

[54] **VAPOR PHASE RESIN FIXATION
PROCESS FOR CELLULOSIC
MATERIAL PERMITTING
SUBSEQUENT CURE**

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[57]

ABSTRACT

Improved crease resistance and smooth drying characteristics are imparted to cellulosic fiber-containing materials, such as cotton fabric, with a minimum sacrifice in physical properties by a process including (1) applying an aqueous solution comprising at least one water-soluble polymer-forming compound possessing reactive N-methylol groups and a latent curing catalyst to the cellulosic material, (2) exposing the material in a water swollen state in the presence of formaldehyde to a reactive vapor atmosphere containing a gaseous acidic catalyst such as sulfur dioxide, and (3) drying the material in preparation for the manufacture of a durable press article therefrom. The latent curing catalyst is conveniently applied to the material from the same bath as the polymer-forming compound, but as an alternative it may be applied to the material from a separate bath, e.g., after the reactive vapor treatment and prior to the final cure. The durable press article may be made by first making the dry uncured material into an article such as a garment having hot pressed creases therein and then curing the article (delayed cure), or by first curing the material and then making the cured material into a final product (precure).

11 Claims, No Drawings

VAPOR PHASE RESIN FIXATION PROCESS FOR CELLULOSIC MATERIAL PERMITTING SUBSEQUENT CURE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to improvements in durable press cellulosic fiber-containing materials, and more particularly to a process for treating such cellulosic materials to impart improved crease resistance and smooth drying characteristics with minimum sacrifice in physical properties.

2. Summary of the Prior Art

There is an ever increasing demand for easy care, durable press garments, that is, for garments which have creases and pleats durably pressed in them, which remain substantially wrinkle-free in normal wear and which can be worn after washing without requiring much, if any, repressing.

It is well known to impart durable wrinkle resistance to cellulosic fabrics such as cotton by impregnation with an aqueous solution of a suitable thermosetting resinous precondensate or cellulose cross-linking agent, usually with an appropriate catalyst, and eventual curing of the impregnated fabric. Such treatments have been effective in improving the shape holding properties of cotton fabrics and have resulted in a greatly increased demand for "wash-and-wear" cotton fabrics because these combine the traditional comfort, washability and economy of the native fibers with the easy care properties desired in today's textile market.

Particularly good shape holding properties have been obtained when the cure of such resin treated fabrics was delayed until after the treated fabric was cut and sewn to produce the desired finished garment and after such garment was given the desired shape by pressing.

A particularly promising approach to the production of easy care, durable press garments has involved the wet fixation of resin- or polymer-forming creaseproofing agents such as formaldehyde-melamine precondensates, as disclosed, for example, in U.S. Pat. No. 3,138,802 which is assigned to the assignee of the present invention. In this type of process, a fiber system such as a cotton fabric is protected against excessive strength loss and presensitized for durable press processing by fixation of a suitable polymer-former and creaseproofing agent within the fibers while they are wet and swollen but without greatly altering the dry crease recovery angle or durable press properties of the fiber system. The latter properties are only imparted in the desired degree during a subsequent dry cure. Such a process accordingly permits ready creasing or other distinct shaping of the fiber system during apparel manufacture or the like subsequent to the wet fixation step and prior to the delayed dry cure. However, wet fixation processes heretofore known have usually required neutralization and wash-off of the strongly acid wet fixation catalyst subsequent to the wet fixing step, to be followed by drying and then recatalyzation and redrying prior to the actual cure, thus requiring additional processing time and effort.

Another promising approach to the production of easy care, durable press garments has involved exposing a conditioned cotton fabric to a reactive atmosphere of formaldehyde and gaseous sulfur dioxide, as disclosed, for example, in U.S. Pat. application, Ser. No. 706,792, filed Feb. 20, 1968, and assigned to the assignee of the present invention. However, this process results directly in a cured fabric and is thus not suitable for delayed cure processing. Moreover, fabrics treated by such a process tend to suffer a substantial strength loss.

OBJECTS AND SUMMARY OF THE INVENTION

Accordingly, a primary object of the present invention is to provide a process for improving the crease resistance and smooth drying characteristics of cellulosic fiber-containing materials, which process substantially prevents or alleviates the problems of the prior art discussed above.

Another object of the present invention is to provide a process for achieving a favorable balance between easy care

and physical properties of cellulosic-fiber containing materials, which process allows both delayed cure and precure procedures to be used.

Yet another object of the present invention is to provide a process for improving the crease resistance of cellulosic fiber-containing materials, which process permits ease of processing while minimizing processing time.

These and other objects of the present invention will become more clearly apparent from the following description.

Accordingly, this invention provides an improved process for imparting crease resistance, that is, wrinkle resistance or shape retention, and smooth drying characteristics to cellulosic fiber-containing materials such as cotton.

Typically, the process comprises (1) applying to the cellulosic material an aqueous solution comprising at least one water-soluble polymer-forming alkaline-reacting compound possessing reactive N-methylol groups and at least one water-soluble solid salt which functions as a latent curing catalyst in the eventual dry cure, (2) exposing the material in a water swollen state at an elevated temperature and in the presence of formaldehyde to a reactive atmosphere or vapor phase which contains a strongly acidic gaseous catalyst which later is driven off by heat to leave the material in a neutral or near neutral condition, e.g., vapor phase may contain sulfur dioxide, acetic acid, formic acid or hydrogen chloride; and (3) drying the material in preparation for the final dry cure. As the latent curing catalyst does not normally perform any essential function in the process prior to the final dry cure step, it need not be included in the initial solution but may be applied later from a separate pad bath, e.g., between the polymerization step (2) and the drying step (3). However, its inclusion in the initial bath may tend to distribute it more effectively throughout the polymer formed in the fixation step and hence make it more efficiently available in the final cure than when it is applied in the same concentration only after the fixation step.

