

1

2

3,518,042

STORABLE POLYMERIC COMPOSITIONS AND PROCESSES

Ildo E. Pensa, Palisades Park, N.J., assignor to J. P. Stevens & Co., Inc., New York, N.Y., a corporation of Delaware

No Drawing. Filed Apr. 28, 1966, Ser. No. 545,832

Int. Cl. D06m 13/12, 13/34

U.S. Cl. 8—116.3

15 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a storable, modifiable textile product having a long term shelf life in the unmodified state. A modifying system is applied to a textile substrate so that a modifying agent is on one side of the textile substrate and an activating agent is on the other side. When the textile product is subjected to an appropriate environment, the modifying agent is activated. In a preferred embodiment, an acid activatable N-methylol crosslinking agent is applied to one side of a cellulosic containing fabric and an acid activating system is applied to the other side.

The term "modifying system(s)" refers to those combinations of modifying agent and activators, which upon being brought into contact with each other in an appropriate environment, permanently modify the substrate in a desired manner.

An "appropriate environment" as used herein refers to that combination of conditions such as time, temperature, humidity and pressure which will bring the particular modifying agents and activators employed into contact with each other and cause permanent deformation or cure of the treated substrate to take place. The term substrate as used herein refers to any textile fabric susceptible to modification with chemical agents.

The modification of textile substrates is well established in the art. Textiles are modified to improve their properties and to make them suitable for new applications. For example, textiles are modified to improve their launderability, to make them resistant to shrinkage and wrinkling, to effect glazing and embossing, impart crease retention and to improve their hand among other things. One of the major problems has been to develop modifying systems which are reactive enough to be activated under mild curing conditions yet can be stored for extended periods of time, without undergoing premature curing.

The use of mild curing conditions is particularly necessary in the garment industry where much of the manufacturing is carried out by small firms having limited resources. These firms cannot afford costly automated equipment and must rely upon the skills of employees to carry out the modification procedures. Since many of the employees are not technically trained the use of complex equipment is generally undesirable. In effect to be commercially acceptable the modifying process must be simple enough to be carried out in the ovens and processing machines routinely employed in garment manufacturing operations.

A second requisite of an acceptable modifying system is long time shelf stability. For example, many textile buyers purchase far in advance of anticipated use to assure availability and price stability. Because of this, custom goods are frequently stored for long periods of time in warehouses which can reach temperatures in excess of 100° F. in the summer months.

A practical illustration of some of these problems is encountered in the modification of the cellulose and their blends. A favored group of modifying agents employed to increase crease retention and improve wash and wear

characteristics in these fabric substrates are reagents of the N-methylol type. These modifying agents are activated under acidic conditions at relatively elevated temperatures to give a modified fabric having improved properties. However, when a stable activating system is used, the activation requires up to 15 minutes even at temperatures as high as 325° F. The same modifying agents can be activated much more quickly for example under ordinary pressing temperatures when a fast acting mixture of acid and salt is used as the activating system. However, due to this high reactivity, the shelf life of the fabric treated in this manner is poor, and premature curing can take place during storage. While the specific system noted above is pertinent to cellulosic fabrics, similar problems are also encountered in the modification of other textile substrates described subsequently.

Because of the aforementioned shortcomings of the prior art there is a real need for improved modifying system and for improved methods of applying them. A desirable modifying system would combine high reactivity with good storage stability. The modifiable materials produced by the inventive process could be cured under mild conditions after the necessary preliminary operations have been performed.

Ideally the novel process would not be confined to any specific modifying system or textile substrate but would be applicable to the chemical modification of textile fabric substrates generally. If, in addition to the aforesaid attributes, a modification process would permit the rapid curing of the modifiable textile under pressing conditions, it would represent a substantial advance in the art.

It is an object of this invention to prepare modifiable textile substrates which can be stored for extended periods of time without undergoing significant premature curing.

It is another object of this invention to provide modifiable textile substrates which can be readily activated under the mild activation conditions produced by textile processing equipment.

It is a further object of this invention to provide sensitized textile substrates which can be activated a considerable period of time after sensitization.

An additional object of this invention is the preparation of storable cellulosic articles treated with reactive crosslinking systems of the N-methylol type.

Yet, an additional object of this invention is to provide a novel application method for improving the storability of modifiable textile substrates, said method being applicable to a variety of substrates and modifying agents.

Another object of this invention is to provide a method of preparing modifiable textile substrates containing all the elements of a highly reactive modifying system in one single, stable package.

Still another object of this invention is to separate the modifying agent of the modifying system from the activator by the use of a permeable textile substrate barrier.

