

[54] **MULTI-STEP REACTION OF TEXTILE MATERIALS WITH MULTI-FUNCTIONAL GROUPS REACTIVE UNDER DIFFERENT CATALYTIC CONDITIONS**

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- [63] Continuation of Ser. No. 244,273, Dec. 13, 1962, abandoned.
[52] **U.S. Cl.**.....**8/116.3**, 8/DIG. 4, 8/DIG. 21, 8/115.7, 8/116.2, 8/116.4, 8/120, 117/139.4, 38/144, 2/243
[51] **Int. Cl.**.....**D06m 15/54**, D06m 15/72
[58] **Field of Search**.....8/116.3, 120; 38/144

References Cited

UNITED STATES PATENTS

- 3,561,916 2/1969 Baitinger 8/116.3

- 3,423,163 1/1969 Magat et al. 8/116.3
2,837,511 6/1958 Mantell.....8/116.3
3,138,802 6/1964 Getchell 8/116.3

OTHER PUBLICATIONS

- Hickner et al., Journal of Organic Chemistry, Vol. 32, pp. 729-733 (1967)
Sumrell et al., Textile Research Journal, Vol. 39, pp. 78-85 (1969)

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[57] **ABSTRACT**

Cellulosic fabrics are modified in two steps with compounds containing at least one group reactive under conditions of acid catalysis and at least one group reactive under conditions of alkaline catalysis, e.g., N-methylol acrylamides. In conducting the process, either the acid or the alkaline catalyzed reaction may be run first; the fabric may be formed into a garment subsequent to the first reaction but prior to the second reaction and an alkaline catalyst may be used which is substantially neutral on the fabric at ambient temperatures but becomes strongly alkaline at elevated temperatures.

8 Claims, No Drawings

MULTI-STEP REACTION OF TEXTILE MATERIALS WITH MULTI-FUNCTIONAL GROUPS REACTIVE UNDER DIFFERENT CATALYTIC CONDITIONS

This application is a continuation of application Ser. No. 244,273, filed Dec. 13, 1962 and now abandoned.

This invention relates to novel processes for producing garments of cellulosic materials which are characterized by a propensity for subsequent durable setting into any desired configuration, for example, creased, pleated, embossed and/or flat, to the fabrics from which said garments are made and to the garments so produced.

Cotton fabrics having varying degrees of dry and wet resiliency properties can be produced by a wide variety of chemical processes which generally involve crosslinking the cellulose molecules of the fabric while the fabric is in a flat state, the wash-and-wear properties being obtained as a result of the fabrics' tendency to return to the flat state after distortion and/or wetting thereof, depending upon the particular treatment given the fabric, i.e., whether the fabric has imparted to it, both dry and wet resiliency properties, or only one type. This tendency to return to a flat state is highly desirable, but this property also greatly complicates the proper creasing or pleating of garments made from the fabric. In general, garments made from flat-set fabrics are difficult to crease or pleat and the distorted configuration obtained is removed from the garment by moisture, such as during laundering.

This difficulty has led to a number of expedients for developing the flat setting property simultaneously with the creasing or pleating operation, such as by spraying the garment with a cross-linking reagent and immediately thereafter conducting the cross-linking reaction while holding the garment in the desired distorted configuration, e.g., creased or pleated.

These processes are generally unsatisfactory in that the garment manufacturer must conduct the process and they are not always equipped to conduct the process under most favorable conditions. The garment manufacturer also must have access to special spray equipment and must use and keep the necessary chemical formulations in his own facilities. Furthermore, these prior procedures generally involve resins, which release large quantities of noxious vapors during pressing. Also, these procedures generally produce only one type of resiliency properties.

It would be highly desirable if the garment manufacturer could be provided with a fabric which he could cut and sew into garments and press in a relatively simple manner, without any chemical treatment, to provide a durably set configuration in addition to both wet and dry resiliency properties, i.e., a fabric which is presensitized, or has a propensity, for subsequent durable setting.

It is an object of this invention to provide a fabric having a propensity for subsequent durable setting into any desired configuration, such as creased, pleated, embossed and/or flat.

Another object of this invention is to produce such fabrics at the mill level and ship them to garment manufacturers in a state whereby no further chemical treatment is necessary in order to provide garments having both wet and dry resiliency properties and sharp creases or pleats.

Yet another object of this invention is to produce garments from such fabrics and set these garments in the desired configuration, so that noxious vapors are not released, and both the desired creased or pleated area and the flat portions of the garment remain substantially in their set configuration after subsequent exposure to wet conditions.

These and other objects are accomplished in accordance with this invention which comprises providing cellulosic material, preferably fabric, corresponding to the general formula:



wherein Cell is the residue of a cellulose molecule and R is an organic radical reactive with cellulose under catalyzed condition: impregnating the cellulosic material with a compound which catalyzes the reaction between R and cellulose at elevated temperatures, most preferably only at elevated tem-

peratures, and drying the cellulosic material under conditions insufficient to initiate substantial reaction.

This fabric is then shipped to the garment manufacturer while being maintained under conditions whereby substantial reaction of the R group with hydroxy groups of cellulose is precluded until after a garment is produced therefrom. The garment is then characterized by a propensity for subsequent durable setting in any desired configuration, merely by holding the garment in the desired configuration while subjecting the garment to conditions whereby the system is activated for substantial reaction, whereby the R group reacts with another hydroxy group of a cellulose molecule to form a stable, cross-linked garment having wet and dry resiliency properties as desired.

The etherified cellulose produce Cell — O — R, which generally already has dry or wet resiliency is preferably produced by impregnating a cellulosic material with (1) a polyfunctional compound containing at least two groups reactive with hydroxy groups of cellulose, at least one of the groups being reactive with hydroxy groups of cellulose under conditions markedly different from the reactivity of at least one other of the groups and (2) a catalyst for the reaction of only one of the reactive groups with hydroxy groups of cellulose. The desired etherified cellulose product is then produced by exposing the cellulosic material to conditions, generally of elevated temperatures, whereby the catalyzed group reacts with hydroxy groups of cellulose to provide either dry or wet resiliency properties, and under which the other class of reactive groups is substantially non-reactive with cellulose.