The durable press article may be made by first making the dry uncured material into a garment having creases hot pressed therein and then curing the garment (delayed cure), or by first curing the material and then making the cured material into a garment (precure).

The essence of the present invention is the discovery that N-methylol compounds can be insolubilized or polymerized within moist swollen cellulosic fibers, i.e., fixed in the material into water insoluble products or resins, by exposure to a reactive atmosphere comprising formaldehyde and a gaseous acidic catalyst, and thereby at the same time usefully control and limit the debilitating effect which otherwise results when a fabric such as cotton is dry cured, and provide a fabric which can ultimately be dry cured without requiring any further application of cross-linking agent or catalyst after the fixation step. By controlling the amounts and relative time sequence in which the gaseous acid catalyst and the formaldehyde vapor are introduced into the process, particularly good process control can be achieved.

It is suggested that the gaseous acid thus introduced into the system promotes the fixation of the methylolated melamine or similar precondensate at the reactive sites in the cellulose fibers of the cotton which are inherently also capable of reacting with a cross-linker such as formaldehyde. By the expedient of exposing the cellulosic material in the processing chamber to formaldehyde only after some preliminary exposure to the acid catalyst, the extent of direct cross-linking of the cellulose fibers with formaldehyde is reduced and so the strength of the cotton is more fully retained.

In this manner, a desirable balance of physical and easy care properties is achieved, but yet no neutralization or washoff of catalyst is needed and the resulting material is suitable for either delayed cure or precure processing.

In accordance with the presently preferred embodiment of the present invention, the cellulosic material is first padded with an aqueous solution containing one or more polymerizable N-methylol compounds and a water-soluble salt serving as

a latent curing catalyst, and then the padded material containing the appropriate amount of moisture is heated and exposed to a reactive atmosphere of gaseous sulfur dioxide and formaldehyde vapor at a temperature of at least about 100° C., thereby causing the N-methylol compound to become fixed in the material and the formaldehyde to become attached thereto so as to be capable of causing the desired cross-linking during a final dry cure step.

In another embodiment of the present invention, the padded material is first exposed to one hot gaseous atmosphere at relatively high moisture conditions to heat the material and optimize distribution and/or fixation or polymerization of the N-methylol compound in the fiber system in the substantial absence of extraneous formaldehyde to effect heating and resin insolubilization in a single stage or in a sequence of stages and the heated and preconditioned material is then exposed to a different atmosphere at lower moisture conditions in a later stage to optimize fixation of formaldehyde in the system for the final cure.

These and other aspects, advantages and embodiments of the present invention will become more clearly apparent from the following more detailed description.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is useful for treating various natural or artificial cellulosic fibers alone or as mixtures with each other in various proportions or as mixtures with other fibers. They include natural cellulosic fibers such as cotton, linen and hemp, as well as regenerated or artificial cellulosic fibers such as viscose rayon and cuprammonium rayon. Other fibers which may be used in blends with one or more of the above mentioned cellulosic fibers are, for example, wool, silk, cellulose acetate, polyamides (e.g., nylon), polyesters (e.g., polyethylene terephthalate), acrylics, polyolefins (e.g., polypropylene), polyvinyl chloride, polyvinylidene chloride, and polyvinyl alcohol fibers. Such blends preferably include at least 20 percent by weight, and most preferably at least 40 percent by weight, of cotton or other natural or regenerated cellulose.

The material may be a knit, woven, nonwoven, or otherwise constructed fabric or the invention may be applied to fibers or yarns before they are converted into more complex structures. The material may be flat, creased, pleated, hemmed, or formed into virtually any shape after contact with the formaldehyde-containing atmosphere. After complete processing, the formed creaseproofed fabric will maintain the desired configuration substantially for the life of the article, that is, a durable press fabric will be produced which will retain its desired shape through numerous wear-wash-dry cycles, requiring little or no pressing.

The practice of the present invention characteristically involves the use of at least one water-soluble polymer-forming compound possessing reactive N-methylol groups, formaldehyde as a cross-linker, and a latent solid curing catalyst. On the one hand, upon exposure to a hot humid acid vapor atmosphere the polymer-forming compound is polymerized inside the cotton fibers while the latter are wet and swollen, so that the polymeric material so formed is fixed within the fibers and protects them against excessive strength loss which normally results from conventional creaseproofing treatments; and, on the other hand, the fixed polymeric material and cross-linker subsequently take part in cross-linking the cellulose when cured in the dry state in the presence of the latent curing catalyst.

The preferred polymer-forming N-methylol compounds at this time include the melamine-formaldehyde and the phenol-formaldehyde precondensates, though other N-methylol containing, polymer-forming compounds such as urea-formaldehyde precondensates are also useful.

The polymer formers useful herein include particularly the easily hardenable precondensates which are substantially water soluble and are obtained by condensation of formal-

dehyde with a compound such as melamine or a lower alkyl substituted melamine, a urea, or a hydroxy benzene such as phenol or resorcinol. The resulting methylol-containing compound or precondensate may further be etherified by reaction with a lower alkanol such as methanol or butanol. As is well known in the fabric treating art, these precondensates are capable of being applied to the cellulosic material from an aqueous solution and to be readily wet fixed or insolubilized therein as described, for instance, in U.S. Pat. No. 3,138,802. Triazines obtained by condensing a methyl or other lower alkyl substituted melamine and formaldehyde are further examples of such precondensates.