Additional objects will become apparent to those skilled in the art after a further perusal of this invention.

The above objects among others are achieved by the process to be described more fully below.

In practice one side of a suitable textile substrate is treated with an activatable modifying agent and upon the other side with the activating agent(s) capable of converting the modifying agent to its active form. The application of the components of the modifying system is arranged so that there is no intermixing of modifying agent and activator. One or more textile adjuvants such as surfactants, brighteners, water-proofing agents, thickeners and the like can be applied with either the modifying agent or activator, or the adjuvant(s) can be applied before modification. Where the activating agent consists of more than one component, part of the activating system can be

incorporated with the modifying agents while the second part is kept separate on the opposite face. However, ordinarily, this results in an inferior product.

The modifying agent(s) or the activator(s) can be applied to the textile substrate by conventional application methods known in the textile art. These include but are not limited to brushing, spraying, coating and the like. The modifying agent(s) and/or activators can be in the form of liquids, slurries, suspensions, emulsions, pastes, gels or solids where appropriate. Ordinarily, it is convenient to apply one set of the modifying components to one side of the substrate and dry before the complementary agents are applied to the opposite face. However, this is not always the case and the preferred procedure depends upon the substrate to be treated, the modifying agent(s) and the catalysts employed.

When both sides of the textile substrate have been treated to create a modifiable material, the substrate can be handled in conventional manufacturing steps such as cutting, sewing, garment manufacturing etc., as long as no contact between the components of the modifying system takes place and the treated substrate is not exposed to an environment where activation or removal of the modifying agents and activators takes place.

The substrates which can be used in this invention vary widely insofar as structure, origin and characteristics are concerned. Virtually any permeable substrate capable of modification can be employed. Both natural and synthetic substrates, inorganic or organic, unblended or in the form of their blends can be used. The substrates can be in the form of woven or knitted fabrics or non-woven assemblies, garments and permeable films. Illustrative substrates include but are not limited to the preferred cellulose such as cotton, linen, jute, flax and rayon fabrics, as well as the proteinaceous substrates such as wool, silk, hair and the like. Fabrics manufactured from synthetic fibers, as typified by the polyamides, polyesters, acrylics and polyolefins among others can also be employed.

"Activatable" as used throughout this application refers to the state of the modifying agents such as resins, resin precondensates or crosslinking agents prior to their activation. To activate the modifying agents in their inactive but modifiable form, they are brought into contact with the activator(s) by exposing the sensitized substrate to the aforesaid appropriate or curing environment.

The operability of the inventive process is not postulated or dependent upon any particular reaction mechanism. However, presumably exposure of the treated permeable textile substrate to an appropriate curing environment causes the reagents to come into contact with each other thus bringing about activation. Whether this contact is brought about by the migration of one or both components or if the contact is caused by leaching, extraction, dissolution or by another phenomenon, is not known except that under these conditions the desired permanent modification of the substrate takes place.

The term "modify" as used herein is the generic term used to describe the alteration of characteristics and/or properties that are to be made in the treated textile substrate. It should be understood that while in many instances modification involves chemical interaction of the substrate and modifying agent; the term also includes modifications of the properties of a substrate that is inert to the agent. In these cases little or no reaction between modifying agent and substrate takes place but the properties are altered by the interaction of modifying agent and activator. While in many instances the modifying agent employed is a resin, resin precondensate or crosslinking agent, the inventive process is not limited to specific agents, their analogues, homologues or derivatives. Rather the inventive process includes the use of any modifying agent or mixture of modifying agents which can be converted from their inactive or precursor state to their active state by contact with activator.

While the inventive process is not limited to any specific substrate, modifying systems or activators, etc., certain substrates and modifying systems lend themselves to the practice of this invention more readily than others and for this reason are favored. In this instance, cellulosic fabrics and cellulosic-synthetic blend fabrics are the preferred textile substrates, particularly when used in conjunction with acid activated N-methylol crosslinking systems defined more fully below.

A second favored group of substrates are wool and wool-cellulosic blends, especially when treated with resins of the alkylated methylol melamine type or mixtures of these resins with other resins such as urea formaldehyde, ethylene urea formaldehyde, guanamine formaldehyde resins and the like.

Other textile substrates, while lending themselves to the practice of this invention, are less favored.