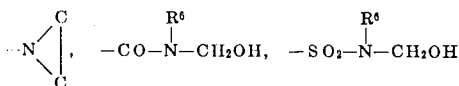
A cellulosic material presensitized for subsequent durable setting can then be produced by impregnating the cellulosic material with a compound which catalyzes the reaction between the remaining class of reactive groups and cellulose at elevated temperatures and drying the cellulosic material at temperatures sufficiently low that substantial reaction does not occur.

Upon subsequent curing, during pressing or afterwards as desired, both wet and dry resiliency properties may be imparted to the fabric, depending on the state of swelling of the fabric at the time the last cure step is conducted, wet resiliency properties being obtained predominantly on highly swollen fabrics with dry resiliency properties being obtained predominantly in an unswollen state. If the initial cure is conducted on the acid side, as when the acid-reactive group of a difunctional compound is reacted first with hydroxy groups of cellulose, and the last cure on the basic side, excellent wet resiliency properties are obtained at higher moisture levels. At low moisture levels, excellent dry resiliency properties are obtained. At some balanced intermediate state of swelling (and this swelling though preferably obtained with water may be accomplished through use of other swelling agents such as organic solvents or inorganic salts), depending in each instance on the particular compounds utilized, a high degree of both wet and dry resiliency properties are obtained. In general, however, some improvement in dry resiliency properties with substantial improvement in wet resiliency properties is obtained at moisture levels no greater than about 20 percent in excess of the regain moisture level of the fabric. For many of the reagents utilized, both wet and dry resiliency properties are well balanced at high levels when the total moisture in the fabric is less than about 10 percent or when the fabric is at a comparable degree of swelling.

It should be realized, however, that regardless of the moisture level during the final cure, durable creases are obtained, when the fabric is creased during the cure, with high levels of dry or wet resiliency.

Preferably, the polyfunctional compound utilized to produce the above presensitized fabrics and garments is one of a class of organic compounds containing at least one terminal group reactive with hydroxy groups of cellulose under acidic conditions and at least one other terminal group reactive with hydroxy groups of cellulose under alkaline conditions.

The acid reactive groups are generally those found in the textile resins presently employed in the resin treatment of cellulosic fabrics, e. g., methylol, epoxy, acetal, alkylated methylol, aldehyde,

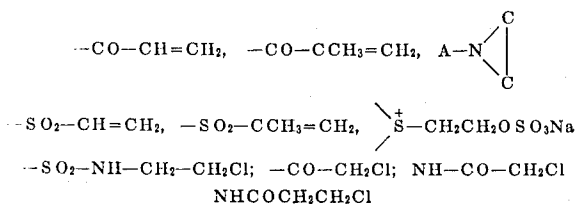


wherein R is hydrogen or alkyl, $-\text{N}=\text{C}=\text{O}$, $-\text{N}=\text{C}=\text{S}$ and the like. These groups are characterized by their ability to combine with the hydroxy groups of the cellulose molecule under textile resin curing conditions. The term "textile resin" as used herein is in conformity with the generally accepted usage in the textile art; i. e., it defines a thermosetting reagent which is applied to a textile fabric and reacted therewith when the dry fabric is heated, usually in the presence of an acid-acting catalyst, at a temperature usually between about 140° to 200° C. These latter conditions are referred to herein as "textile resin curing conditions." At these temperatures, the reagent, even by itself, will ordinarily resinify in the presence of an appropriate catalyst, thus probably contributing to the use of the term "resin treatment." However, it is to be understood that the term as used in the textile art is a misnomer in that in contradistinction to the generally accepted meaning of the term resin, "textile resins" are of relatively low molecular weights, are almost always water soluble and are often liquids.

Included in the class of textile resins are urea-formaldehyde and the melamine-formaldehydes, e. g., dimethylol-urea and tetra- and penta-methylol-melamines; the acrolein-urea-formaldehyde resins; the cyclic ethylene urea-formaldehyde resins, e. g., dimethylol cyclic ethylene urea and dimethylol dihydroxy cyclic ethylene urea; trimethylol-acetylene diurea and tetra-methylol-acetylene diurea; the triazines, e. g., dimethylol-N-ethyl-triazine, dimethylol-N-hydroxyethyl-triazine and N, N'-ethylene-bis-dimethyloltriazine; and the urons, e. g., dimethylol uron.

These aminoplast textile resins exemplify the wide variety of structures which can be used to contribute an acid reactive group to the polyfunctional compounds employed in the process of this invention. Other non-nitrogen containing textile resins can also be employed, e. g., the epoxy and acetal textile resins. It will be obvious to one skilled in the art that the choice of compound employed to contribute the base reactive group will be influenced by the functional groups present in the compound contributing the acid reactive group.

The base-reactive groups are those which have the capacity of reacting with the hydroxy groups of the cellulose molecule in the presence of strong base at elevated temperatures and include epoxy and halohydrin groups, and carbonyl, acetylenic, sulfone and sulfoxide activated groups, e. g., of the formula $-\text{CH}_2\text{CH}_2-\text{A}-\text{A}'$ wherein A is a carbonyl, sulfone, sulfoxide or acetylenic group and A' is sulfatoethyl, alkali-metal sulfatoethyl, phosphatoethyl, alkali-metal phosphatoethyl, thiosulfatoethyl, and alkali-metal thiosulfatoethyl, quaternary ammonium ethyl halides, e. g., pyridinium ethyl chloride, vinyl or substituted, e. g., lower alkyl vinyl, sulfonylhalide, such as sulfonylfluoride



chloro-S-triazine and the like.

Both the acid reactive and base reactive groups can be epoxy if one of the epoxy groups has a lower order of activity

than the other under textile resin curing conditions so that it does not, at that step, react with the cellulose. Employing a mild catalyst such as, for example, zinc chloride, magnesium chloride or an amine hydrochloride will facilitate such a preferential reaction.