Good results are obtained, for instance, using precondensates obtained by condensing 1 mole of melamine or an alkyl substituted melamine with 2 to 6 moles of formaldehyde, i.e., using di-, tri-, tetra-, penta-, or hexa-methylol melamine. Such products function well as polymer-formers which can be readily wet fixed in the material by heating or steaming as described herein.

Commercially available products of this kind include Aerotex 23, an alkylated melamine-formaldehyde precondensate; Aerotex M-3, a dimethoxymethylhydroxymethyl-melamine; Aerotex P-225, a hexakis (methoxymethyl) melamine; and Aerotex 19, which is a less completely fractionated modification of Aerotex P-225. These products are supplied in the form of aqueous solutions by American Cyanamid Company. Equivalent products are commercially available from other manufacturers.

The practice of the present invention also involves the use of a conventional latent curing catalyst. For example, one can use a water-soluble salt of a strong acid with a weak base such as ammonium salts of hydrochloric, sulfuric, nitric, oxalic, lactic, or other inorganic or organic acid, various amine hydrochlorides, as well as acid acting salts of metals such as zinc or magnesium, e.g., zinc nitrate or magnesium chloride or a mixed catalyst such as $MgCl_2/ZnCl_2$, $MgCl_2$ /citric acid or $Zn(NO_3)_2$ /tartaric acid. Zinc nitrate, zinc chloride, magnesium chloride and ammonium chloride represent latent curing catalysts the use of which is particularly preferred in conjunction with the present invention.

To treat the cellulosic materials in accordance with the present invention, it is most convenient to apply the required N-methylol polymer-forming compound such as a methylolated melamine or a mixture of such compounds and a latent curing catalyst to the fabric initially from a common aqueous solution or pad bath. However, the curing catalyst may be omitted from this initial stage and only applied at a later stage of the process, as its presence is only required in the final dry curing step.

For example, when applying by conventional padding using customary equipment, or by spraying or other known processes, the polymerizable N-methylol compound or precondensate may be dissolved in water to form a solution containing from about 3 to 25 percent, and preferably from about 5 to 15 percent, of the N-methylol compound. To facilitate its ultimate cure in the cellulosic material, a curing catalyst may be included in this same solution, or in a separate solution, in an amount of between about 1 and 10 percent, and preferably between about 4 and 6 percent, based on the weight of the N-methylol compound. The optimum concentration depends somewhat on the particular catalyst and particular N-methylol compound used, and may be determined by routine preliminary tests.

Depending on the requirements of the finished materials or fabrics, the padding or impregnation is carried out in such a manner that the add-on of N-methylol compound deposited on the material is between about 3 and 12 percent, and preferably between about 6 and 8 percent, calculated as dry solid deposit based on the weight of dry fibrous material ("owf"). The padding is normally performed at ambient temperature, e.g., between about 10° and 30° C.

An essential feature of this part of the process is that the deposited N-methylol compound is fixed in the fibrous materi-

al together with a cross-linking component while the fibers are distended or swollen with water, so that the compound or precondensate becomes insolubilized in the fibrous cellulosic material without, however, converting the latter to a shape holding, crease resistant form at this stage, i.e., without altering the dry crease recovery angle of the fiber system to such an extent as to impede the creasing or other distinct shaping of such a fiber system during subsequent manufacture of garments or other products therefrom. Without wishing to be bound by any particular theory, it is believed by way of possible explanation that such fixation may achieve this result because the water swollen state of the fibers either prevents extensive cross-linking of the cellulose by any cross-linking compound present or, even if such cross-linking takes place, the fibers are greatly distended when so treated and hence the treated structure still retains a high degree of mobility when dried.

The aqueous padding bath may also contain other conventional fabric treating agents, for instance, wetting agents and fabric softeners, i.e., polymers capable of forming a soft film on the material or fabric. For example, suitable fabric softeners include a latex or fine aqueous dispersion of polyethylene, various alkyl acrylate polymers, acrylonitrile-butadiene copolymers, deacetylated ethylene-vinyl acetate copolymers, polyurethanes, and the like. Polymeric additives suitable for this general purpose are otherwise well known in the art and in most cases are commercially available in concentrated aqueous latex form. For use in the present invention, such a dispersion is preferably diluted to provide about 0.1 to 4 percent of softener based on the weight of the fabric ("owf").

After the cellulosic material has had the N-methylol compound padded on or otherwise applied, the fabric is heated while its moisture content is between about 15 and about 90 percent, preferably between 30 and 70 percent ("owf"), in the presence of a gaseous acid catalyst, so that the N-methylol compound is fixed in the material.

Maintaining an appropriate amount of moisture in the fabric, within the limits indicated, is important as it undergoes exposure to the hot vapor atmosphere or atmospheres. In the absence of sufficient moisture it appears that not enough polymer is fixed inside the fibers in the early stages of the vapor treatment to prop the fibers open and protect them against excessive cross-linking by formaldehyde during the later stages of the vapor treatment or during the final cure. As a result, the final product in such a case tends to suffer from a high strength loss analogous to the loss suffered in the conventional pad-dry-cure process.