In the favored process, one side of a cellulosic fabric substrate containing a plurality of reactive hydroxyl groups is coated with a paste containing an acid activatable crosslinking agent having reactive functional groups, until a sufficient quantity of crosslinking agent is deposited upon the side of the cellulosic substrate. A "sufficient quantity" of crosslinking agent is defined as that amount of crosslinking agent which upon activation will impart the desired degree of modification to the textile substrate in a curing environment. After drying, the opposite side of the substrate is treated with appropriate activating catalyst(s), preferably in the form of a paste, so that enough catalyst is deposited upon the substrate to activate it. When the sensitized substrate is cured at elevated temperature, the catalyst activates the modifying agent and the aforesaid permanent modification of the textile substrate is effected.

A preferred group of modifying agents of the acid activated type are those nitrogen containing compositions referred to as N-methylols. These include methylol derivatives of cyclic ureas such as cyclic ethylene urea, urea-formaldehyde, dimethylol ureas and triazones, dimethylol carbamates, dimethylol imidazolidones among many others. These modifying agents are preferably activated by a mixed catalyst system comprising a salt of an inorganic acid, for example a metallic salt or salts such as magnesium chloride, magnesium nitrate, zinc chloride, zinc nitrate, zinc fluoroborate or the like combined with a carboxylic acid such as acetic, propionic, citric, tartaric, lactic, glycolic, etc. Such mixed catalyst systems have been found to quickly activate the above modifying agents under mild heating conditions. The organic acids preferred are water soluble, non-volatile, hydroxy acids whose pH in 1-normal aqueous solution varies between about 3.0 to about 5.0. Illustrative catalyst formulations are described more fully below. Since the treated fabric is exposed, albeit briefly, to elevated temperatures, acids having a boiling point above about 120° C. are preferred.

Ordinarily the mixed acid catalyst contains by weight from about 15 parts to 3 parts of acid for each part of salt. Usually, the catalyst is applied in the form of a paste suitably formulated. Preferably, the mixed catalyst system contains by weight from about 7 to 10 parts of organic acid for each part of salt. The amount of the catalyst system on the substrate fabric can be varied by controlling the paste formulation and the amount of paste deposited on the substrate.

As indicated above, while the preferred embodiments of this invention are cellulosic containing substrates which are made modifiable through treatment with modifying systems of the N-methylol type, other combinations of substrate and modifying agents can be used.

For example, a valuable group of substrates are those of proteinaceous origin. The most important of these are wool, silk, animal hairs and their blends, particularly their blends with the cellulose. To modify these wool containing substrates a number of modifying systems can be used.

These include mixtures of certain resins such as the alkylated methylol melamines and/or melamine formaldehyde resins as well as certain non-resinous modifying systems.

The modifiable wool containing substrates, like the cellulose, are most conveniently prepared by coating one side of the substrate with a paste consisting essentially of a thixotropic agent plus the modifying compound, and the opposite side with activator. As in the case of the cellulose, ordinarily one side of the substrate is treated and dried before the second and opposite side is treated. This is done to minimize accidental contact between the modifying agent activator which can promote undesirable premature curing.

The thickening agents used as the paste base in treating the wool, cellulose or other substrates can be selected from a variety of synthetic and natural products. Illustrative thickeners include gums such as arabic, guar and tragacanth, gelatine, alkylated celluloses and hydroxyalkylated celluloses such as the methyl-, ethyl-, and propyl-celluloses, hydroxymethyl, hydroxyethyl, and hydroxypropyl celluloses, Irish moss, albumin, alginic acid and its derivatives, particulated silica, sulfonated castor oil among many others.

As in the case of the cellulose, the amount of modifying agent and activator cannot be stated with precision. The amounts employed are dependent upon the effect sought, the modifying agent and the activators employed, the substrate, the mode of application and the curing environment among other experimental conditions.

In the foregoing description of this invention, modification of the textile substrate involved *chemical interaction of the substrate and modifying agent*. One such instance was modification of cellulosic textile by chemical reaction with a poly-N-methylol compound (the modifying agent), in which a crosslinking of cellulose by the reagent was induced by an acid activator system.

As indicated earlier, the invention is also applicable to the modification of textile substrates wherein little or no interaction between the modifying agent and the substrate takes place. In these embodiments the same general objectives are achieved, e.g., modifiable textile substrates which can be:

(a) Stored for extended periods without undergoing significant premature curing, and

(b) Activated a considerable period of time after preparation. Again, modification results in desirable properties being imparted to the fabric; however, in these instances the modification is achieved by physical means without significant alteration of the chemical bonds of the textile substrate.