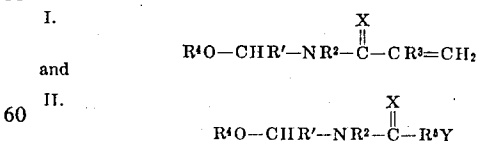
Compounds which can be employed to contribute the base-reactive group to the polyfunctional compounds employed in the process of this invention include polyhydroxy compounds, at least one hydroxy group of which is activated and esterified. Esters of activated hydroxy groups can be carried through the heating step under textile resin curing conditions and will then be available to react with the cellulose molecule in the presence of strong aqueous base. The unesterified hydroxy group is available to react with the compound contributing the acid reactive group, e. g., an amino-plast textile resin, thereby producing a polyfunctional compound having both acid and base reactive groups. Within the above definition are included the mono-esters of di-β-hydroxyethyl-sulfone and di-β-hydroxyethyl-sulfoxide. The mono-ester can be the sulfate, phosphate, or thiosulfate, preferably in the form of their alkali-metal salts, or an organic ester, e. g., lower alkanoate, or other alkyl, aryl, alkaryl, or arylalkyl ester, preferably hydrocarbon and containing from one to 12 carbon atoms.

Because of the activated character of the hydroxy groups of the starting compounds, the mono-esters thereof can readily be prepared by employing a mole of the esterifying reagent per mole of the starting dihydroxy compound. Only very mild esterification conditions are required. For example, the sulfato mono-ester can be prepared at room temperature with about two molar equivalents of concentrated sulfuric acid. The reaction product can be converted to an alkali-metal salt by pouring into ice water and then carefully neutralizing to a pH of about 4 with, e. g., sodium carbonate.

A method of producing an alkali-metal salt directly involves mixing the starting dihydroxy compound with about a molecular equivalent of sodium or potassium bi-sulfate and then heating while removing the water of reaction, usually with an azeotropic solvent. These mono-esters can then be reacted with an aminoplast polymethylol textile resin either prior to applying the compounds to the selected textile material or subsequent thereto.

Examples of compounds containing acid and base-reactive groups which can be used in the process of this invention are the reaction products of the sodium salt of the sulfato mono-ester of di-β-hydroxyethyl-sulfone with dimethylol urea, dimethylol-N-ethyl-triazine, dimethylol-N-hydroxyethyl-triazine, dimethylol cyclic ethylene urea, or dimethylol-dihydroxy-cyclic ethylene urea, and the reaction products of the corresponding acetic acid mono-ester with each of the above textile resins.

While the above compounds are entirely suitable for use in accordance with this invention, preferred compounds include those characterized by the formulae:



wherein R' is selected from hydrogen, lower alkyl, and the residue of a saturated or unsaturated aldehyde; R² is selected from hydrogen, lower alkyl, and $-\text{CX}-\text{CR}^3=\text{CH}_2$; R³ is selected from hydrogen and methyl; R⁴ is selected from hydrogen and lower alkyl; R⁵ is selected from $-\text{CHR}^3$, $-\text{CH}_2\text{CH}_2-$, and

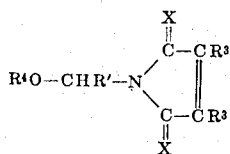


X is selected from sulfur and oxygen and Y is halogen, such as chlorine, bromine or iodine.

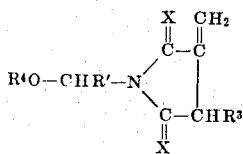
Additional suitable compounds include imides, such as

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III.

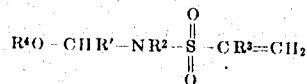


IV.



and the like; vinyl sulfonamides, such as

V.

and the like, wherein R¹, R², R³, R⁴ and X are as defined above. The

can have substituted therefor



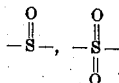
and sulfonium if desired.

In any of the compounds shown herein particularly those characterized by formulae I and II above, the

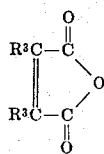


groups have substituted

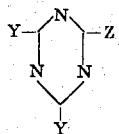
therefor



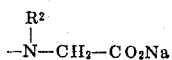
and sulfonium if desired. Additional compounds having reactive groups of markedly different orders of reactivity include anhydrides, such as



and the like; halotriazones, such as



wherein Z is an organic radical, such as



and the like. The base-acting catalysts shown herein may be utilized to initiate the desired reactions.

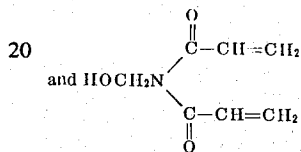
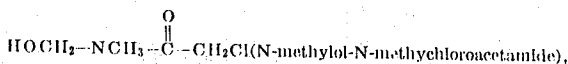
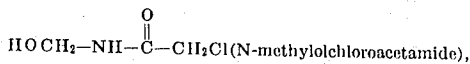
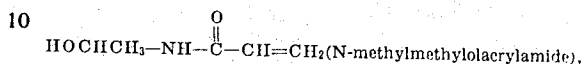
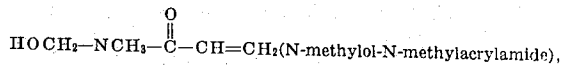
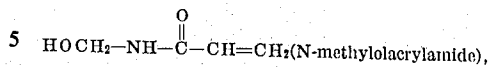
Included in the above polyfunctional compounds are those wherein the methylol group is derived from aldehydes other than formaldehyde, such as those derived from saturated or unsaturated aldehydes, whereby R² would be lower alkyl, e.g., acetaldehyde; vinyl, e.g., acrolein; acetyl, e.g., pyruvaldehyde; CH₃CH=CH-, e.g., crotonaldehyde;



e.g., methacrolein; OCH(CH₂)_N- wherein N=0-4, e.g., glyoxal (N=1); OCH(CH₂)₃CHOH-, e.g., hydroxy adipaldehyde and the like.

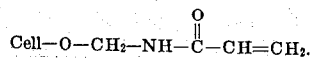
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Preferred compounds characterized above are the methylol acrylamides and halo-acetamides, e.g.,



25 the methylol groups of which are reactive with the hydroxy groups of cellulose under textile resin curing conditions, as with an acid-acting catalyst at elevated temperatures, the CH₂CH- and -CH₂Cl groups being reactive with hydroxy groups of cellulose under the influence of strong base at elevated temperatures.

For example, when a cellulosic fabric impregnated with N-methylolacrylamide and an acid-acting catalyst is exposed to textile resin curing conditions, the following cellulose ether is formed:



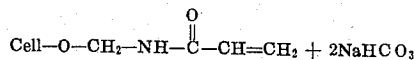
The fabric is then padded with a catalyst which catalyzes the reaction between the ethylenically unsaturated group and hydroxy groups of cellulose only at elevated temperatures, e.g., NaHCO₃ which forms strongly basic Na₂CO₃ upon heating to temperatures in excess of about 65° C. After drying at lower temperatures, the fabric may be shipped to a garment manufacturer who can store the mildly alkaline fabric until ready for use, so long as activating conditions are not produced.

Activating conditions generally arise as a result of a combination of pH of the fabric and temperature. Generally temperatures in excess of about 80° C. and pH levels of 9 or greater are reached before substantial reaction occurs.

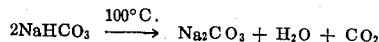
In some instances, pH alone will initiate the reaction, e.g., as when sodium hydroxide is utilized. If so, and this is not a preferred technique, retarding agents should accompany the strong base. It is preferred, however, to utilize one of the preferred latent base-acting catalysts set forth below. Garments can then be made from the fabric. These garments can then be folded and pressed on conventional equipment, e.g., a Hoffman press, where activating conditions are produced as a result of the high temperature. For example, a pair of trousers made from the "presensitized" fabric can be placed on the press in the desired configuration. The press is then closed and the trousers are steamed and pressed for a sufficient period of time, e.g., 30 seconds to 1-5 minutes or more, to effect substantial reaction between the ethylenically unsaturated group and hydroxy groups of cellulose.

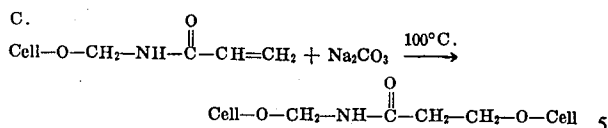
During this second cure under basic conditions, the cellulose is cross-linked as follows:

A.



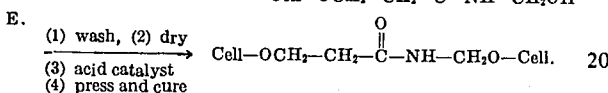
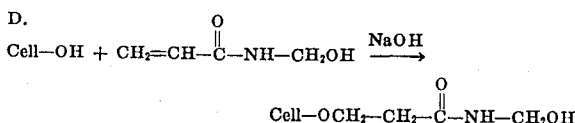
B.





The configuration of the garment when reaction C. takes place, both creased or pleated and flat or otherwise, will be substantially retained after exposure to wet conditions, e.g., as during laundering of the garment.

In a less preferred embodiment, the procedure could be reversed, i.e.,



The highly preferred steam setting medium may be moist, but preferably should contain less than about 10 % in excess of the moisture regain level of the fabric, for optimum wet and dry resiliency properties. The use of steam greatly decreases curing and setting time.

Alternatively, the garments may be set in the desired configuration by hot, dry conditions, such as by hot-pressing without steaming, e.g., by pressing at temperatures up to about 200° C. for as long as necessary to produce the desired reaction, e.g., less than a minute.

United States Pat. Nos. 2,837,511 and 2,837,512 disclose the reaction of cellulose with N-methylolacrylamide and similar compounds in a two-step operation whereby the acid-curing groups are first monofunctionally attached to cellulose (U.S. Pat. No. 2,837,512), after which the resulting cellulose ether is soaked in strong base solution at room temperature (U.S. Pat. No. 2,837,511) to produce a cross-linked product. These patents, however, are wholly deficient in disclosing a presensitized fabric, that is, an essentially dry fabric containing a catalyst for the subsequent reaction of terminal unsaturated groups at elevated temperatures. Also, these patents fail completely to disclose garments made from a fabric presensitized with a latent base-acting catalyst or suitable techniques for imparting sharp, durable creases or pleats to such garments. Furthermore, no procedure is disclosed for imparting simultaneously both wet and dry resiliency properties in a cellulosic material.

The amount of acid and base reactive group containing compound which can be employed is not critical and the exact amount to be employed depends, in part, on the properties desired in the final product and the efficiency of the selected compound. For example, amounts in the range of from about 1 to 40 percent, preferably about 5 to 25 percent, calculated on the weight of the dry textile material, or more or less, can be applied to the textile material as desired. As the pick-up of solution of the selected compound, if it is supplied as a solution, will range from about 50 to 200 percent of the weight of the textile material, a solution concentration should be selected which will provide the desired deposition of compound on the selected textile material under the conditions of pick-up.

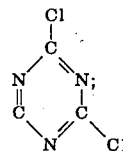
Although it is sometimes advantageous to apply to the textile material a single compound having both acid-reactive and base-reactive groups in the molecule, it is often more convenient to apply to the textile material a mixture of compounds which under the textile resin curing conditions or conditions employed prior thereto, is converted to a compound having the requisite acid and base-reactive groups. For example, a solution containing acrylamide, the desired amount of formaldehyde (generally equimolar proportions of acrylamide and formaldehyde are utilized for production of N-methylol acrylamide) and the desired acid-acting catalyst may be

prepared and padded onto the cellulosic material being treated. The acrylamide and formaldehyde may react in an aqueous solution of a mixture of these compounds, especially if heated, in which case the resulting product would fall within the definition of a compound having both acid-reactive and base-reactive groups in the molecule.

Alternatively, the fabric may first be impregnated with a conventional acid-reacting textile resin and a suitable acid-acting catalyst and cured after which a base-reacting cross-linking reagent and a suitable latent base-acting catalyst are applied to the fabric. After drying under conditions insufficient to initiate substantial reaction between the cross-linking reagent and hydroxy groups of cellulose, the fabric may be shipped and made into garments which can be pressed and cured to obtain durable configurations as desired, along with improved wet and dry resiliency properties.

This procedure can be reversed so that the basic cure can be conducted initially followed by impregnating of the fabric with a textile resin and latent acid-acting catalyst. In any of the procedures of this invention, where optimum storage and an optimum degree of wet resiliency properties, along with dry resiliency properties, are desired, the final cure should be on the basic side, i.e., the fabric supplied the garment manufacturer already has been reacted on the acid side.

In another procedure, the fabric may be impregnated with the acid-reacting textile resin, an acid-acting catalyst and a base-reacting reagent which does not volatilize during the curing under textile resin curing conditions. Suitable non-volatilizing base-reactive compounds include $\text{XH}_2\text{CH}_2\text{CSO}_2\text{CH}_2\text{CH}_2\text{X}$, wherein HX is volatilized only under basic conditions, e.g., $\text{NaO}_3\text{SCH}_2\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ and dihydroxymethyl sulfone;



methylene-bis-acrylamide, and the like.

In yet another embodiment of this invention, single compounds containing both acid-reactive and base-reactive groups may be combined with any of the textile resin formulations set forth herein. For example, the N-methylol acrylamide or chloroacetamide may be combined with a conventional triazone resin to provide a sometimes better performing product, though of course, less economical.

The textile resin catalysts employed during the heating step under textile resin conditions are well-known class of compounds and include the "acid-acting" compounds, i.e., those compounds which are acidic in character under the curing conditions. The most common are the metal salts, e.g., magnesium chloride, zinc nitrate, and zinc fluoroborate, and the amino salts, e.g., monoethanolamine hydrochloride and 2-amino-2-methyl-propanol nitrate. The amounts of catalyst to be employed are the same as those employed when using the usual textile resins, e.g., up to about 20 percent by weight of the acid-reacting compound employed, with the preferred range being from about 0.5 percent to about 10 percent.

While any acid-acting catalyst may be utilized, it may be preferable in some instances to use a mild or strong catalyst depending on the polyfunctional compound. For example, if both the acid-reactive and base-reactive groups are epoxides, it is preferred to use a mild acid-acting catalyst to induce the required preferential reaction. On the other hand, when utilizing N-methylol acrylamide, it is often preferred to utilize a strong acid-acting catalyst, such as zinc nitrate and the like in that improved properties, such as less chlorine retention, are obtained using the stronger acid catalysts. In this regard, compounds like zinc nitrate, which produce relatively low pH values in the fabric during curing, are considered strongly acidic, whereas compounds like magnesium chloride are considered mildly acidic.

Selection of the base-acting catalyst is particularly critical for the production of a "presensitized" fabric which will withstand normal storage. The base-acting catalyst is pH of compound which does not initiate substantial reaction between the base-reactive group and hydroxy groups of cellulose under normal conditions, but does initiate substantial reaction under prescribed conditions, such as elevated temperature or some other activating means, as by use of another chemical compound. For example, an alkali-metal sulfite can be padded onto the fabric and be decomposed into strongly basic alkali-metal hydroxide by including small amounts of formaldehyde in the steam used for curing. The latent base-acting catalyst utilized herein, however, preferably comprises alkaline-earth salts, such as alkali-metal carbonates like sodium bicarbonate, which is neutral to mildly alkaline, e.g., pH of about 8.5, on the fabric but decomposes at temperatures in excess of about 80° C. to form the stronger base sodium carbonate, which will initiate substantial reaction at the elevated temperatures utilized during press-curing. Sodium carbonate may be utilized if desired, since the pH of 9.5 in the fabric produced by this compound under normal conditions is generally insufficient to initiate the desired degree of reaction to any appreciable extent under normal temperature conditions. Fabrics at pH levels above about 10, however, gradually degrade during storage and essentially neutral or mildly alkaline catalysts are preferred where storage properties are desired.

Additional base-acting catalysts include potassium bicarbonate, potassium carbonate, sodium silicate, alkali-metal phosphates, such as sodium or potassium phosphates; barium carbonate; quaternary ammonium hydroxides and carbonates, e.g., lauryl trimethylammonium hydroxide and carbonate, and the like.

These bases are usually employed as about 0.2 percent to about 16 percent solutions, preferably about 2 percent to about 16 percent. The exact concentration, while not critical, will affect the results obtained. The concentration which gives the optimum result will depend, in part, on the percent pick-up of the base by the textile material, the temperature at which the reaction is conducted, and the amount of base consumed in the reaction. If a highly acidic group is released during the reaction, the amount of base applied to the textile material should be at least the amount that will be consumed by that group. Generally, a 3 percent to 10 percent aqueous solution of base is preferred when the pick-up is between about 30 percent to 130 percent, calculated on the weight of the dry textile material. In carrying out the initial heating step of the process of this invention the cellulosic material, uniformly impregnated with a polyfunctional organic compound having at least one acid reactive group and at least one base reactive group is heated under textile resin curing conditions in the presence of an acidic catalyst. As stated before, this acid and base reactive compound can be that which is initially applied to the textile material or can be the product of an in situ reaction of an acid reactive group containing compound and a base reactive group containing compound. Under ordinary conditions, this step employs conditions identical to that of a conventional resin treatment. For example, the selected reagents can be applied to the textile material by padding, spraying, or applicator roll and then passing through squeeze rolls, if necessary, to achieve the desired pick-up of the reagents. As these reagents are ordinarily applied as aqueous solutions, the textile material is dried and then heated to the appropriate temperature, e.g., about 100° to 200° C., preferably about 140° to 190° C., to fix the compound to the textile material. When employing fabric these steps of drying and curing are conducted while the fabric is free from extraneous wrinkles, usually in a smooth, open width condition.

Conventional curing equipment is suitable for this operation. For example, when employing a fabric, the reagents can be applied with the usual equipment and then passed through squeeze rolls and dried, e.g., at room temperature or while the fabric passes through a hot air oven or over heated cans. In

production, it is preferred to conduct the heating operations in a tenter frame to maintain the desired dimensions.

The thus treated textile material is then ordinarily given a thorough wash to remove the catalyst and any unreacted reagents. If sufficient reagents are employed in this step, the textile material will be found to possess a high degree of dry resiliency at this stage.

The step of contacting the textile material with the desired base-acting catalyst employs conditions generally employed in the textile trade, and the necessary techniques will be apparent to those skilled in the art. For example, impregnating the textile material with the selected catalyst can be accomplished in a manner similar to those employed in the previous step. The material can be moistened by dipping in an aqueous solution of the selected base, and squeezed through rollers to achieve the desired pick-up of the base.