On the other hand, when too much moisture is present, and particularly when water vapor present in the reactive vapor phase condenses as a liquid on the fabric, it appears that this unduly dilutes the acid which migrates from the vapor phase into the fabric. As a result the polymer-forming compound is left insufficiently catalyzed to produce the desired degree of polymerization or amount of fixed polymer in the fibers. Consequently, much of the potential advantage which the present invention is capable of providing can be lost either because of too much or because of too little moisture in the system. However, moisture conditions conducive to the production of optimum results are readily determined by preliminary empirical tests.

To obtain optimum process flexibility or process control, it is advantageous to separate the process into a plurality of more or less distinct stages, either by providing separate chambers for each such stage or by introducing the various treating fluids in a spatial and chronological sequence along the path on which the fabric moves. For instance, after the fabric is padded in the liquid bath containing the polymer-former, it is useful to pass it between squeeze rolls where excess liquid is squeezed out in preparation for the vapor treatment which represents the essential part of the present invention.

The squeezed padded fabric is then introduced into a first stage of a reaction chamber where it is heated to the desired reaction temperature, e.g., at least 80° C., but preferably between about 100° and 170° C., in a steam atmosphere while the moisture in the fabric is maintained at or adjusted to the appropriate level. The hot fabric is then passed over rollers to a second stage of the chamber where an acid gas, e.g., SO₂ or formic acid, is introduced such that it impinges upon the fabric while the latter remains at a predetermined temperature and moisture content. This causes the polymer-former to become substantially fixed inside the fibers. This, one can suggest, keeps the reactive sites on the cellulose from subsequently reacting to excess with the active cross-linker, e.g., formaldehyde.

From the preliminary polymerization stage the fabric is then passed to a third stage where formaldehyde is introduced such that it impinges upon the fabric while maintaining appropriate controlled conditions of temperature, moisture and acidity, which may be the same as or different from the corresponding conditions maintained in the earlier stages. For instance, after the polymer-former has been sufficiently fixed in the fibers while passing through the second stage, it is permissible and may be advantageous to maintain a substantially lower moisture content in the third stage than in the earlier stages. Such lower moisture level in the third stage can have the effect of facilitating not only the further polymerization of the polymer-former in the fibers but also the fixation of formaldehyde in the system.

By dividing the treatment into such separate stages, suitable adjustments in reaction temperature, moisture level, acidity and formaldehyde fixation can be most conveniently made as may be needed or desired. Separation of the process into stages can be satisfactorily achieved by passing the fabric through a single reaction chamber over a series of rollers arranged along a path defining the shape of an inverted V. Steam is produced from the residual moisture in the fabric after the fabric enters the heated chamber. SO₂ or other acid vapor is introduced and impinged upon the fabric near the entrance of the chamber. The formaldehyde in reactive form is introduced near the crest of the inverted V and impinged upon the heated fabric. The heated fabric having the polymer-former at least partially polymerized therein then passes along the downward leg of the inverted V toward the exit from the chamber.

Alternatively, the several phases of the process can be performed by passing the fabric through a series of completely separate consecutive chambers, or the entire vapor treatment can be performed by passing the padded fabric straight through a single stage containing a mixed atmosphere of water vapor, gaseous acid catalyst and formaldehyde. However, even in the latter embodiment it is advantageous to have at least some spatial separation between the points of introduction of the acid vapor and of the reactive formaldehyde, so as to permit at least some protective polymer to become fixed inside the moisture swollen fibers before the fabric is exposed to any high concentration of formaldehyde.

While the moisture content of the fabric being treated is important, the concentrations of water, acid and formaldehyde vapors present in the treating atmosphere or gas phase can be varied within wide limits and are not particularly important in and of themselves. To produce optimum results for any particular case, they can be readily coordinated with other factors such as kind and amount of polymer-former padded on, species of acid vapor employed, reaction temperature and fabric exposure time on the basis of preliminary trial runs and fabric evaluations. Generally speaking, the amounts of acid vapor and formaldehyde present in the vapor phase or phases filling the treating chambers are well in excess of the small amounts of such chemicals which are actually required for accomplishing the desired chemical reactions in the fabric being treated.

Sulfur dioxide has been found to give particularly good results and is the most preferred gaseous acid catalyst in the present invention, because it is especially adapted to form a

strong acid in the presence of formaldehyde, probably taking the form of a sulfonic acid, and yet is easy to remove from the fabric by drying subsequent to the vapor treatment. However, other acids which have a boiling point below about 120° C., e.g., formic or acetic acid, may be used instead of SO₂. Hydrochloric acid is similarly useful, though it may cause greater tendering of the fabric if it is left in the fabric without any counteracting acid acceptor over an extended period prior to final cure and washing.

In the preferred procedure, the wet cotton fabric is passed in a continuous manner through one or more zones containing the reactive acid and formaldehyde vapors and maintained at a temperature of at least 80° C., preferably from about 100° to 170° C. The fabric is passed through such a chamber or plurality of chambers or reaction stages at such a rate as to provide a total exposure time of from about 10 seconds to about 15 minutes, preferably 30 seconds to 2 minutes. Typically, in a multistage process as described earlier herein a fabric exposure time of about 1 minute at 102° C. to an atmosphere of water vapor and SO₂ in the first stage or stages and from about another 30 seconds to 1 minute in a subsequent formaldehyde-containing stage at a like temperature should be considered representative of satisfactory operating conditions.