In practice, one side of a suitable textile substrate is coated with a semi-resinous or resinous modifying agent inert to the substrate, the modifying agent being in an intermediate stage of polymerization. After the addition of resin is complete the other side of the substrate is coated with the activating agent in suitable form. Once more care is taken to assure that no intermixing of modifying agent and activator takes place during the pre-storage and storage periods. Textile adjuvants can be applied to the fabric before coating with said resinous agents, or either or both of said agents may be formulated with compatible adjuvants.

Particularly suitable inert fabric substrates include those of certain organic and inorganic fibers, and the organic fibers embrace man-made fibers which are completely synthetic (as polyesters) or partially so (cellulose triacetate). Some representative non-reactive fibers are listed in the technical literature. See for example Table 30 of the book by Kaswell, "Wellington Sears Handbook of Industrial Textiles" (1963), pages 382-383; and pages 53-65.

In some instances, it is desirable to utilize the semi-resinous or resinous modifying agent in an intermediate stage of polymerization, referred to in the art as an A-stage resin, a precondensate, or a prepolymer. Such agents,

which usually have a molecular weight range of about 1000 to 4000, are fusible under the application of heat or heat and pressure, or can be solubilized in any of several common solvents or their mixtures. If desired, the "A-stage" resins can be applied in the form of an aqueous dispersion or emulsion to one side of the fabric. As usual, the opposite side of the substrate is treated with appropriate activator. When the treated substrates are exposed to elevated temperatures the resin and activator come into contact with each other and the resin is polymerized to a much higher molecular weight thus modifying the substrate's properties.

Illustrative of such a resinous system is a melamine-formaldehyde precondensate resin coated on one side of a nonreactive fabric (e.g., Dacron polyester), with an acid activator of a type described hereinbefore is coated on the other side. Activation takes place upon exposing the treated substrate to temperatures of about 200 to 500° F. for 1 to 20 minutes. Comparable modifications can be achieved using the alkylated type of resins (e.g., methylated or butylated melamine-formaldehyde), although higher-than-methylated types are not so efficient for the purpose of this invention. Moreover, precondensates of other aminoplasts are operable, such as a urea-formaldehyde precondensate resin. The ratio of precondensate to acid activator should be between 100:2 and 100:20, preferably near 100:7, but depending on the average equivalent weight and strength of the acids involved.

Another type of prepolymer system which can be used advantageously in this invention is the acetone-soluble, fusible prepolymer form of diallyl or bis(2-methylallyl) esters of dibasic acids. Such prepolymers are generally obtainable in solid form as precipitated powders. Representative prepolymers of this class are those of diallyl adipate, succinate, isophthalate, phthalate, and diglycolate, as well as bis(2-methylallyl) maleate. Allyl acrylate prepolymer is also operable. Activators for these allylic prepolymers are peroxy compounds, preferably solid peroxides, either organic or inorganic, which are coated on the back side of the fabric, preferably from an aqueous system. For instance, urea peroxide is conveniently applied from an aqueous solution, followed by drying, as is potassium persulfate. Benzoyl peroxide or solid peroxides made by the action of hydrogen peroxide on certain ketones are applied in dispersed or emulsified form, followed by evaporation of the water. The ratio of prepolymer to peroxide will generally be between 100:0.3 and 100:8, with 100:2 usually being effective. Curing to complete polymerization is accomplished at temperatures ranging between about 70 and 150° C., the latter being preferred with less active catalysts, such as di-tert-butyl diperterephthalate.

Systems utilizing epoxy resins of molecular weights of the order of 300 to approximately 2000 along with hardeners or curing agents of the aromatic diamine type are exemplary of still another chemical class which find applicability for advantageously modifying non-reactive fabrics. Solid epoxy resins are preferable. Examples of solid epoxies are Shell Epons 1001, 1004, and 1007, as well as Ciba Araldites 6084, 6097, 7097, 6071 and 7071. Curatives are exemplified by meta-phenylenediamine, methylenedianiline, and mixed hindered aromatic diamines (e.g., Naugatuck Curalon-L). The preferable ratio of epoxy to curative ranges from about 100:4 to about 100:90, the optimum generally being near to 100:30.

In known practice epoxy and curative can be melted and blended, then coated in the molten state on exclusively the back side of the fabric. Alternatively, they can be blended as powders and applied from an organic solvent (as toluene or xylene), or from aqueous dispersion, to only the back side of the fabric. According to the present invention, the epoxy is coated on one side of the fabric and the curative on the other side and as a result storage conditions can be less mild. Curing is accomplished at about 140 to 250° C., so the resistance of the

fabric to such temperatures is a factor in selecting the upper limit. Particular care is required when utilizing an epoxy-diamine system to modify a so-called olefin (poly-olefin) fabric, such as polypropylene, or a modacrylic fabric, such as Dynel or Verel, because of limitations above 150° C. Longer cures are required at lower temperatures.

