $R_3$ represent, in each instance, hydrogen or a monovalent, nonfunctional radical, $R_4$ represents a divalent connecting radical and Z, in each instance, represents a divalent radical represented by one of the formulae:



wherein $R_5$ and $R_6$, in each instance, represent hydrogen or a monovalent nonfunctional radical, and X represents halogen, preferably chlorine or bromine.

$R_1$, $R_2$, $R_5$, and $R_6$ in the above formulae, in each instance, preferably represent hydrogen, as such compounds are the most readily prepared, but they can in one or more instances represent lower alkyl groups, e.g., methyl or ethyl, hydroxyalkyl groups, e.g., hydroxymethyl or hydroxyethyl, monocyclic aryl groups, e.g., phenyl or tolyl, cycloalkyl groups, e.g., cyclohexyl, haloalkyl groups, e.g., chloromethyl or chloroethyl, or $R_1$ and $R_3$ can together represent a divalent connecting radical, e.g., methylene, ethylene or other lower alkylene radicals. $R_4$ can represent any divalent connecting radical group but in most instances will represent either an alkylene group, e.g., methylene, ethylene, or propylene, a hydroxyalkylene group, e.g., hydroxypropylene or a group of the formula —R—Y—R′—Y—R″, wherein Y represents oxygen or sulfur, R and R″ represent lower alkylene groups, e.g., methylene or ethylene, and R′ represents any divalent connecting radical, as illustrated by a lower alkylene group, a lower hydroxyalkylene group, e.g., 2-hydroxypropylene, a monocyclic aryl radical, e.g., phenyl or tolyl, a radical of the formula $—C_2H_5(O—C_2H_5)_n—$ wherein $n$ is an integer of from 1 to about 20, or a radical of the formula $—(R'''—O—CH_2—CH—CH_2—O)_n—R'''—$, wherein $n$

represents an integer of from 1 to about 5 and R''' represents a divalent hydrocarbon radical as illustrated by



Compounds of the latter type results when epichlorohydrin is reacted with less than an equal molar quantity of a dihydric alcohol or phenol. When a wet cross linking compound corresponding to one of the formulae in the preceding paragraph contains two Z groups, the group may be the same or different. Examples of suitable cross linking compounds are: 1,3-dichloropropanol-2,2,3-dichloropropanol, 2,3-dibromopropanol, m-di(β,γ-epoxypropoxy)benzene, 1,3 - di(β-hydroxy-γ-chloropropoxy)-propanol - 2, 1,2-di(β-hydroxy-γ-chloropropoxy)ethane, 1,2-di(β,γ-epoxypropoxy)-ethane, 1,2;3,4-diepoxybutane, 1,2;5,6-diepoxyhexane, 1,5-dihydroxy-2,4-dichloro-cyclohexane and 2,6-dichloro-3,4,5-trihydroxy-methyl-heptane. The preferred cross linking compounds are epichlorohydrin, 1,3-dichloropropanol-2, 2,3-dichloropropanol, and mixtures theroef.

The type and amount of catalyst to be employed depends upon whether an acid or alkaline catalyzed wet cross linking agent is employed and upon the reactivity of the selected wet cross linking agents. These catalysts and the amounts to be employed are known in the art.

Suitable alkaline catalysts for the alkaline catalyzed wet cross linking agents include the alkali metal hydroxides, e.g., sodium hydroxide and potassium hydroxide, the quaternary ammonium hydroxides, e.g., trimethylphenylammonium hydroxide, tetrabenzylammonium hydroxide, and tetramethylammonium hydroxide, and alkali metal salts which, in the presence of water, produce a strongly alkaline solution, e.g., the alkali metal sulfides. When the salts are employed, they should be employed in an amount which will impart an alkalinity to the solution in the same range as that obtained when an alkali metal hydroxide or quaternary ammonium hydroxide is employed. Generally speaking, a molar equivalent or more of the salt, based on the amount of an alkali metal hydroxide which would give satisfactory results, should be employed.

The acid catalyzed wet cross linking agents are ordinarily catalyzed with strong mineral acids, including hydrochloric, sulfuric and phosphoric acids, although the stronger organic acids are also operable. The amounts of these acids to be employed generally correspond to the amounts employed when an alkali metal hydroxide is employed in conjunction with an alkaline catalyzed wet cross linking agent.

The term "cellulosic textile material" when used herein means any textile material comprising fibers having the free hydroxy groups characteristic of cellulose, e.g., cotton, unmodified cellulose and cellulose modified by etherification or esterification of a portion of the hydroxy groups. Textile materials within this definition include those comprising natural cellulose fibers, e.g., cotton, linen, jute, flax, regenerated cellulose fibers, e.g., viscose rayon fabrics, and cellulosic fibers some of the hydroxy groups of which have been replaced by ester or ether groups, so long as some free hydroxy groups are present so as to obtain the desired cross linkage. Normally, cellulosic fibers which contain as few as 1.8 free hydroxy groups per anhydroglucose unit will result in sufficient cross linkage for satisfactory results. Thus, cellulosic textile materials the fibers of which contain a limited number of acetyl groups, such as cellulose acetate fabrics of a relatively low acetyl content, or textile materials the fibers of which contain a limited number of methyl ether groups, such as partially methylated cellulose, can be processed according to this invention. However, textile materials which do not comprise cellulosic fibers having free hydroxy groups are not normally suitable for use in the process of this invention and are not within the term "cellulosic textile material" as used herein.