The optimum vapor phase reaction condition is one which is just long enough to effect the desired degree of fixation of N-methylol compound (e.g., 3 to 12 percent of polymer based on the fabric) and active formaldehyde cross-linker (e.g., 0.2 to 5.0 percent on the fabric), without overexposing the fabric to the reactive atmosphere. In addition to the formaldehyde vapor and gaseous acidic catalyst the reactive vapor phase may also contain inert gases such as air, nitrogen, carbon dioxide, helium, and the like. Of course, steam is present in the hot vapor phase at least as a result of evaporation of water from the passing padded fabric or may be deliberately introduced as such into the treating chamber as a means of heating the padded fabric to the desired temperature or as a means of controlling the moisture content of the fabric at the desired level or levels while it is being treated. However, instead of using steam to maintain the desired reaction temperature, other sources of heat such as infrared lamps may be used.

The formaldehyde may be obtained for the process in any convenient manner, such as by heating a suspension of paraformaldehyde in mineral oil to generate formaldehyde gas or by passing air through an aqueous formaldehyde solution and metering the resulting formaldehyde vapor or vapor mixture in a suitable proportion into the reaction zone. When a highly methylolated melamine is used as the polymer-former, such a compound of itself may also furnish some active formaldehyde cross-linker when subjected to a high temperature in the eventual dry curing step.

After exposure to the reactive atmosphere, if the initial pad bath contained a latent curing catalyst, the cellulosic material is directly dried in preparation for the manufacture of a durable press article therefrom. No other intervening rinsing or other processing is required in such a case. Only if a latent catalyst was not included in the initial pad bath is it necessary to pass the fabric after the vapor treatment and before the drying step through a second pad bath containing an aqueous solution of a suitable latent curing catalyst, whereby the fabric becomes catalyzed for the eventual dry cure. Drying conditions are not especially critical but drying should be restricted so that the moisture content of the fabric does not fall below 6 to 10 percent and so that inadvertent precuring is avoided. For example, the treated cellulosic material may be dried at temperatures between about 20° and 60° C. for an appropriate time.

The durable press article may be made by first making the dry uncured material into a garment having creases hot pressed therein and then curing the garment ("delayed cure"), or by first curing the material in a flat state and then making a final product from the cured material ("precure").

The curing or final setting or creaseproofing of the treated fabric may be effected by dry curing in a walk-in air oven at

temperatures between about 100° C. and the charring temperature of the fabric, preferably at a temperature of about 120° to 180° C., or in any other convenient heating equipment. Curing may, for example, also be accomplished in equipment such as a garment press which has been provided with adequate heating and dwell time control means. A residence or dwell time of about 5 minutes in an air oven at 160° C. gives satisfactory cure in a typical case although curing times in the range from between about 2 to 10 minutes can commonly be used.

It will be understood, of course, that the cellulosic materials of the present invention may be treated with other conventional textile treating agents such as water repellants, antimicrobial agents, flame proofing agents, soil release agents, stain repellants, and the like as is otherwise well known to those skilled in the art.

The invention is additionally illustrated by the following examples. All parts and percentages are by weight in the examples, as well as in other parts of the specification and claims, unless otherwise indicated.

All these examples were conducted in accordance with the present invention using 100 percent cotton twill fabric having a weight of 7.6 ounces per square yard and a thread count of 166×52.

EXAMPLES 1-4

These examples were conducted using the preferred single pad procedure.

Samples of the cotton twill fabric about 5 yards long and 17 inches wide, weighing about 500 grams, were fed from a feed roll and padded to about a 70 percent wet pickup in aqueous baths maintained at room temperature (about 22° C.) and containing various amounts of hexakis (methoxymethyl) melamine precondensate ("Aerotex P-225") or dimethoxymethylhydroxymethylmelamine precondensate ("Aerotex M-3"), 0.5 percent zinc nitrate hexahydrate, 0.5 percent "Triton X-100" nonionic wetting agent, and 1.0 percent finely dispersed polyethylene fabric softener ("Velvamine 732"), as further indicated in Table I.

After lightly squeezing out excess liquid by passage through a pair of squeeze rolls, each of these samples was then passed over three transport rollers through a treating chamber having a volume of about 2½ cubic feet (about 18 inches wide, 12 inches long and 24 inches high), one of said rollers being disposed adjacent the fabric inlet slot at one side of the base of the chamber, the second roller being disposed near the top of the chamber on a line intermediate the two sidewalls of the chamber and the third roller being disposed adjacent the fabric outlet slot at the base of the chamber across from the inlet slot, whereby the fabric is passed through the chamber along an inverted V-shaped path about 4 feet in length.

Formaldehyde was generated by heating a paraformaldehyde-mineral oil mixture in a stainless steel tank. The heated vapor was carried by metered compressed air through heated tubes and one of several gas inlet manifolds into the reaction chamber. Sulfur dioxide was introduced from a tank and metered through the same or similar feed lines. In some tests both sulfur dioxide and formaldehyde gas were introduced into the chamber through a manifold located near the fabric entrance, but in the preferred operation only the SO₂ was introduced near the fabric entrance at the bottom while the formaldehyde was introduced in the interior of the chamber near the top roller. Steam injection was also available and was used in a few runs, but generally was found unnecessary in this small scale equipment because an adequate moisture content was easy to maintain in the padded fabric without steam injection. However, in commercial scale equipment steam injection may offer improved moisture control for optimum resin fixation.

By varying the fabric speed, exposure times of fabric in the chamber were capable of variation from 30 seconds to 3 minutes, as desired.