To indicate the workings of this invention in the greatest possible detail, the following illustrative examples are submitted.

In all the examples that follow, the pastes are applied by supported knife coating procedures using a gap opening of 2 mils. The padding solutions used as controls are applied to the fabric by impregnation and squeezing through rolls. Both the coated and padded fabrics are dried in a forced draft oven. The exact compositions of the solutions and pastes are listed under the designated letter in the table which follows. The testing and rating systems employed are described below.

Crease recovery in angular degrees.—Monsanto method, ASTM D-1295-60T.

Crease retention.—AATCC-88C-1964T, Test IIC Scale: 1 (no crease left), 2 (slight crease), 3 (moderate crease), 4 (sharp crease), and 5 (unchanged very sharp crease).

Wash-and-wear rating.—AATCC-88A-1964T, Test IIC Scale: 1 (most seriously wrinkled) to 5 (perfectly smooth).

EXAMPLE 1

(A) Experimental

Five (5) sets of 8 oz. 100% cotton twill samples are treated as follows:

Sets 1 and 2 are treated with an aqueous padding solution (L) containing zinc nitrate and N,N-dimethylol dihydroxyethylene urea (DMDHEU). This solution is a conventional, stable but slow acting crosslinking system known in the prior art and is included for comparison.

Set 3 is treated with an aqueous padding solution (M) containing magnesium chloride, citric acid and DMDHEU. This is a fast acting, crosslinking system of the prior art known to have limited storage stability. This is also included for comparison.

Set 4 is treated on the back with the same reactive system of set 3 (magnesium chloride, citric acid and DMDHEU) but prepared in a paste form as given by (G).

Set 5 is treated on the back with paste (D) containing the crosslinking agent, then dried. The opposite side of the fabric is treated with paste (C) containing the catalyst system consisting of magnesium chloride and citric acid. This set illustrates the inventive process.

The above five (5) sets are divided into two groups (a) and (b) according to the lapse of time between the treatment and setting by pressing or pressing and curing.

Set 1, group (a) is creased along the warp direction, pressed for 10-15 seconds on a steam press and cured for 15 minutes at 325° F. in an oven.

Sets 2-5, group (a) are creased along the warp direction and pressed for 65-75 seconds on a steam press.

Set 1, group (b) is pressed and cured after an aging period of 4 weeks at 110°±5° F.

Sets 2-5, group (b) are pressed after an aging period of 4 weeks at 110°±5° F.

Table I below summarizes the crease retention ratings obtained on the above samples after 10 laundering and drying cycles.

TABLE I

Time of curing	Crease retention appearance after 10 launderings				
	Set 1	Set 2	Set 3	Set 4	Set 5
Initial: Group (a)-----	5.0	2.5	4.8	5.0	4.8
After aging 4 weeks: Group (b)-	4.5	2.5	2.0	4.0	4.5

(B) Results

The high ratings of set 1, group (a) establishes that the conventional salt catalysed crosslinking system of the prior art cures slowly at elevated temperatures. The substantially similar ratings obtained before and after aging are indicative that no appreciable crosslinking takes place during storage.

The low ratings of set 2, both before (group (a)) and after aging (group (b)), confirm that the activating conditions obtained in a pressing cycle on a steam press are too mild to activate this system.

The high initial rating of set 3, as shown by group (a), confirms the reactivity of the mixed acid catalyst system of the prior art, while the low rating obtained after aging, as shown by group (b) reflects the poor storage characteristics of the system.

The results of set 4 (group (b)) indicate that on storage the initial high ratings shown by group (a) begin to drop due to crosslinking that takes place during aging.

The high initial ratings of set 5, shown in group (a), is indicative of two facts: (1) that the high reactivity of the prior art systems of sets 3 and 4 are retained by the inventive process, (2) that a considerable gain in stability is obtained. The latter is illustrated by the small drop in the initial rating after aging.

EXAMPLE 2

To establish the criticality of separating the complete catalyst system from the crosslinking agent the following experimental work is submitted:

Five (5) sets of 8 oz., 100% cotton twill samples are treated as follows:

Set (1) is coated on its back with a paste (F) containing the prior art system of zinc nitrate and DMDHEU.

Set (2) is coated on its back with paste (H) containing magnesium chloride and DMDHEU. After drying, the face is coated with a paste (B) containing citric acid. This set illustrates the effect of splitting the mixed acid catalyst system by placing the acid salt with the DMDHEU.