Although this invention is directed primarily and preferably to cellulosic textile fabrics, both knitted and woven, the advantages of this invention can also be achieved by treating the cellulosic yarns or threads employed to produce these fabrics. Ordinarily, this will be cotton thread or yarn. The thus treated thread or yarn, when woven into fabric, will produce a fabric having better flat drying properties than identical fabric woven from untreated yarn or thread.

Satisfactory results, according to this invention, can be achieved employing cellulosic fabrics containing both cellulosic and noncellulosic fibers, especially if the noncellulosic fibers have some minimum care characteristics of their own. For example, the minimum care characteristics of fabrics formed from a mixture of glycol-terephthalate fibers and cotton fibers can be improved by the process of this invention even if the percentage of cotton fibers is small, e.g., 10% to 40%. Satisfactory results can also be obtained with fabrics formed from a mixture of nylon fibers and cellulosic fibers or a mixture of cellulosic fibers and polyacrylic fibers, e.g., those sold under the trademark Orlon. As would be expected, if the noncellulosic fibers have little or no minimum care characteristics, the improved characteristics of the fabric treated according to the process of this invention will be more readily apparent if the cellulosic, e.g., cotton, content of the fabric is substantial, e.g., about 40% or more by weight.

Because woven fabrics consisting essentially of cotton, e.g., 90–100% cotton, ordinarily have the poorest flat drying and dry crease recovery among the common cellulosic textile fabrics, the advantages of the process of this invention is most readily apparent with these fabrics and it is to these fabrics that this invention is preferably directed.

The resin fixation is performed while the cellulosic fibers are in an essentially dry, i.e., unswollen configuration. It appears that the resin fixation tends to fix or stabilize the fibers so that the resultant fabric tends to maintain itself in the configuration it possessed during the resin treatment, thus giving it improved dry crease recovery, i.e., wrinkle resistance. However, it is well recognized that when the fabric is subsequently moistened, the fibers become mobile and, if wrinkled or creased while in this moist state, they will dry with some of the creases or wrinkles retained. It is for this reason that it is recommended that the so-called "wash and wear" resin treated fabrics of the prior art be drip dried, i.e., dried while the fabric is substantially wrinkle free. Thus, the housewife, in washing this fabric in an automatic washer, must remove the fabric without spin drying. The inconvenience of this procedure has tended to limit the commercial acceptance of wash and wear resin treated fabrics, although these fabrics, when properly dried, do reduce ironing time.

The wet cross linking process of the prior art, while improving dimensional stability and shrinkage resistance, generally have not produced a commercially acceptable spin dryable product, i.e., one having suitable wet configuration memory. In my copending application Serial Number 575,716, there is described a technique for achieving the desired spin drying properties, employing classes of reagents some of which are known to the art. The products produced by this improved process produce an excellent spin drying product, an important and desired property. Thus, the housewife can spin dry and then line dry a garment made of the thus treated fabric, thereby eliminating the necessity of interrupting the normal cycle of an automatic washer and hanging dripping wet garments to dry.

Such improved products do not, however, possess dry crease recovery to the desired degree. Retailers, for example, desire a product which will hang substantially wrinkle-free when removed from shipping boxes or storage drawers. It appears that wet cross linked fabrics, while tending to retain a desired configuration while in a moist or wet condition, do not have this characteristic to an appreciable degree when the cellulosic fibers are in

a dry, unswollen condition. Thus, tumble drying tends to impair the appearance of a spin dried garment or fabric which has been wet cross linked.

The process of this invention produces a fabric having both good spin drying properties and good dry crease recovery. Not only is the combined advantages of resin treatment and of wet cross linking observed, but additional surprising advantages are obtained that could not be predicted from the results obtained from either of these treatments alone. Some of these advantages are described hereinbefore.

In carrying out the process of this invention, the cellulosic textile material is "dry" treated, cross linked, e.g., by a conventional resin treatment, and then "wet" treated, i.e., wet cross linked, while the material is in a wrinkle free configuration. This can be accomplished according to techniques known in the art.

The resin treatment involves the well known steps of applying a textile resin and catalyst, if necessary, usually as an aqueous solution thereof, ordinarily squeezing the material through rollers to achieve the desired solution take-up, drying and then curing the material at an elevated temperature to achieve the desired reaction of the textile resin with the cellulosic fibers, with the latter step being performed while the material is maintained in a wrinkle free configuration, i.e., ordinarily an essentially flat condition. Flat, in this sense, includes rolling up smooth into a roll.

Conventional equipment is suitable for this operation. For example, the textile resin can be applied with the usual padding equipment, the material then passed through squeeze rolls, and then dried, e.g., at room temperature or while the material passes through a hot air oven and, if fabric is being treated, preferably while in a tenter frame to maintain the desired dimensions. The usual curing equipment can be employed for the curing step, so long as the material is maintained in a wrinkle free condition. If a flat fabric is desired, the usual stationary or rotating tenter apparatus can be employed. However, if a novelty fabric is desired, e.g., an embossed or a pleated fabric, drying and curing of the fabric should be performed under conditions approximating this condition, but nevertheless free from extraneous wrinkles. The material can then, if desired or necessary, be scoured to remove any excess reactants or residual catalyst.