At the beginning of each run the formaldehyde generator was loaded with 200 grams of paraformaldehyde. Airflow into the generator was generally 5 cubic feet/hour while sulfur dioxide was supplied at 4 cubic feet/hour, measured at about 22° C. and about 1 atmosphere. The formaldehyde generator temperature ranged from 120° to 140° C. and the treating chamber was in most cases maintained either at about 102° C. or at about 118° C. depending on the desired reaction conditions.

In typical runs about 100 grams SO₂ and 50 grams formaldehyde was introduced into the treating chamber while treating a 500 gram, 5 yard long sample of cotton fabric. However,

Data pertaining to a number of runs which are representative of the invention, as well as the run in which the sample was treated according to the earlier steam wet fix procedures, are summarized in Table I.

As may be seen from Table I, fabrics treated in accordance with the present invention have a desired balance between easy care properties (durable press, crease retention, wrinkle recovery) and physical properties (breaking and tearing strength, Stoll flex abrasion), along with the commercially significant advantage of short processing times (no washoff needed and only 1 to 2 minutes reaction time). A comparison between Example 5 and Examples 1-4, points to the fact that

TABLE I.—PROPERTIES OF FABRICS, UNCURED AND CURED, HAVING POLYMER FIXED THEREIN BY VAPOR TREATMENT

Example number.....	1		2		3		4		5		Conventional steam wet fix
Precondensate in bath.....	10% P-225 ¹		7% F-225 ¹		10% M-3		5% M-3 plus 5% P-225		10% P-225		
Reaction time.....	1 min. ²		1 min. ³		1 min. ²		1 min. ²		3 min. ³		As prescribed in text
Reaction temperature.....	120° C.		120° C.		120° C.		102° C.		102° C.		
Cure 160° C./5 min.....	No	Yes	No	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes
Appearance:											
Durable press rating.....	3.1	4.0	3.1	3.4	2.6	3.8	3.8	3.7	3.2		
Crease retention rating.....		4.3		4.6		4.2	4.1	4.2	44.7		
Wrinkle recovery (W+F) (AATCC 66-1959T):											
Dry, deg.....	211	282	235	273	225	282	286	276	282		
Wet, deg.....		250		236		234					
Breaking strength (Fill, Grab) (ASTM D-39-49):											
Pounds.....	65	43	71	47	74	58	48	42			
Percent retention.....	89	59	97	64	99	77	62	48	72		
Tearing strength (fill) (ASTM D-1425-59):											
Grams.....	2,240	1,205	2,380	1,290	2,660	1,850	1,860	1,015			
Percent retention.....	91	49	97	53	105	73	69	36	73		
Stoll flex abrasion (fill) (ASTM D-1175-61T using heat and tension loads of 0.5 and 2 pounds, respectively):											
Cycles to failure.....						1,013	792	235			
Percent retention.....						116	86	40			
Add-on polymer: (Percent, 1 L+D).....		10.7		8.4		11.4	8.3	8.8	74		

¹ The polyethylene softener was padded on in a separate bath after the vapor phase treatment but before drying.

² SO₂ was jetted into bottom of chamber at fabric inlet, formaldehyde was jetted in separately near top of chamber.

³ Mixed SO₂ and formaldehyde vapors were jetted in together at fabric inlet near bottom of chamber.

these amounts of vapors were several times in excess of minimum requirements. In a commercial size chamber having a much larger volume and proportionately less gas leakage satisfactory results should be achievable while introducing into such a chamber as little as 3 to 5 grams SO₂ and 2 to 3 grams formaldehyde per 100 grams of cotton fabric.

Following vapor treatment, the fabrics were dried in an air oven at 52° C. for about 20 minutes and, after pressing, air cured at 160° C. for 5 minutes, laundered (AATCC 124-1967 III B), and the appearance and other properties evaluated after one cycle of laundering and tumble drying (1 L+D). In addition, in some cases the fabrics were also evaluated prior to curing, after the vapor treatment and drying. Moreover, some of the treated dried samples were laundered before curing and their properties measured.

For comparison, a sample of the same cotton twill sample was also treated by a previously used steam wet fix procedure, similar to that described in copending application, Ser. No. 764,950. More particularly, in this run the fabric was padded at 60 percent wet pickup in a bath containing 29 percent Aerotex 19 methylolated melamine (65 percent active compound), 38 percent Fixapret PCL modified methylolated propylene acid (50 percent active compound), 0.1 percent Triton X-100 wetting agent, the bath being adjusted to a pH of 2 by addition of an appropriate amount of sulfuric acid.

After padding, this sample was steamed in the steam chamber at 102° C. for 45 seconds, neutralized in 0.5 percent sodium carbonate solution, rinsed, washed and dried. Thereafter it was catalyzed by padding at 60 percent wet pickup in a solution containing 0.8 percent ZnNO₃·6H₂O and 2 percent polyethylene softeners. After drying, the sample was dried, pressed and air cured at 160° C. for 10 minutes, the same as all the other samples, and its appearance and other physical properties determined.

injecting SO₂ and formaldehyde in sequence rather than simultaneously results in better strength retention. In all cases, the wrinkle recovery of the uncured fabric was low enough for delayed cure processing. Further, when compared to the same cotton twill fabric treated by conventional steam wet fix procedure, the cured fabrics processed according to the present invention generally had better easy care properties with comparable physical properties.