Set (3) is coated on its back with paste (I) containing citric acid and DMDHEU. After drying, the face is coated with paste (A) containing magnesium chloride. This set shows the effect of splitting the activating mixed acid catalyst system by placing the free acid with the DMDHEU and keeping the acid salt on the other side of the substrate.

Set (4) samples are coated on their back with paste (D) containing DMDHEU. After drying the face is coated with paste (C) containing the mixed acid catalyst system of magnesium chloride and citric acid. This set illustrates the inventive process.

Set (5) samples are coated on their back with paste (D) containing DMDHEU. After drying, the face of the samples are coated with paste (C) containing zinc nitrate. This set shows the use of a conventional slow acting system of the prior art wherein the crosslinking agent and catalyst components are separated.

The sample from the five sets are creased along the warp direction and pressed on a steam press for 60-75 seconds. Crease retention performance is rated after five and ten washing and drying cycles. The table (II) below summarizes these ratings:

TABLE II

	Crease retention appearance				
	Set (1)	Set (2)	Set (3)	Set (4)	Set (5)
After 5 launderings-----	2.5	3.5	3.5	4.8	1.5
After 10 launderings-----	1.5	3.0	2.5	4.5	1.0

The above ratings indicate that only the inventive compositions (set 4) set a good crease under the mild cur-

ing conditions obtained by pressing on a steam press. Further, the crease obtained is highly resistant to laundering.

EXAMPLE 3

This example illustrates the long-term crease retention properties that are obtained using the inventive process. Standard slow setting and fast setting systems of the prior art are used as controls.

Set (1) is treated with a padding solution L containing the slow acting system of zinc nitrate and DMDHEU.

Set (2) is treated with padding solution M containing a reactive system of magnesium chloride, citric acid and DMDHEU.

Set (3) is treated on its back with paste (D) containing DMDHEU and after drying the face is coated with paste (C) containing magnesium chloride and citric acid. This set illustrates the inventive process.

The samples are handled as follows:

Set (1) samples creased, pressed for 10-15 seconds on a steam press and cured for 15 minutes at 325° F. in a forced draft oven immediately after treatment. The creasing and pressing operation is repeated after intervals of two weeks for a total of eight weeks.

Sets (2) and (3) are creased and pressed on a steam press for 65-75 seconds immediately after treatment and after intervals of two weeks for a total of 8 weeks.

Table III below summarizes the wash and wear appearance and crease retention ratings obtained after ten washing and drying cycles.

	Original	2 weeks	4 weeks	6 weeks	8 weeks
Set (1) 10 laundings					
tumble dried:					
Wash/wear.....	5.0	4.8	4.5	4.5	4.8
Crease retention..	5.0	4.8	4.5	4.5	4.0
Set (2) 10 laundings					
tumble dried:					
Wash/wear.....	4.5	4.0	4.0	4.0	4.0
Crease retention..	4.5	4.0	2.0	1.0	1.0
Set (3) 10 laundings					
tumble dried:					
Wash/wear.....	4.8	4.8	4.5	4.5	4.5
Crease retention..	5.0	4.8	4.5	4.5	4.5

The above ratings indicate that applicant's process of separating the catalyst and crosslinking agent (set 3) gives better wash and wear and crease retention appearance on aging than can be obtained using the same crosslinking system but where the catalyst and crosslinking components are kept together. The slower acting system of set (1) gives almost comparable results but requires much longer curing times at a high temperature.

EXAMPLE 4

This example illustrates that prior treatment of the substrate with textile adjuvants such as waterproofing agents does not interfere with the operation of the process of this invention.

Samples of 8 oz. 100% cotton twill are treated with padding solution (N) containing a fluorocarbon waterproofing agent. The samples are dried and cured at 300° F. for 3 minutes. The dried samples are coated on their back with paste (D) containing DMDHEU and dried, then coated on their face with paste (C) containing magnesium chloride and citric acid, and dried one more.

The treated samples are creased along the warp and pressed on a steam press for 70-80 seconds. The creases are durable to repeated laundering indicating that textile adjuvants can be used without any apparent interference with the practice of this invention.

EXAMPLE 5

This example illustrates the direct inclusion of a textile adjuvant into the compositions of this invention.

Two sets of 8 oz. 100% cotton twill samples are prepared. Set (1) is coated on the back with paste (D) containing DMDHEU. After drying, the face side of the samples is coated with paste (K) containing magnesium chloride, citric acid and fluorocarbon water proofing agent. Set (2) is coated on the back side with paste (J) containing DMDHEU and fluorocarbon water proofing agent. After drying, the opposite side is coated with paste (C) containing magnesium chloride and citric acid.