Further details of the general methods of textile resin treatment are set forth in publications such as, for example, Marsh's "An Introduction to Textile Finishing," Wiley Publishers (1951), and Ward's "Chemistry and Chemical Technology of Cotton," Interscience Publishers (1955).

The amount of textile resin which is applied to the cellulosic textile material according to this invention can be varied within wide limits, e.g., between about 2% and about 10% resin solids, calculated on the weight of the dry fabric. The most advantageous amount is dependent upon a number of variables. For example, the amount of resin which can most advantageously be applied depends somewhat upon the degree of cross linking of the cellulosic fibers effected during the wet cross linking operation, and the particular type of resin being employed. It is a general rule that the greater the degree of wet cross linkage, the smaller the amount of textile resin which need be employed, and one can obtain good results by employing only a relatively small amount of resin on a highly wet cross linked cellulosic fabric which are comparable to those obtained by employing a larger amount of textile resin on a cellulosic material whose fibers have been wet cross linked to only a slight degree. In most instances, it is desirable to employ only a small amount of the resin material and between about 2% to about 7% resin solids, calculated on the weight of the dry material, generally gives the desired results. Due to the synergistic action of the wet cross linking agents and the textile resins employed in the process of this invention, the effectiveness of the textile resin is greatly increased as compared to the prior art procedures of resin applications to cellulosic fabrics and satisfactory minimum care characteristics, e.g., flat drying properties and wrinkle resistance, can sometimes be obtained by the procedure of this invention employing as little as 0.5% resin solids, based on the weight of the material. At the other extreme, as much as 10% to 15% resin solids, by weight of the material, can be employed, but the use of such large amounts of resin is generally not necessary and is not economically desirable.

In a standard resin treatment, following the resin application, the material is dried and then cured at any suitable curing temperature. Usually the material is dried at a temperature lower than the curing temperature, e.g., from about room temperature to 140° C. The most advantageous curing temperature depends upon the particular resin and catalyst employed, but as a general rule a curing temperature in the range of from about 100° C. to 200° C. with a temperature between about 140° C. and about 180° C. being more commonly employed. The curing temperature can be maintained for from 10 seconds to about 30 minutes or more with the preferred range being from 30 seconds to 5 minutes, depending on the temperature, amount and type of catalyst, and the particular textile resin employed.

The wet cross linking step of the general type employed with the process of this invention has also been employed in the textile trade, and the necessary techniques will be apparent those skilled in the art. For example, the impregnating of the textile material with the selected reagents can be accomplished in a manner similar to those employed in resin treatment. The material can be moistened by dipping in water, preferably containing the necessary catalyst, squeezed through rollers to achieve the desired take-up, and then contacted with the wet cross linking reagent. If the alkaline or acidic catalyst is applied first, the usual procedure involves thereafter padding on the wet cross linking agent or passing the material through a bath of the reagent per se or a concentrated solution thereof in water or organic solvent. Excessive tension in this wet cross linking step is not ordinarily desired because of the tendency of tension to squeeze the moisture and reagents from the fibers and fabric, thus tending to interfere with the proper take-up of reactants, although some tension appears to have a favorable effect upon the tensile strength of the resulting material. Tension can be applied fillwise by means of a tenter frame, which can also be adjusted to supply warpwise tension. If the fabric is then immediately tightly wound on a roll, some of this tension and stretching of the fabric can be retained during the cross linking reaction.

The amount of the wet cross linking agent which should be reacted with the cellulosic fabric can vary within relatively wide limits. Between about 3% and about 30% calculated on the weight of the dry material, of wet cross linking agent is ordinarily employed and more desirably especially when epichlorohydrin is used as the wet cross linking agent, between about 8% and about 12%. The wet cross linking agent or mixture of wet cross linking agents is preferably applied in relatively pure form, i.e., without the use of a solvent or diluent, but due to the small degree of cross linkage necessary in accordance with this invention, the wet cross linking agent can be employed in an organic solvent or in most instances even in the form of an aqueous solution.

The wet cross linking agent can be applied by any suitable procedure and where a solution of the cross linking reagent is employed, the solution is preferably applied by padding followed by passing the material through squeeze rolls to remove excess solution. It is generally preferable to apply the cross linking reagent per se to the material by a distributing technique so that a limited quantity of the reagent can be applied, thus avoiding loss of excess reagent. Distribution of the pure reagent

upon the material can be achieved by the use of sprays, Scotch rolls or other apparatus of this type which permits one to evenly distribute a relatively small quantity of a reagent upon a textile material.

The catalyst for the wet cross linking reaction is ordinarily employed in the form of an aqueous solution. The catalyst solution can be applied to the material either before or after the wet cross linking agent is applied. If precautions are taken to prevent excessive side reactions, e.g., reaction of the wet cross linking agent with itself or with water, the catalyst and the cross linking agent can also be applied to the material simultaneously. Generally, it is preferred that an aqueous solution of the catalyst be applied to the dry material prior to the application of the cross linking agent, e.g., by means of conventional padding equipment which permits the material to be immersed in an aqueous solution of the catalyst and thereafter squeezed or extracted to remove excess solution. Alternatively, the catalyst solution can be applied by means of sprays, Scotch rolls, or in instances where the wet cross linking agent is applied first, the material can simply be immersed in an excess of the basic solution of a proper concentration and the reaction allowed to take place during the time the material is so immersed.