The fabric is then dried under conditions insufficient for the base-acting catalyst to initiate substantial reaction between the base-reactive group and hydroxy groups of cellulose. The fabric containing the latent catalyst is then shipped to garment manufacturers for production of garments which can be subsequently pressed to obtain both wet and dry resiliency properties, in addition to sharp, durable creases or pleats.

When the base reactive step is conducted first, strong aqueous bases having a pH of at least 10 as a 1 percent aqueous solution are preferably utilized. The bases most commonly employed are the alkali-metal hydroxides, although other compounds such as sodium silicate, sodium carbonate, and potassium carbonate can also be employed. These bases are usually employed as about 0.2 percent to about 16 percent solutions, preferably about 2 percent to about 16 percent. The exact concentration, while not critical, will affect the result obtained. The concentration which gives the optimum result will depend, in part, on the percent pick-up of the base by the textile material, the temperature at which the reaction is conducted, and the amount of base consumed in the reaction. If a highly acidic group is released during the reaction, e.g., when employing a sulfato ester-containing compound, the amount of base applied to the textile material should be at least the amount that will be consumed by that group. Generally, a 3 percent to 10 percent aqueous solution of base is preferred when the pick-up is between about 30 percent to 130 percent, calculated on the weight of the dry textile material.

A latent acid catalyst, for example, any of the above recited catalysts can be then padded onto the cellulosic material, though preferably a mild catalyst is applied. After drying under conditions insufficient to produce substantial reaction between the acid-reactive group and hydroxy groups of cellulose, a presensitized fabric is obtained. Garments produced from these fabrics can be durably set by pressing under textile resin curing conditions. Storage time and wet resiliency properties will generally be lower in this embodiment of the invention.

Textile materials which can be treated according to the processes of this invention are those in which the anhydroglucose units are chemically substantially unmodified. Thus, the term "cellulosic textile material" when used herein means any textile material comprising fibers within the above definition, e.g., cotton, paper, linen, jute, flax, regenerated cellulose fibers, including viscose rayon, in the form of staple, yarn and fabrics. This invention is directed primarily and preferably to cellulosic textile fabrics, either knitted or woven, preferably woven. However, the advantages of this invention can be achieved by treated the cellulosic fibers, yarns, or threads employed to produce these fabrics. The thus treated material, when woven or knitted into fabric will produce a fabric having better wet and dry resiliency than identical fabric woven from identical untreated yarn or thread. Moreover, the properties of the staple yarn and thread are modified in a desirable fashion. For example, the staple is less prone to compression into hard masses during wet or dry processing.

Satisfactory results can be achieved employing cellulosic materials containing both cellulosic and non-cellulosic fibers,

especially if the non-cellulosic fibers have minimum care characteristics of their own. For example, the wet and dry resiliency of fabrics formed from a mixture of polyester, such as poly(ethylene terephthalate), polyamide such as poly(hexamethylene adipamide) or acrylic fibers, such as polyacrylonitrile and copolymers containing at least about 85 percent combined acrylonitrile filaments or fibers with cotton or rayon can be improved by this process. Obviously, if the non-cellulosic fibers have low minimum care characteristics, the improved characteristics of the materials treated according to the processes of this invention will be more readily apparent when the cellulosic content of the fabric is substantial, e.g., about 40 percent or more by weight. As stated above, the invention is primarily directed to fabrics, preferably consisting essentially of cellulosic materials, especially cotton. Bleached and usually also commercially mercerized or printed fabric, e.g., printcloth, broadcloth, and oxfordcloth, is usually employed as the starting fabric.

After the initial curing step, the cellulosic material preferably contains at least about 1.8 unsubstituted hydroxy groups and at least 0.05 hydroxy groups per anhydroglucose unit substituted through an ether linkage by a radical having a terminal grouping reactive towards hydroxy groups of cellulose. In the usual instance, as where the acid-reactive group of the polyfunctional compound is reacted first, the substituent is base-reactive.

Such degree of substitution is preferred for the desired cross-linking reaction to take place to a satisfactory extent. Preferably, there are at least two unsubstituted and, more preferably, at least 2.5 unsubstituted hydroxy groups per anhydroglucose unit for the same reason. Of the remaining hydroxy groups, an average of at least 0.05, more preferably 0.2-0.5 hydroxy groups per anhydroglucose unit is substituted through an ether linkage to one of the R groups set forth above.

In addition to the preferred number of free hydroxy groups and reactive radical-substituted groups, the cellulosic material can have a minor proportion of hydroxy groups substituted with ether or ester groups, e.g., lower-hydrocarbon esters including the acetate, propionate, butyrate, benzoate, sulfate, phosphate, aryl and alkyl esters; and lower alkyl ethers including methyl and ethyl; and hydroxyalkyl, such as hydroxyethyl and carboxymethyl ethers.

In some instances, the addition of reducing agents, such as alkali-metal borohydride, such as sodium and potassium borohydride; alkanolamine sulfites, such as monoethanolamine sulfite, monoisopropanolamine sulfite and others containing up to about eight carbon atoms in the alkyl chain and the like can be applied to the cellulosic material being treated to inhibit any yellowing which may tend to occur under setting conditions in the garment state. Furthermore, when sodium borohydride is applied along with sodium bicarbonate or sodium carbonate, the time of pressing on the Hoffman press is reduced, e.g., to 30-60 seconds with no yellowing of the fabric when steam is used, whereas without steam as much as 5 minutes would be required to get the same result. Durable creases are also produced in as little as 10 seconds using a hot platen press at 350° F.

Preferred embodiments of the present invention are shown in the following Examples.

EXAMPLE I

The physical properties of the fabrics treated according to the process of this invention were determined according to accepted standard methods. Tear strength was determined by A.S.T.M. Test designation D-1424-59. Tensile strength was determined by A.S.T.M. Test designation D-39-59 (No. 10). Crease recovery angle was determined by A.S.T.M. Test designation D 1295-53 T. See "A.S.T.M. Standards for Committee D-13 on Textiles," (1959). Flat dry ratings were by A.A.T.C.C. Test designation T-88-1958.

Preparation of N-methylolchloroacetamide:

Eighty-one gms. of a 37 percent formaldehyde solution (1 mole) are adjusted to a pH of 8.0 by the addition of 1 N-sodium hydroxide solution. To the solution are added 93.5 gms. (1 mole) of 2-chloroacetamide. The mixture is heated for 1 hour at 60° C. with the concomitant addition of 1 N-sodium hydroxide to maintain the pH in the range 6-8. Towards the end of the heating period, 240 gms. of water are added. After cooling, the clear solution weigh 435 gms. and therefore contain 28.4 percent by weight of N-methylolchloroacetamide.

EXAMPLE II

The N-methylolchloroacetamide solution of Example I is applied to 80 × 80 bleached and mercerized cotton print cloth in the following manner. The print cloth is padded through a solution comprising 10 percent solids N-methylolchloroacetamide, a zinc nitrate catalyst (1% OF $Zn(NO_3)_2 \cdot H_2O$), 6 percent of a polyethylene softener (Moropol 700) and ½ percent of the surfactant (Surfonic N-95). The wet fabric is then squeezed through nip rolls at 60 lbs. per square inch pressure to provide a pick-up of about 75 percent based on the weight of the dry fabric. The fabric is dried over hot cans and then cured by passing through a curing oven about 175° C. for 90 seconds.

The cured fabric is then washed to remove all unreacted chemicals, air dried and padded and squeezed to 75 percent pick-up with 5 percent aqueous solution bicarbonate. The fabrics are then air dried to give the presensitized cotton fabric.

The presensitized fabrics so produced give sharp creases substantially durable to laundering when pressed while steaming on the Hoffman press for 1 minute. In addition, good wet and dry resiliency properties are produced.

EXAMPLE III

The procedure of Example II is repeated except that aqueous solutions containing 1 percent, 3 percent 5 percent and 70 percent sodium carbonate, respectively are substituted for the sodium bicarbonate catalyst. Essentially the same results are obtained as before, with best results being obtained with the 3 percent solution.

This procedure is again repeated, except that the fabric swatches impregnated with sodium carbonate are dried over hot cans, heated to 110° C. Under these conditions, the fabric does not reach the temperature of the hot cans so that the reaction between the acetyl halide groups and hydroxy groups of cellulose does not occur to a degree sufficient to destroy the fabrics propensity for subsequent durable setting. Upon pressing on a Hoffman press for 2 minutes as before, sharp creases substantially durable to laundering are obtained, with good wet and dry resiliency properties.

EXAMPLE IV

Samples of the same starting fabric as that described in Example II are padded in the manner described therein with a solution comprising 15 percent of a 60 percent aqueous solution of N-methylolacrylamide (obtained from the American Cyanamid Company), 2 percent catalyst AC (a solution of 2-amino-2-methyl-1-propanol hydrochloride), 6 percent of a polyethylene softener (Moropol 700) and ½ percent of a surfactant (Surfonic N-95). The fabrics are dried over hot cans, then cured by passing through a curing oven at 182° C. for 90 seconds. After washing and drying, the fabrics exhibit a tensile strength of 27.6 lb. a tear strength of 456 gm., crease recovery angles (warp and fill) of 210° (dry) and 230° (wet), and spin and tumble ratings of 1.7 and 2.8, respectively.

The fabric samples are further padded to a pick-up of approximately 85 percent, with 4 percent aqueous sodium bicarbonate and 2 percent aqueous sodium carbonate and air dried to give the presensitized cotton fabrics.

The presensitized fabrics yield crease or creases durable to laundering when pressed on the Hoffman press in the presence

of steam for 3 minutes. The creases have a good appearance irrespective of whether the fabrics are spun dried followed by line drying, or tumble dried. The sodium carbonate catalyst gives slightly better creases than the sodium bicarbonate.

EXAMPLE V

Samples of the starting fabric of Example II are padded as described therein with a solution comprising N-methylolacrylamide (15 percent or 25 percent of a 60 percent solution, being equivalent to 9 percent and 15 percent solids, respectively), 3 percent catalyst AC, 6 percent Moropol 700 polyethylene softener and $\frac{1}{2}$ percent Surfonic N-95 surfactant. After drying over hot cans, the fabrics are cured at 182° C. for 90 seconds, washed and dried.

EXAMPLE VI

Padding of the samples prepared in Example V to a pick-up of about 85 percent with aqueous solutions containing 4 percent sodium bicarbonate and 3 percent sodium carbonate together with $\frac{1}{2}$ percent sodium borohydride, followed by air-drying, yield presensitized fabrics which are given durable pleats or creases in the presence of steam in the Hoffman press. The presence of the sodium borohydride completely eliminated any tendency of the fabrics to yellow during the pressing operation. However, the pressing time for production of a good durable crease is now only 30–60 seconds.

It may be noted that the fabrics impregnated with sodium bicarbonate solutions must be dried at less than 65° C. to avoid conversion of the bicarbonate to carbonate. The fabrics impregnated with sodium carbonate solutions may be dried over hot cans at temperatures up to 110° C., since this temperature time is insufficient to cause the vinyl group to react with the cellulose.

Good durable creases are also imparted to these presensitized fabrics on the Hoffman press in the absence of steam if the pressing time was extended to 5 minutes.

Good durable creases are also produced on a hot Platen press (177° C.) in 15 seconds with virtually no yellowing.

Good durable creases are also produced by pressing the samples in the presence of steam on the Hoffman press for 5 seconds, followed by setting in dry air in an oven at 160° C. for 2 minutes. The bicarbonate catalyzed samples have 4.0 × 4.0 spin and tumble ratings after this latter press-curing operation.

EXAMPLE VII

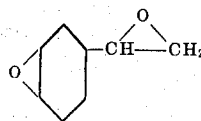
The examples thus far enumerated have involved the production of presensitized fabrics by the acid-catalyzed reaction, with the cellulose hydroxy groups, of one functional group in a difunctional reagent. The second functional group is then subsequently reacted under conditions of base-catalysts. It is also possible to reverse this procedure as the present example will show.

The starting fabric of Example II is padded as described therein with solutions comprising N-methylolacrylamide (9 percent or 18 percent solids) and 3 percent sodium hydroxide. After ageing overnight at room temperature, the fabrics are washed and dried, and at this point exhibit spin and tumble ratings both equal to 1.0. The fabrics are then padded to about 85 percent pick-up with a magnesium chloride catalyst (catalyst MX; 2 percent or 3 percent and air-dried. The presensitized fabrics thereby obtained are given creases durable to laundering by pressing on a Platen press at 177° C. for, 60 seconds. No yellowing of the fabrics occurred. Similar results are obtained with catalyst AC.

EXAMPLE VIII

This example illustrates the use of a difunctional presensitizing agent where advantage is taken of the very different reactivities of the two epoxide groups contained therein. In this case, both steps in the process involve acid catalysts.

The starting fabric of Example II is padded as described therein with a solution containing 20 percent of vinylcyclohexene diepoxide



and 2% zinc fluoroborate ($\text{Zn}(\text{BF}_4)_2$) and dried

at a temperature of 140° C. The fabric is washed, dried, re-padded to about 85 percent pick-up with 1.5 percent $\text{Zn}(\text{BF}_4)_2$ and dried, to yield the presensitized fabric.

Durable creases are imparted to this fabric by pressing in the Platen press at a temperature of 177° C. for 60 seconds.

EXAMPLE IX

The reaction product of glyoxal with two molar equivalents of acrylamide is also employed as a presensitizing agent. Two hundred eighty-five grams of 40 % glyoxal (2 moles) and 95 gm. water are adjusted to a pH of 8.0 with 1.0 N-sodium hydroxide solution. Two hundred eighty-four gm. of acrylamide and 3 gm. of methylhydroquinone inhibitor are added and the mixture is heated at 50° C. for 1.5 hours and cooled. The starting fabric of Example II is padded as described therein with a solution comprising 20 percent of the above solution, an acid catalyst (1 percent $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), or 2 percent catalyst MX), 6 percent Moropol 700 polyethylene softener and $\frac{1}{2}$ percent Surfonic N-95 surfactant. After drying over hot cans, the fabrics are cured at 177° C. for 90 seconds, washed and dried.

These fabrics are padded to approximately 100 percent pick-up with a solution comprising 4 percent sodium bicarbonate and 0.2 percent sodium borohydride, and air dried to give the presensitized fabrics. Sixty seconds pressing in the presence of steam on the Hoffman press is sufficient to impart moderately good creases to the presensitized fabrics, which are durable to laundering.

EXAMPLE X

The procedure of Example IX is repeated except that the reaction product of 1 mole acrolein and 3 moles acrylamide, condensed at pH 2 by heating at 60° C. for 30 minutes, is utilized as the presensitizing agent. The fabric is padded with a 50 percent solution (adjusted to pH 9) of the reaction product containing 3 moles formaldehyde. Substantially similar results are obtained.

EXAMPLE XI

The procedure of Example II is repeated except that an aqueous solution containing 10 percent of the sodium salt of the sulfato mono-ester of di- β -hydroxy-ethyl-sulfone, 10 percent dimethylol urea along with the same catalyst, softener and surfactant. Substantially similar results are obtained.

EXAMPLE XII

The procedure of Example IV is repeated except that 5 percent hydroxyethyl triazone is added to the initial treating solution. The pressed products are characterized by higher strength properties and better tumble ratings.

I claim:

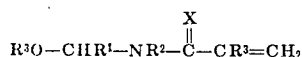
1. A process for producing a durable press garment which comprises

a. impregnating a cellulosic textile fabric with a polyfunctional, organic creaseproofing compound having at least one vinyl group or a precursor thereof and at least one N methylol group and an alkaline catalyst which is substantially neutral on the fabric but becomes strongly alkaline at temperatures in excess of 80° C;

b. reacting said creaseproofing compound and hydroxy groups of cellulose to form an ether linkage therebetween;

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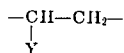
- c. thereafter impregnating said fabric with an acidic catalyst;
 d. drying said fabric at a temperature insufficient to initiate substantial reaction;
 e. cutting said fabric into garment sections;
 f. sewing said sections to form a garment;
 g. pressing said garment in a desired configuration; and
 h. subjecting said garment to conditions whereby said impregnated fabric is activated for substantial reaction to form a stable, crosslinked garment.
2. A process for producing a durable press garment which comprises
- a. impregnating a cellulosic textile fabric with (1) a polyfunctional, organic creaseproofing compound selected from the group consisting of



and



wherein R¹ is selected from the group consisting of hydrogen, lower alkyl; R² is selected from the group consisting of hydrogen and lower alkyl; R³ is selected from the group consisting of hydrogen and methyl; X is selected from the group consisting of sulfur and oxygen; R⁵ is selected from the group consisting of -CH₂CH₂- and



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- and Y is a halogen; and (2) an acidic catalyst;
- b. reacting said creaseproofing compound and hydroxy groups of cellulose to form an ether linkage therebetween;
- 5 c. thereafter impregnating said cellulosic textile material with an alkaline catalyst which is substantially neutral on the fabric but becomes strongly alkaline at temperatures in excess of 80° C;
- d. drying said fabric at a temperature insufficient to initiate substantial reaction
- 10 e. cutting said fabric into garment sections;
 f. sewing said sections to form a garment;
 g. pressing said garment in a desired configuration; and
 h. subjecting said garment to conditions whereby said impregnated fabric is activated for substantial reaction to form a stable, crosslinked garment.
- 15 3. The process of claim 2 wherein during the final curing the moisture level of the fabric is maintained below about 20 percent in excess of the regain moisture level of said fabric until
- 20 after the crosslinking reaction has occurred.
4. The process as defined in claim 2 wherein the pressing step and the reaction step are conducted simultaneously.
5. The process as defined in claim 2 wherein the polyfunctional compound is N-methylol acrylamide.
- 25 6. The process as defined in claim 2 wherein the polyfunctional compound is N-methylol haloacetamide.
7. A cellulosic textile fabric produced according to the process of claim 1.
8. A cellulosic textile fabric produced according to the
- 30 process of claim 2.

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