Both sets of sample are creased along the warp and pressed for 70-80 seconds on a steam press. The creased swatches are laundered in an agitation type machine and are tumble dried ten times. All the laundered samples rated 4.0+ in both wash and wear appearance and crease retention.

EXAMPLE 6

This example shows the application varying the textile substrate to be modified and varying the curing conditions.

Samples of 6.5 oz. 65% polyester-50% cotton blend twill are coated on the back with paste (D) containing DMDHEU, a crosslinking agent. After drying, the face is coated with paste (C) containing magnesium chloride and citric acid.

Three sets (1, 2 and 3) of samples are then creased along the warp and pressed or pressed and cured under the following conditions:

Set (1) is pressed 65-75 seconds on a steam press.

Set (2) is pressed 15 seconds on a steam press and is then cured for 90-150 seconds at 275°-325° F. in a forced draft oven.

Set (3) is pressed 10 seconds on a steam press and is then cured for 5 minutes at 250° to 275° F. in a forced draft oven.

All samples are then laundered in an agitation type machine and dried in a tumble drier for ten cycles. In all cases the wash and wear appearance rated 4.5-5.0 and the crease retention appearance rated 4.0+.

In a comparable experiment samples of a 50% rayon-50% wool blend fabric are treated on the back side with paste (D) containing DMDHEU, a crosslinking agent. After drying, the opposite side is treated with paste (C) containing magnesium chloride and citric acid and dried. The treated fabric samples are creased along the warp pressed for 15 seconds on a steam press then cured at 250-300° F. for 90-180 seconds in a forced draft oven. The fabric samples are laundered and tumble dried as above. Good shrinkage control and satisfactory crease retention are obtained.

As the foregoing example indicate, this invention has numerous advantages, both in its process and compositional aspects.

For instance, the inventive process of preparing storable modifiable substrate compositions by coating opposite side of the substrate with the components of the modifying system is simple and economical. No special skills or equipment are required. Further, because of the high reactivity of the favored mixed catalyst systems, the fabric substrates can be modified under relatively mild conditions, that is, the coated substrates need only be exposed to temperatures ranging from about 250 to 325° F. for brief periods of time to effect permanent modification.

In its compositional aspect the novel coated substrates of this invention represent modifiable substrate compositions that can be stored at/or about room temperature or below for extended periods of time without undergoing significant modification. This minimizes waste from premature curing of treated fabrics and reduces the risks of storage to the buyer of treated textiles. Further advantages will suggest themselves to those skilled in the

TABLE OF EXAMPLES

[The table below gives the composition of the waterbased coating pastes (A through K) and aqueous padding solutions (L through N) used in the preceding examples]

	Percent													
	A	B	C	D	E	F	G	H	I	J	K	L	M	N
30% aqueous solution of $Zn(NO_3)_2$					4.0	4.0						2.5		
30% aqueous solution of $MgCl_2$	3.0		3.0				3.0	3.0			3.0		1.5	
Citric acid crystals.....		9.0	9.0				9.0		9.0		9.0		3.5	
45% aqueous solution of DMDHEU ¹				25.0		25.0	25.0	25.0	25.0	25.0		15.0	15.0	
Hydroxyethyl cellulose ²	0.95	0.90	0.90	0.75	0.95	0.75	0.65	0.75	0.65	0.60	0.75			
28% emulsion of fluorochemical ³										10.0	10.0			3.5

¹ DMDHEU—N,N-dimethylol dihydroxyethylene urea.

² Natrosol 250H (high viscosity type).

³ Scotchgard FC-208.

What is claimed is:

1. A textile product modifiable upon exposure to a curing environment and having long term shelf life in the unmodified state, said textile product comprising a cellulosic containing fabric having applied to one side an acid activated N-methylol crosslinking agent for cellulose and having applied to its opposite side a catalyst system for said crosslinking agent consisting essentially of a metallic salt of an inorganic acid wherein said metal is magnesium or zinc and a carboxylic acid selected from the group consisting of acetic acid, propionic acid, and water soluble, non-volatile, hydroxy acid.

2. A textile produce as claimed in claim 1 wherein said carboxylic acid is selected from the group consisting of citric acid, tartaric acid, lactic acid and glycolic acid.

3. A textile product as claimed in claim 1 wherein said N-methylol crosslinking agent is dimethylol dihydroxyethylene urea.