The amount of alkaline catalyst to be employed should be between about 0.1% to about 20%, calculated on the weight of the dry material, i.e., it can be varied over a wide range. An amount less than about 13% and ordinarily less than 10% is employed. As the alkaline catalyst is ordinarily applied as an aqueous solution to the dry material, these amounts are conveniently expressed in terms of the concentration of the aqueous catalyst solution. Thus an aqueous catalyst solution of the catalyst of between about 0.5% and about 16% concentration will ordinarily provide the desired amount of catalyst, the exact concentration being governed in part by the catalyst, the amount of the solution applied to the material, and the selected wet cross linking agent.

If the wet cross linking agent consumes two chemical equivalents of alkaline catalyst, as in the case of 1,3-dichloropropanol-2, then about 1.5 to 2.5 chemical equivalents of catalyst, calculated in the amount of cross linking agent applied to the material, can suitably be employed. If a cross linking agent is employed which consumes only a chemical equivalent of alkaline catalyst, as in the case of epichlorohydrin, then about 0.5 to 1.5 chemical equivalents of catalyst, calculated in the amount of cross linking agent applied to the material can be employed. With wet cross linking agents which do not consume the catalyst, e.g., the diepoxides and divinyl sulfone, correspondingly lesser amounts can be employed. The pH of the treated material can be controlled by adjusting the ratio of wet cross linking agent to alkaline catalyst. A nonalkaline product can be achieved by employing a wet cross linking agent which consumes the catalyst and less than a chemical equivalent of the catalyst. For example, excellent results are obtained using 8% to 12% epichlorohydrin as the wet cross linking agent, calculated on the weight of the dry material, and between about 2.5% and 3.5% of sodium hydroxide, calculated on the weight of the dry material, as a 3.5% to 4.5% aqueous solution with an 80% to 90% uptake thereof. A stoichiometrically equivalent amount of another alkali metal hydroxide gives comparable results.

The amount of water in and on the material during the cross linking reaction while not always critical, can affect the result obtained, depending on the cross linking agent employed. For example, if a high degree of cross linkage is desired, the total amount of water present in and on the material during the cross linking reaction is of greater importance and should be limited so that the total amount of water present in the material is equal to not more than 130% and preferably not more than about 100%, of the weight of the dry material, especially when the dihalohydrins and their equivalents are employed. Ordinarily, more desirable results are obtained when not more than about 90%, e.g., between about 60% and about 90%, of the weight of the dry material of water is present. These preferred conditions are conveniently achieved by dipping the material in water containing the selected catalyst, squeezing the material to achieve the desired degree of moisture uptake and then padding or spraying on the wet cross linking agent per se in the desired amount. If the wet cross linking agent or catalyst is volatile, it is preferred to maintain the treated material in a closed container until the cross linking reaction has gone to completion to prevent excess loss of the reagent.

As previously mentioned, the wet cross linking reaction is conducted while the cellulosic fibers are in a wet, swollen condition and more specifically the reaction should be conducted with the fibers sufficiently wet so as to have an average diameter at least about 25% greater than the average diameter of the dry fibers. Usually as little as 15%, calculated on the weight of the dry material, of water is required to achieve a wet, swollen condition for the cellulosic fibers, although at least 30% is preferred. It is not normally necessary, however, to measure the degree of swelling of the fibers for the reason that only minimal amounts of water is necessary to achieve measurable and adequate swelling. Quite obviously, because the fibers must be in a wet, swollen condition, the reaction should be conducted at a temperature and under conditions which will not prematurely dry out the fibers. Normally, the reaction should be conducted at a temperature considerably below 100° C., although temperatures as high as 90° C. give satisfactory results. The preferred temperature for conducting the wet cross linking reaction is usually from about room temperature to about 60° C. More reactive wet cross linking agents do not ordinarily require external heat for the reaction to process at a satisfactory rate, especially when at least 3% alkaline catalyst is employed.

The time required for completion of the wet cross linking reaction depends upon the temperature, the type and amount of catalyst employed, and the particular wet cross linking agent used. Under conditions favoring a fast reaction and with highly reactive cross linking agents, sufficient cross linkage can be obtained in only a minute or less, but in most instances at least about 5 minutes to 7 hours should be allowed for the cross linking reaction to occur to a satisfactory extent. If only sufficient cross linking agent or catalyst is applied to the material to give the desired degree of cross linkage, there is no need to control reaction time other than to insure that adequate time is allowed, e.g., a period of 24 or even 48 hours can be provided. However, if the cross linking reaction is conducted with the material in contact with an excess of cross linking agent and catalyst, precautions should be exercised to avoid excessive cross linkage of the material. For this reason a procedure which involves applying limited quantities of the wet cross linking reagent or catalyst to the material is preferred.

As in the resin treatment, the wet cross linking is conducted in an essentially wrinkle free configuration. Usually this is an essentially flat condition unless a novelty finish is desired. Thus, the wrinkle free configuration is ordinarily the same in both the resin and wet cross linkage steps. The term "flat" when used herein means smooth and fabric rolled up in a smooth roll is within the term flat as used herein.

As stated hereinbefore, outstandingly superior results are obtained when the resin treatment is conducted before the wet cross linking step. It is known that a resin treated fabric will lose some of its dry crease recovery upon treatment with alkali and the results of extensive experiments have been published correlating this loss with a comitant gain in tensile strength. It has also been found that such treatment increases chlorine retention

of resins tending to be sensitive to chlorine bleaches, an undesirable result. However, when a resin treated material is wet cross linked with an alkaline catalyzed wet cross linking agent, not only is the dry crease recovery of the resulting material not impaired, it is often substantially improved, even when the alkaline catalyst is applied before the cross linking agent. Equally surprising, the chlorine retentivity of the material is decreased instead of increased. Furthermore, the staining tendency of the fabric, e.g., when washed with other material which tend to lose their dyes, is less than material which is wet cross linked first.

These and other surprising features of a resin first, wet cross linked material renders the process comprising a resin treatment followed by an alkaline catalyzed wet cross link treatment distinctive from and preferred over the reverse treatment.

In the example given hereinbelow, the treated fabrics were tested according to accepted standard methods. Tear strength was determined by Test A.S.T.M.D. Designation D1424–59. Dry Crease Recovery Angle was determined by Test A.S.T.M.D. Designation D1295–53T. See "A.S.T.M. Standards for Committee D–13 on Textiles" (1959). Flat dry ratings were by Test A.A.T.C.C. Designation T–88–1958.

The following examples are illustrative of the processes and products of this invention, but are not to be construed as limiting.

## EXAMPLE I

A sample of type 180 sheeting is padded with a 5% aqueous solution of dimethylol methyl triazone resin containing 1% zinc nitrate, dried and then cured for 10 minutes at 150° C. The fabric is then immersed in a freshly prepared aqueous solution containing 10% divinyl sulfone and 1% sodium hydroxide, and the cloth is thereafter squeezed between rubber rolls to remove excess solution such that the pick up is about 80%. The wet fabric is rolled up into a neat roll, wrapped in polyethylene plastic and aged for 30 minutes. It is then neutralized with dilute acetic acid and thoroughly washed and dried. The thus treated fabric has excellent minimum care characteristics.

Similarly, the above fabric can be reacted with any of the other textile resins described herein and then passed into the alkaline divinyl sulfone solution. Alternatively, in the above-described reaction, the desired amount of alkali-metal hydroxide solution, e.g., of a concentration of from about 0.5 to about 5% and in an amount of from about 30 to about 130% of the weight of the dry fabric, can be applied to the fabric and the fabric then passed into an aqueous solution of divinyl sulfone, e.g., of a concentration of from about 2 to about 20%.

## EXAMPLE II

A desized and bleached piece of 80 square cotton fabric is treated with an 8% aqueous solution of cyclic ethylene urea formaldehyde resin containing 1% zinc nitrate catalyst, dried and then cured for two minutes at 170° C. The fabric is then immersed in an aqueous solution containing 6% divinyl sulfone and 2% sodium hydroxide, squeezed out between rubber rolls to a pickup of 60%, batched into a roll, wrapped with polyethylene plastic and allowed to stand 30 minutes. The fabric is then washed thoroughly and dried. The thus treated fabric has excellent dry crease recovery.

## EXAMPLE III

Example II is repeated except that the fabric is treated with a 10% aqueous solution of dimethyl ether of dimethylol ethyl triazone resin containing 2% monoethanol amine hydrochloride instead of cyclic ethylene urea resin of Example II. The results are substantially the same as in Example II.



## EXAMPLE IV

A fabric is treated with dimethylol methyl triazone resin in the manner described in Example III and the cured fabric is immersed in an aqueous solution containing 14% 1,3-dichloropropanol-2 maintained at 75° C. The fabric is then squeezed between rubber rolls to a pickup of 60% and is subsequently immersed into an aqueous solution containing 10% sodium hydroxide and 15% sodium sulfate. This alkaline solution is maintained at 90° C. and the resin treated fabric is maintained under the surface of the alkaline liquid for a period of 30 seconds. It is then squeezed out by the rubber rolls to remove excess liquid and is washed until free of alkali. The thus treated fabric has excellent wrinkle resistance.

## EXAMPLE V

An 80 square cotton fabric is immersed in an aqueous solution containing 7% Aerotex 23 modified melamine type textile resin (50% solids), 1% Surfonic N–95 polyethylene glycol nonylphenol wetting agent, 0.85% zinc nitrate catalyst, and 6% Moropol 700 emulsified polyethylene softening agent and then squeezed through rubber rollers at 60 lbs. pressure to provide about an 85% solution uptake, calculated on the dry fabric. The fabric is then dried and cured while smooth in an oven at 140° C., for one minute.

A portion of the above thus-treated fabric is then immersed in a 5% aqueous solution of sodium hydroxide and squeezed to provide about an 80% uptake based on the dry fabric. The wet cloth is then contacted with epichlorohydrin so as to provide about a 10% uptake of epichlorohydrin, rolled up in a smooth roll and maintained at 55° C. overnight in a sealed polyethylene bag.

The two portions of the fabric are then tested along with an untreated control for flat drying properties. The results of such tests are shown below.

*Table I*

| Sample | Flat Dry Rating | |
|---|---|---|
| | Spin Plus Line Drying | Spin Plus Tumble Drying |
| 1. Control (untreated) | 1.2 | 1.0 |
| 2. 3.5% resin solids | 3.4 | 3.8 |
| 3. 3.5% resin solids plus wet cross linking | 4.8 | 4.6 |

Increasing the resin solids to 4% and heating for one minute at 140° C. does not significantly alter the results. Note that both spin plus line dry and spin plus tumble dry flat dry ratings are improved to a commercially acceptable level.

## EXAMPLE VI

Portions of an 80 square cotton fabric which has been resin treated with about 9% (50% resin solids) Zeset MC dimethylcyclicethyleneurea textile resin catalyzed with zinc nitrate is treated with aqueous solutions of potassium hydroxide of varying concentration to provide about an 80% pickup, rolled up smooth in a plastic bag and maintained at 55° C. overnight and then washed thoroughly and dried.

Other portions of the same cotton fabric is subject to the same treatment, but about 10–12% epichlorohydrin, calculated on the weight of the dry fabric, is padded onto the fabric wet with alkali before being heated.

The samples are then tested for dry crease recovery, a measure of the loss or gain in the effectiveness of the resin, the alkali plus epichlorohydrin treatment, by itself, not materially affecting the dry crease recovery angle.

*Table II*

| Sample | Dry Crease Recovery Angle (Average of Warp and Fill), degrees |
|---|---|
| 1. Control (resin treated fabric) | 98 |
| 2. 4% KOH | 90 |
| 3. 5% KOH | 92 |
| 4. 7% KOH | 82 |
| 5. 10% KOH | 88 |
| 6. 4% KOH plus epichlorohydrin | 96 |
| 7. 5% KOH plus epichlorohydrin | 104 |
| 8. 7% KOH plus epichlorohydrin | 112 |
| 9. 10% KOH plus epichlorohydrin | 112 |

Increasing the concentration of the alkali alone from 4 to 10% causes increasing impairment of dry crease recovery whereas increasing the concentration of the alkali from 4 to 10% with 10–12% epichlorohydrin takeup cause increasing improvement of dry crease recovery.

## EXAMPLE VII

An 80 square, 4 yard/pound cotton fabric, resin treated in the manner described in Example VI, is treated with 7% aqueous potassium hydroxide, squeezed through rollers to provide about an 80% upstake, and then padded with epichlorohydrin so as to provide various percentages of uptake, calculated on the dry fabric. The fabric is rolled up smooth, sealed in a polyethylene bag, heated at 55° C. overnight, and washed thoroughly and dried.

A cotton fabric which is identical to the above fabric, but not resin treated, is similarly treated.

The resulting samples are tested for flat drying properties and dry crease recovery.

*Table III*

| Sample | Percent Epichlorohydrin Takeup | Flat Dry Properties | | Dry Crease Recovery Angle (Average Warp and Fill), degrees |
|---|---|---|---|---|
| | | Spin With Line Drying | Spin With Tumble Drying | |
| 1. No resin | 4.8 | 2.6 | 1.0 | 68 |
| 2. No resin | 7.0 | 3.2 | 1.0 | 71 |
| 3. No resin | 10.0 | 2.8 | 1.0 | 62 |
| 4. No resin | 15.5 | 2.2 | 1.0 | 70 |
| 5. No resin | 16 | 2.6 | 1.0 | 69 |
| 6. No resin | 21 | 2.3 | 1.0 | 62 |
| 7. Resin treated | 2.5 | 3.1 | 3.2 | 115 |
| 8. Resin treated | 5.5 | 4.6 | 3.0 | 117 |
| 9. Resin treated | 8.5 | 4.5 | 3.0 | 117 |
| 10. Resin treated | 11.5 | 4.9 | 3.1 | 127 |
| 11. Resin treated | 14 | 4.6 | 3.1 | 117 |
| 12. Resin treated | 19 | 4.3 | 3.3 | 119 |
| 13. Resin only | | 1.0 | 2.5 | 98 |

The fabric which is not resin treated but is wet cross linked does not have acceptable flat dry properties or dry crease recovery. The fabric which is resin treated and then wet cross linked has markedly superior flat dry properties and dry crease recovery.

The relatively low spin dry ratings of the wet cross linked only samples (1–6) is due to "rope lines" present in the original fabric, i.e., warpwise wrinkles present in the original fabric and resulting from bleaching, scouring and drying operations while the fabric is twisted in a rope-like state. Resin treatment alone or wet cross linking alone does not successfully remove these rope lines.

What is claimed is:

1. A process for improving the minimum care characteristics of a cellulosic textile material containing at least 1.8 free hydroxy groups per anhydroglucose unit by cross linking the free hydroxy groups thereof consisting essentially of the combination of steps of first applying to the cellulosic material a textile crease-proofing resin chemical cross linking agent and chemically cross linking with the cross linking agent a sufficient portion of the free hydroxy groups of the cellulosic material while the material is in an essentially dry, unswollen condition and in an essentially wrinkle free configuration to impart drip dry flat drying properties to the material by increasing its dry crease recovery and thereafter again applying to the cellulosic material a wet textile crease-proofing chemical cross linking agent and chemically cross linking with the cross linking agent a sufficient portion of the free hydroxy groups of the cellulosic material while the material is in an essentially water wet, swollen condition and in an essentially wrinkle free configuration to impart spin dry flat drying properties to the material by increasing its wet crease recovery.

2. A process according to claim 1 wherein the cellulosic material is cotton.

3. A process according to claim 1 wherein the cellulosic material is in the form of fabric.

4. A process according to claim 1 wherein the chemical cross linking agent employed while the cellulosic material is in a dry, unswollen condition is an acid catalyzed textile resin.

5. A process according to claim 4 wherein the textile resin is an aminoplast.

6. A process according to claim 1 wherein the chemical cross linking agent employed while the cellulosic material is in a wet, swollen condition is alkaline catalyzed.

7. A process according to claim 6 wherein the alkaline catalyzed cross linking agent is epichlorohydrin and the amount of water present during the wet cross linking step is not more than about 100% calculated on the weight of the dry cellulosic material.

8. A process for improving the minimum care characteristics of a cellulosic textile fabric material containing at least 1.8 free hydroxy groups per anhydroglucose unit by chemically cross linking the free hydroxy groups of the cellulosic fabric consisting essentially of the steps of first applying to the fabric an acid catalyzed textile crease-proofing resin chemical cross linking agent and a catalyst for the resin and chemically cross linking with the textile resin a sufficient portion of the free hydroxy groups of the cellulosic material while the material is in an essentially dry, unswollen condition and the fabric is in an essentially wrinkle free configuration to impart drip dry flat drying properties to the fabric by increasing its dry crease recovery and thereafter applying to the fabric an alkaline catalyzed wet textile crease-proofing chemical cross linking agent and an alkaline catalyst for the cross linking agent and chemically cross linking with the cross linking agent a sufficient portion of the free hydroxy groups of the cellulosic material while the material is in an essentially water wet, swollen condition and the fabric is in an essentially wrinkle free configuration to impart spin dry flat drying properties to the fabric by increasing its wet crease recovery.

9. A process according to claim 8 wherein the fabric consists essentially of cotton.

10. A process according to claim 8 wherein the textile resin is selected from the group consisting of cyclic ethylene urea formaldehyde resins, melamine formaldehyde resins and triazone formaldehyde resins.

11. A process according to claim 8 wherein the alkaline catalyzed cross linking agent is epichlorohyrin and the amount of water present during the wet cross linking step is not more than about 100%, calculated on the weight of the dry fabric.

12. A process according to claim 8 wherein the alkaline catalyzed cross linking agent is dichloropropanol and the amount of water present during the wet cross linking step is not more than about 100%, calculated on the weight of the dry fabric.

13. A process according to claim 8 wherein the alkaline catalyzed cross linking agent is a polyepoxide textile crease-proofing cross-linking agent and the amount of water present during the wet cross linking step is not more than about 100%, calculated on the weight of the dry fabric.

14. A process according to claim 8 wherein the alkaline catalyzed cross linking agent is a sulfone activated divinyl compound.

15. A process for improving the minimum care characteristics of a cellulosic textile fabric material containing at least 1.8 free hydroxy groups per anhydroglucose unit and consisting essentially of cotton by cross linking the free hydroxy groups thereof consisting essentially of the combination of steps of first applying to the fabric an acid-catalyzed textile crease-proofing resin selected from the group consisting of cyclic ethylene urea formaldehyde resins, melamine formaldehyde resins, and triazone formaldehyde resins and a catalyst for the resin and chemically cross linking with the textile resin a sufficient portion of the free hydroxy groups of the cotton while the cotton fibers are in a dry, unswollen condition and the fabric is in an essentially wrinkle free condition to impart drip dry flat drying properties to the fabric by increasing its dry crease recovery, and thereafter applying to the fabric epichlorohydrin and an alkali-metal hydroxide and chemically cross linking with the epichlorohydrin, in the presence of not more than 100% water, calculated on the dry weight of the fabric, a sufficient portion of the free hydroxy groups of the cotton, while the cotton fibers are in a water wet, swollen condition and the fabric is in an essentially wrinkle free condition to impart spin dry flat drying properties to the fabric by increasing its wet crease recovery.

16. A process for improving the minimum care characteristics of a cellulosic textile fabric material containing at least 1.8 free hydroxy groups per anhydroglucose unit and consisting essentially of cotton by cross linking the free hydroxy groups thereof consisting essentially of the combination of steps of first applying to the fabric an acid-catalyzed textile crease-proofing resin selected from the group consisting of cyclic ethylene urea formaldehyde resins, melamine formaldehyde resins, and triazone formaldehyde resins and a catalyst for the resin and chemically cross linking with the textile resin a sufficient portion of the free hydroxy groups of the cotton while the cotton fibers are in a dry, unswollen condition and the fabric is in an essentially wrinkle free condition to impart drip dry flat drying properties to the fabric by increasing its dry crease recovery, and thereafter applying to the fabric dichloropropanol and an alkali-metal hydroxide and chemically cross linking with the dichloropropanol, in the presence of not more than 100% water, calculated on the dry weight of the fabric, a sufficient portion of the free hydroxy groups of the cotton, while the cotton fibers are in a water wet, swollen condition and the fabric is in an essentially wrinkle free condition to impart spin dry flat drying properties to the fabric by increasing its wet crease recovery.

17. A process for improving the minimum care characteristics of a cellulosic textile fabric material containing at least 1.8 free hydroxy groups per anhydroglucose unit and consisting essentially of cotton by cross linking the free hydroxy groups thereof consisting essentially of the combination of steps of first applying to the fabric an acid-catalyzed textile crease-proofing resin selected from the group consisting of cyclic ethylene urea formaldehyde resins, melamine formaldehyde resins, and triazone formaldehyde resins and a catalyst for the resin and chemically cross linking with the textile resin a sufficient portion of the free hydroxy groups of the cotton while the cotton fibers are in a dry, unswollen condition and the fabric is in an essentially wrinkle free condition to impart drip dry flat drying properties to the fabric by increasing its dry crease recovery, and thereafter applying to the fabric a polyepoxide textile crease-proofing cross-linking agent and an alkali-metal hydroxide and chemically cross linking with the polyepoxide, in the presence of not more than 100% water, calculated on the dry weight of the fabric, a sufficient portion of the free hydroxy groups of the cotton, while the cotton fibers are in a water wet, swollen condition and the fabric is in an essentially wrinkle free condition to impart spin dry flat drying properties to the fabric by increasing its wet crease recovery.



18. A process for improving the minimum care characteristics of a cellulosic textile fabric material containing at least 1.8 free hydroxy groups per anhydroglucose unit and consisting essentially of cotton by cross linking the free hydroxy groups thereof consisting essentially of the combination of steps of first applying to the fabric an acid-catalyzed textile crease-proofing resin selected from the group consisting of cyclic ethylene urea formaldehyde resins, melamine formaldehyde resins, and triazone formaldehyde resins and a catalyst for the resin and chemically cross linking with the textile resin a sufficient portion of the free hydroxy groups of the cotton while the cotton fibers are in a dry, unswollen condition and the fabric is in an essentially wrinkle free condition to impart drip dry flat drying properties to the fabric by increasing its dry crease recovery, and thereafter applying to the fabic divinyl sulfone and an alkali-metal hydroxide and chemically cross linking with the divinyl sulfone, in the presence of not more than 100% water, calculated on the dry weight of the fabric, a sufficient portion of the free hydroxy groups of the cotton, while the cotton fibers are in a water wet, swollen condition and the fabric is in an essentially wrinkle free condition to impart spin dry flat drying properties to the fabric by increasing its wet crease recovery.

19. A process for improving the minimum care characteristics of a cellulosic textile fabric containing at least 1.8 free hydroxy groups per anhydroglucose unit and consisting essentially of cotton by cross linking the free hydroxy groups thereof, consisting essentially of the combination of steps of first applying to the fabric an aqueous solution of between 2% and 7%, based on solids, of an acid-catalyzed textile crease-proofing resin selected from the group consisting of cyclic ethylene urea formaldehyde resins, melamine formaldehyde resins and triazone formaldehyde resins, and an acid acting catalyst for the resin; drying the fabric and chemically cross linking a portion of the free hydroxy groups of the cotton with the textile resin while the fabric is dry and in an essentially wrinkle free condition by heating the fabric to a curing temperature between 100° C. and 200° C., thereby improving the dry crease recovery of the fabric; and thereafter applying to the fabric less than 10% of an alkali-metal hydroxide as an aqueous solution, followed by an alkaline catalyzed wet cross linking agent, and chemically cross linking a portion of the free hydroxy groups of the cotton fibers of the wet fabric with the cross linking agent, at a temperature between room temperature and 90° C., in the presence of beween about 15% and 90% water, thereby improving the wet crease recovery and further improving the dry crease recovery of the fabric, the percentages of textile resin, alkali-metal hydroxide and water being calculated on the dry weight of the fabric.

20. A process according to claim 19 wherein the alkaline catalyzed wet cross linking agent is epichlorohydrin.

21. A process according to claim 19 wherein the wet cross linking agent is dichloropropanol.

22. A process according to claim 19 wherein the wet cross linking agent is a polyepoxide textile crease-proofing cross-linking agent.

23. A process according to claim 19 wherein the wet cross linking agent is divinyl sulfone.

24. A process for improving the minimum care characteristics of a cellulosic textile fabric containing at least 1.8 free hydroxy groups per anhydroglucose unit and consisting essentially of cotton by cross linking the free hydroxy groups thereof, consisting essentially of the combination of steps of first applying to the fabric an aqueous solution of betwen 2% and 7%, based on solids, of a melamine formaldehyde textile resin, and an acid acting catalyst for the resin; drying the fabric and chemically cross linking a portion of the free hydroxy groups of the cotton with the textile resin while the fabric is dry and in an essentially wrinkle free condition by heating the fabric to a curing temperature between 100° C. and 200°

C., thereby improving the dry crease recovery of the fabric; and thereafter applying to the fabric an amount of an alkali-metal hydroxide stoichiometrically equal to between about 2.5% and 3.5% of sodium hydroxide as an aqueous solution, followed by epichlorohydrin and chemically cross linking a portion of the free hydroxy groups of the cotton fibers of the wet fabric with the epichlorohydrin, at a temperature between room temperature and 90° C., in the presence of between about 15% and 90% water, thereby improving the wet crease recovery and further improving the dry crease recovery of the fabric, the percentages of textile resin, alkali-metal hydroxide and water being calculated on the dry weight of the fabric.

25. Fabric produced according to the process of claim 1.

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