EXAMPLES 2/1-2/4

In another series of runs, samples of the cotton twill fabric were padded to about a 70 percent wet pickup in aqueous baths containing 10 percent Aerotex P-225 precondensate of Aerotex M-3 precondensate, 0.5 percent ("owf") zinc nitrate, 0.5 percent Triton X-100 nonionic wetting agent, and 1.0 percent ("owf") finely dispersed polyethylene fabric softener (Velvamine 732), and then treated consecutively in two different vapor atmospheres as indicated. The data from these runs are summarized in Table II.

In the first vapor pass, the samples were exposed to an atmosphere consisting of saturated steam, or an atmosphere comprising gaseous sulfur dioxide and saturated steam, at about 102° C. for either 1 or 3 minutes to deposit or fix the precondensate inside the fibers, as indicated in Table II.

In the second vapor pass, the samples were exposed to an atmosphere comprising a mixture of formaldehyde vapor, air and gaseous sulfur dioxide at 102° C. for 3 minutes in runs 2/1, 2/2 and 2/3, and at 115° C. for 1 minute in run 2/4.

The thus treated samples were then air dried at about 50° C. Some of the dried samples were laundered and their fabric properties measured as was done in Examples 1-5.

The remaining samples were creased by hot iron pressing, air cured at about 160° C. for 5 minutes, laundered, and their fabric properties measured as was done in Examples 1-5.

TABLE II.—Properties of Fabrics, Uncured and Cured, After Various Steaming and SO₂/Formaldehyde Treatments

Example Number	2/1		2/2		2/3		2/4	
Precondensate in bath	10% M-3		10% P-225		10% M-3		5% M-3 plus 5% P-225	
Steaming stage, 102° C./3 min.	Saturated steam only		Saturated steam plus SO ₂		Saturated steam plus SO ₂		Saturated steam (102° C./1 min.)	
Vapor fixation stage 102° C./3 min.	SO ₂ plus formaldehyde		SO ₂ plus formaldehyde		SO ₂ plus formaldehyde		SO ₂ plus formaldehyde (115° C./1 min.)	
Cure, 160° C./5 min.	No		No		No		Yes	
Appearance (1 L+TD): durable press rating	3.1	3.3	2.8	3.4	2.9	3.4	3.6	3.6
Crease retention rating		4.0		4.0		3.2		3.4
Wrinkle recovery (W+F):								
Dry, deg.	270	286	252	301	241	287	299	
Wet, deg.		245		251		227		
Breaking strength (F, grab):								
Pounds	65	40	62	40	70	50	53	
Percent retention	83	51	79	51	90	64	55	
Tearing strength (F):								
Grams	2,415	1,520	2,125	1,285	2,590	1,765	1,915	
Percent retention	82	51	72	43	88	60	74	
Stoll flex abrasion (F):								
Cycles to failure	1,950		1,915		2,850		679	
Percent Retention	175		176		262		68	
Add-on polymer: Percent, 1 L+D		11.3		9.8		10.3		

As may be seen from Table II, fabrics treated in accordance with this aspect of the present invention also have a useful level of easy care and physical properties. Generally speaking, however, they do not exhibit any significant advantage over the fabrics from Examples 1-5 which were treated by the more rapid and somewhat simpler procedure, without any added steam.

EXAMPLE 3/1

To illustrate the effectiveness of the vapor phase treatment in fixing a polymer-former in cellulosic fibers, a pair of comparative tests was conducted, one of which included a vapor treatment in accordance with this invention while the other one did not.

More particularly, two samples of the cotton twill fabric described earlier herein was padded in a bath containing 4 percent M-3 methylolated melamine plus 4 percent P-225 methylolated melamine, and 0.8 percent Zn(NO₃)₂·6H₂O. After such padding, one of these samples was subjected to vapor phase fixation treatment with SO₂ and formaldehyde analogous to that described earlier for Examples 1-4 (Table I), after which it was laundered, recatalyzed by padding in a solution containing 0.8 percent ZnNO₃·6H₂O, dried, cured for 5 minutes at 160° C., and again laundered and dried, while the other sample was laundered, catalyzed, dried, cured, relaundered and dried in exactly the same manner but without any intervening vapor phase fixation step.

The results are summed up in Table III.

TABLE III.—COMPARISON OF FABRICS PADDED WITH "MELAMINES", WITH AND WITHOUT VAPOR PHASE TREATMENT.

Example	3/1-A	3/1-B
Precondensate in bath	4% M-3 plus 4% P-225	None
Vapor treatment with HOCHO/SO ₂	1 min./120° C.	
Durable press rating	3.4	2.4
Wrinkle recovery (W+F) dry, deg.	272	221
Breaking strength (F):		
Pounds	60	74
Percent retention	62	71
Tearing strength (F):		
Grams	2,020	2,900
Percent retention	76	103
Stoll flex abrasion (F):		
Cycles to failure	1,147	
Percent retention	116	
Add-on, percent	4.0	1.2

As is evident from Table III, the vapor treatment of the present invention converts the aminoplast precondensate to an insoluble form which resists laundering and upon recatalyzing of the fabric can serve to impart durable press properties to the fabric when dry cured. By contrast, in the absence of any such vapor treatment most of the precondensate remains water soluble such that it is removed by laundering and a subsequent cure is then incapable of producing satisfactory durable press properties. The difference in add-on determined on

the final cured samples further confirms the effectiveness of the invention in fixing the aminoplast in a substantially insoluble form in the fabric while in the absence of such vapor treatment only a small fraction of the initially applied aminoplast remains on the fabric after laundering.

It should be noted that in comparing the procedure of Example 3/1-A with the procedure used in all earlier examples, a laundering step and a recatalyzing step were interposed between the vapor treating step and the dry curing step. This procedure permits the evaluation of the effectiveness of the resin fixation achieved by the vapor treatment, but is not required for any practical reasons. As shown in Table III, the easy care properties of the fabric in Example 3/1-B are not developed because in the absence of the vapor treatment there is insufficient resin fixation.

While the foregoing specification describes the general principles and nature as well as preferred embodiments and modifications of the present invention, still other modifications may be made by those skilled in the art without departing from the scope and spirit of the appended claims.

We claim:

1. A process for treating a cellulosic fiber-containing textile material so as to make it susceptible to improvement of its crease retention and smooth drying characteristics by a subsequent cure, which process comprises

a. applying to the material an aqueous solution comprising at least one water-soluble polymer-forming precondensate possessing reactive N-methylol groups;

b. exposing the material while swollen by moisture at a temperature of at least 80° C. to a reactive atmosphere comprising formaldehyde vapor and a gaseous acid whereby said polymer-forming precondensate becomes fixed in the material;

c. applying to the material a latent acid curing catalyst either as a component of the aqueous solution of step (a) or in the form of a separate aqueous solution which is applied after fixation step (b) and prior to drying step (d); and

d. drying the material in preparation for the manufacture of a durable press article therefrom.

2. In combination with the process of claim 1, the further steps of making the dried material into a garment having at least one hot pressed crease therein, and thereafter heating the garment in a substantially dry state at a temperature between about 120° and 180° C., thereby imparting durable press properties thereto.

3. The process of claim 1 wherein the gaseous acid is selected from the group consisting of sulfur dioxide, formic acid, acetic acid and hydrogen chloride.

4. The process of claim 3 wherein the cellulosic fiber-containing material comprises at least 20 percent cellulosic fibers, and wherein the aqueous N-methylol precondensate solution

applied to the material comprises a hardenable methylolated melamine compound and precondensate is fixed inside the cellulosic fibers by heating the material at a temperature of at least about 80° C. in a vapor phase comprising a gaseous acid and formaldehyde while maintaining the moisture content of the material between about 15 and 90 percent based on the weight of the material.

5 The process of claim 3 wherein the material having the aqueous solution of the N-methylol compound applied thereto is heated at a temperature of at least about 100° C. under controlled moisture conditions prior to exposing the material to the reactive atmosphere comprising a mixture of gaseous acid and formaldehyde.

6. The process of claim 5 wherein the material having the N-methylol precondensate applied thereto is heated under controlled moisture conditions in an atmosphere comprising sulfur dioxide before exposure to a mixture comprising reactive formaldehyde and sulfur dioxide.

7. A process for making a cotton-containing fabric suitable for having improved crease resistance and smooth drying characteristics imparted to it upon eventual curing, which process comprises

a. applying to the fabric an aqueous solution comprising (i) at least one water-soluble formaldehyde-melamine precondensate having reactive N-methylol groups and (ii) a latent acid curing catalyst;

b. heating the fabric at a temperature between about 100° and 170° C. in a vapor treating zone while the moisture content of the fabric is maintained between about 30 and 70 percent and exposing the fabric to a reactive vapor atmosphere comprising formaldehyde vapor and gaseous sulfur dioxide, thereby fixing the precondensate and formaldehyde inside the cotton fibers; and

c. drying the vapor treated fabric to a moisture content no lower than 6 percent.

8. The process of claim 7 wherein the latent curing catalyst is selected from the group consisting of zinc nitrate, zinc chloride, ammonium chloride, and magnesium chloride, and wherein the vapor treated and dried fabric is heated at a tem-

perature between about 120° and 180° C., thereby imparting durable press properties thereto.

9. The process of claim 7 wherein the fabric is maintained in said vapor treating zone for a period of from about 10 seconds to about 15 minutes, and wherein the vapor treating zone comprises a plurality of successive treating stages, sulfur dioxide being introduced principally into a first stage while formaldehyde is introduced primarily into a succeeding stage.

10. A process for improving the crease resistance and smooth drying characteristics of a cotton fabric, which process comprises

a. padding an aqueous solution comprising about 3 to 25 percent of a water-soluble, hardenable formaldehyde-melamine precondensate having reactive N-methylol groups and a formaldehyde to melamine ratio of between about 2:1 and 6:1 and about 1 to 10 percent, based on the amount of formaldehyde-melamine precondensate, of a water-soluble curing catalyst selected from the group consisting of zinc nitrate, zinc chloride, ammonium chloride and magnesium chloride;

b. passing the padded fabric at a moisture content between about 30 and 70 percent through a sequence of vapor treating stages comprising gaseous sulfur dioxide and formaldehyde vapor at a temperature between about 100° and about 120° C. at a rate resulting in a vapor exposure time of from about 30 seconds to 6 minutes, thereby fixing between about 6 and 8 percent of the N-methylol compound and between about 0.2 to about 5 percent active formaldehyde in the fabric;

c. drying the exposed fabric;

d. making the dried fabric into a garment;

e. curing the garment at a temperature of about 120° to 180° C.; and

f. laundering residual soluble chemicals from the cured garment.

11. A process according to claim 10 wherein sulfur dioxide is introduced into a first vapor treating stage and formaldehyde vapor is introduced into a succeeding vapor stage.

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