4. A textile product as claimed in claim 1 wherein said metallic salt is selected from the group consisting of magnesium chloride, magnesium nitrate, zinc chloride, zinc nitrate and zinc fluoroborate.

5. A textile product as claimed in claim 1 wherein said cellulosic containing fabric is a cellulosic-synthetic blend.

6. A textile product as claimed in claim 1 wherein said cellulosic containing fabric is a cellulosic-wool blend.

7. A textile product as claimed in claim 1 wherein a thixotropic agent is admixed with both said crosslinking agent and said catalyst system.

8. A process for preparing a modifiable textile product curable under mild conditions and storable in the uncured state for long periods of time, said process comprising applying to one side of a cellulosic containing fabric an activatable N-methylol crosslinking agent for cellulose and applying to the other side of said fabric a catalyst system for said crosslinking agent consisting essentially of a metallic salt of an inorganic acid wherein said metal is magnesium or zinc and a carboxylic acid selected from the group consisting of acetic acid, propionic acid, and water soluble, non-volatile, hydroxy acid.

9. A process as claimed in claim 8 wherein said metallic salt is selected from the group consisting of magnesium chloride, magnesium nitrate, zinc chloride, zinc nitrate and zinc fluoroborate and said carboxylic acid is selected from the group consisting of citric acid, tartaric acid, lactic acid and glycolic acid, about 3 to 15 parts by weight of said carboxylic acid being present for each part by weight of said metallic salt.

10. A process of preparing garments having a permanent configuration from cellulosic containing fabric, said process comprising

(a) applying an N-methylol crosslinking agent for cellulose to one side of a cellulosic containing fabric and applying to the other side of said fabric a catalyst system for said crosslinking agent consisting essentially of a metallic salt of an inorganic acid wherein said metal is magnesium or zinc and a carboxylic acid selected from the group consisting of

acetic acid, propionic acid, and water soluble, non-volatile hydroxy acid;
(b) forming a garment from said fabric;
(c) shaping said garment into a desired configuration, and
(d) heating said garment to activate said crosslinking agent and set the garment in said configuration.

11. A process as claimed in claim 10 wherein said metallic salt is selected from the group consisting of magnesium chloride, magnesium nitrate, zinc chloride, zinc nitrate and zinc fluoroborate, said carboxylic acid is selected from the group consisting of citric acid, tartaric acid, lactic acid and glycolic acid, and about 3 to 15 parts by weight of said carboxylic acid are present for each part by weight of said metallic salt.

12. A process as claimed in claim 10 wherein said crosslinking agent and said catalyst system are applied in the form of a paste and the side of the fabric treated first is dried before the opposite side is treated.

13. A process as claimed in claim 12 wherein said crosslinking agent is activated by heating at a temperature of at least about 250° F.

14. A process as claimed in claim 12 wherein said crosslinking agent is dimethylol dihydroxyethylene urea, said salt of an inorganic acid is at least one member of the group consisting of zinc nitrate and magnesium chloride and said carboxylic acid is citric acid.

15. A textile product modifiable upon exposure to a curing environment and having long term shelf life in the unmodified state, said textile product comprising a cellulosic containing fabric having applied to one side an acid activatable N-methylol crosslinking agent for cellulose and having applied to its opposite side a catalyst system for said crosslinking agent comprising a metallic salt selected from the group consisting of magnesium chloride, magnesium nitrate, zinc chloride, zinc nitrate and zinc fluoroborate and a carboxylic acid selected from the group consisting of acetic acid, propionic acid, citric acid, tartaric acid, lactic acid and glycolic acid, about 3 to 15 parts by weight of said carboxylic acid being present for each part by weight of metallic salt.

References Cited

UNITED STATES PATENTS

2,974,432 3/1961 Warnock et al. 38—144
3,366,440 1/1968 Nuwayser 8—115.6

OTHER REFERENCES

Wash-Wear Finishing of Cotton Fabric, using deferred curing, Kullman et al., American Dyestuff Reporter, May 14, 1962, pages 47, 48.

MAYER WEINBLATT, Primary Examiner

U.S. Cl. X.R.

8—115.6, 116.2; 117—139.4; 38—144

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,518,042 Dated June 30, 1970

Inventor(s) Ildo E. Pensa

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

Column 5, line 52, "resinousu" should read -- resinous --;
Column 10, line 23, "65% polyester" should read
-- 50% polyester --; Claim 1, Column 11, line 20,
"acid activated" should read -- acid activatable --.

Signed and sealed this 26th day of September 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents