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PROCESS OF TREATING NATURAL CELLULOSE TEXTILES TO PARTIALLY ESTERIFY THEM AND THEN TREATING WITH A RESIN CONDENSATION PRODUCT AND PRODUCTS RESULTING THEREFROM

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1

This invention relates to improvements in the manufacture of crush and wrinkle resistant textile materials and particularly natural cellulosic textile materials.

It has been possible heretofore to treat natural cellulosic textile materials such as cotton and linen textiles with urea-aldehyde and melamine-aldehyde condensation products and thereby alter the physical characteristics of the textile materials after the condensation product was insolubilized thereon. When relatively small amounts of such condensation products are deposited on the natural cellulosic textile materials, it is possible to prepare a textile product having a fair degree of dimensional stability against washing, that is, the textile product is relatively resistant to shrinkage on laundering. When relatively large amounts of such condensation products are deposited on a natural cellulosic textile product, it is not only possible to achieve a higher degree of dimensional stability, but it is also possible to produce a textile product having resistance to crushing or wrinkling, that is, the textile product is adapted to return to its normal configuration or dimension after being creased or crushed. However, textile products of the latter type, especially, have certain disadvantages which have been objectionable to the trade with the result that they have not been accepted commercially on a large scale. Such textile products are objectionable because they are embrittled and undergo excessive loss in tensile strength as a result of the treatment with the above described condensation products. These disadvantages become more apparent as the amount of condensation product deposited on the textile material is increased.

It is one object of the present invention to provide a method of improving the dimensional stability and particularly the crush and/or wrinkle resistance of natural cellulosic textile materials without appreciably embrittling and lowering the tensile strength of such materials.

A further object of the present invention is to provide crush and/or wrinkle resistant natural cellulosic textile materials which are characterized by excellent dimensional stability and good flexibility and tensile strength.

Still further objects and advantages of the present invention will appear from the following description and the appended claims.

In accordance with the present invention a cellulosic textile material such as cotton, linen, ramie and the like is first given a pre-treatment with an organic agent which is capable of react-

2

ing with the accessible hydroxyl groups of the cellulose micellae or molecules under such conditions that only a partial esterification or etherification of the cellulose is effected and the cellulose is not swollen to an appreciably greater extent than it would be swollen in water alone. This pre-treatment is preferably carried out with an organic esterifying agent and more particularly with formic acid.

The resulting product is readily distinguished from textile materials which have been highly esterified or etherified or which have been spun from solutions of cellulose esters or ethers in that the first mentioned material swells readily in water in much the same manner as unmodified cellulose or regenerated cellulose while the latter type of materials are quite resistant to swelling in water and are soluble in certain organic solvents which do not appreciably affect unmodified or regenerated cellulose or the aforementioned partially esterified or etherified cellulosic materials.

After the cellulosic textile materials have been partially esterified or etherified to the desired extent, they are washed free of unreacted agent and are preferably dried for convenience in handling and are then impregnated with an aqueous solution of a substantially unpolymerized urea-aldehyde condensation product or an aqueous solution of a substantially unpolymerized melamine-aldehyde condensation product or in an aqueous solution comprising mixtures of such condensation products. Other thermosetting condensation products may also be employed as will appear hereinafter, but the two mentioned above are preferred for the purposes of the present invention. The amount of condensation product deposited on the cellulosic material may be varied to a considerable extent depending on the particular cellulosic textile which is being treated. Best results have been obtained by depositing from about 6 to 16% by weight condensation product, based on the textile, on natural celluloses such as cottons and linens.

The cellulosic textile, after it has been impregnated with the above described condensation product or products, is then heat-treated to cure or insolubilize the condensation product or resin, that is, the condensation product is rendered water resistant by converting it, through polymerization or condensation, to its infusible form. This is accomplished by heating the impregnated textile, preferably after it has been dried, to a temperature of from about 275° to 350° F. for a period of from 30 to 2 minutes de-

3

pending on the temperature employed. The condensation product is cured or insolubilized in the presence of a suitable catalyst which becomes acid at the above temperatures. Such catalyst is preferably added to the aqueous solution of condensation product before the impregnation of the cellulosic textile material. It is preferable to give the finished textile materials a neutralizing wash in a dilute alkaline solution after the heat treatment referred to above in order to remove the major portion of catalyst from the textile. The finished textile product possesses a high degree of crease and wrinkle resistance and has a tensile strength which is substantially the same as the untreated material from which it is prepared.

In carrying out the pre-treatment of the cellulosic textile as described above, almost any organic hydrogen-replacing agent which yields a stable product with cellulose may be employed. It is believed that by replacing the hydrogen of the cellulose hydroxyl groups with such agents the cross-linking of the cellulose molecules by the urea-aldehyde or melamine-aldehyde condensation product or other condensation product is substantially prevented. Therefore, the cellulosic textile is not appreciably embrittled and does not appreciably lose its tensile strength as a result of the treatment. However, it is not intended that the present invention be limited by any theory presented herein. Formic acid, as previously pointed out, is the preferred organic hydrogen-replacing agent for use in the pre-treatment of cellulose because it is easier to control the esterification and a superior product is produced after resin treatment. However, other esterifying agents such as acetic acid, acetic anhydride, propionic acid and propionic anhydride may also be used instead of formic acid, if an esterifying catalyst is employed. Etherifying agents such as dimethyl and diethyl sulfate may be used in place of esterifying agents, if the cellulose has been prepared to react with such agents, for example, by pre-treating the cellulose with caustic soda. When formic acid in concentrations of 85 to 100% by weight is employed, satisfactory results are obtained by treating the cellulosic textile for 30 minutes at 60° C. or for 16 hours at 20° C. Formic acid in concentrations of less than about 80% by weight is not an effective esterifying agent without strong esterifying catalysts which are undesirable. Other esterifying conditions may also be employed. However, it is not desirable to carry the esterification or etherification reaction too far as the physical properties of the textile may be adversely affected.

It has presently been found that an esterification of at least 1% and not more than 10% of the available hydroxyl groups of the cellulose yields a very satisfactory product when further treated with a urea-formaldehyde or melamine-formaldehyde condensation product. The degree of esterification can readily be determined by taking an aliquot portion of the textile, washing out the unreacted esterifying agent, saponifying the aliquot with caustic soda or caustic potash solution of known strength and then titrating the caustic solution with an acid to determine the amount of esterifying agent combined with the cellulose. Since there are only three available hydroxy groups for each $C_6H_{10}O_5$ unit of cellulose, the percentage of esterification of the cellulose textile may be readily calculated.

It is preferable to carry out the partial esterification of the cellulosic textile with the esterify-

4

ing agents of the invention by employing an excess of the esterifying agent. This may be accomplished, for example, by employing from 25 to 50 parts of esterifying agent for 1 part of cellulosic textile. Relatively low esterification temperatures are also preferred since it thus is easier to avoid excessive esterification of the cellulosic materials. Temperatures of from about 15 to 35° C. have been found to be very satisfactory for this purpose.

After the esterification treatment is completed, it is essential to wash out unreacted esterifying or etherifying agent from the cellulose textile prior to the treatment with urea or melamine-aldehyde condensation product, otherwise the textile may be excessively tendered when it is heat-treated to cure or insolubilize the condensation product. This may be followed by drying prior to resin treatment for ease in handling, but the drying step is not essential.

The partially esterified cellulosic textile may be impregnated with a urea-aldehyde or melamine-aldehyde condensation product in a variety of ways as, for example, by padding the textile through an aqueous solution of the condensation product, by immersing the textile in the aqueous solution of condensation product and then centrifuging the textile to remove excess solution or by spraying the aqueous solution of condensation product on the textile. The concentration of condensation product in the aqueous solution is preferably such as will deposit the quantity of condensation product as hereinbefore described depending upon the impregnation method employed. Generally an aqueous solution having a concentration of condensation product of from 6 to 20% by weight is suitable for the treatment of partially esterified or etherified natural celluloses such as cotton and linen. The aqueous impregnating solution preferably comprises about 0.2 to 0.4% by weight of a latent curing catalyst for the condensation product and may also comprise other additives such as penetrants, softening agents and the like. A small amount, say about 0.5 to 2% by weight of a penetrant such as anionic and nonionic wetting agents aids the penetration of the condensation product into the textile fibers especially if the fibers are slightly oily or greasy. Sodium salts of alkylated benzene sulfonic acids having a long alkyl chain and polyethylene glycol derivatives of alkylated phenols having a long alkyl chain are respective examples of an anionic and nonionic wetting agent.

The urea or melamine-aldehyde condensation products employed in the present invention are substantially unpolymerized or are substantially uncondensed, that is, they are essentially monomeric or only slightly polymerized when applied to the cellulosic textile. The condensation products of urea or melamine with formaldehyde or mixtures thereof are particularly useful for the purposes of the present invention and are preferred over other condensation products prepared from other amines and aldehydes. However, alkylated urea-aldehyde condensation products and alkylated melamine-aldehyde condensation products and particularly the methylated urea formaldehyde or melamine-formaldehyde condensation products or mixtures of the above described condensation products may also be employed, although they are not as desirable as the urea-formaldehyde or melamine-formaldehyde condensation products for producing crush resistance.

5

6

The aqueous solutions of urea or melamine-aldehyde condensation products employed herein may be prepared according to the known methods of the prior art. A suitable method for preparing aqueous solutions of substantially un-
polymerized condensation products from urea and formaldehyde is to react urea with a neutral aqueous formaldehyde solution under refluxing conditions and in a mildly alkaline solution, that is, a solution having a pH of about 7.5 to 9 until the urea dissolves, after which, the solution is cooled and diluted to the desired concentration. Aqueous solutions containing a melamine-formaldehyde condensation product are suitably prepared by reacting melamine and an aqueous solution of neutralized formaldehyde under refluxing conditions and in an alkaline solution until solution of the melamine occurs, after which, the solution is cooled and diluted to the desired concentration. Alkylated derivatives of urea or melamine-aldehyde condensation product are prepared satisfactorily by further reacting the above condensation products at temperatures of from 60 to 100° C. with a monohydric alcohol having from 1 to 3 carbon atoms such as methanol, ethanol and the like or with a dihydric alcohol having from 2 to 6 carbon atoms such as ethylene glycol, diethylene glycol and the like. The reaction with monohydric or dihydric alcohol is preferably carried out under acid conditions by adjusting the acidity of the original condensation product and the alcohol below about pH 3 using a mineral acid such as hydrochloric acid, phosphoric acid and the like.

In carrying out the condensation of urea or melamine with an aldehyde, formaldehyde is preferably employed as the aldehyde since the condensation product prepared therefrom possesses better water solubility than condensation products prepared from other aldehydes. However, aldehydes such as acetaldehyde, glyoxal, furfural, propion aldehyde and the like may also be employed. In addition, products such as para-formaldehyde which yield formaldehyde under the conditions of reaction may also be used instead of formaldehyde.

A further understanding of the invention will be obtained from the following examples which are intended to be illustrative, but not limitative of the present invention, parts and percentages being by weight unless otherwise specified.

Example I

An aqueous solution of melamine-formaldehyde condensation product (hereinafter referred to as resin solution A) was prepared as follows:

One mol of melamine was reacted with 4 mols of formaldehyde in the form of a 37% aqueous solution at a temperature of 80° C. using a reflux condenser and at a pH of about 9 (glass electrode). The pH was adjusted to the above value by the addition of a 25% aqueous solution of caustic soda. The mixture was heated at a temperature of 80° C. for a period of 5 minutes by which time solution of the melamine had occurred. The solution was then cooled to room temperature and employed as described below. The solution contained about 54% of substantially unpolymersized or monomeric melamine-formaldehyde condensation product.

A linen fabric was pre-treated for about 16 hours and at room temperature in an 85% solution of formic acid. Approximately 30 parts of 85% formic acid were employed for 1 part of linen fabric. After this treatment excess formic

acid was removed by extracting the fabric in a centrifuge and the unreacted acid still remaining in the fabric was then removed by washing the fabric with cold water. The fabric was air-dried after the washing step.

The above air-dried fabric was padded through an aqueous solution prepared by diluting resin solution A (prepared as described above) until it contained 16% resin solids. The solution also contained about 0.3% of 2-amino-2-methyl propanol phosphate as a catalyst and 1% of sodium dodecyl benzene sulfonate as a penetrant. The pad pick-up was adjusted so that the fabric would pick up a weight of solution equal to 75% of the dry fabric weight (12% condensation product being thereby deposited on the fabric). The fabric was then framed, dried for 5 minutes at 180° F. and cured for 5 minutes at 300° F. Finally, the fabric was given a neutralization wash in a very dilute soap solution containing 0.25% sodium carbonate, rinsed and then dried.

A linen fabric, which had not been pre-heated with formic acid, was treated with melamine-formaldehyde condensation product substantially in the same manner as set forth immediately above. After curing, this fabric ruptured on mere bending.

The following table indicates the relative wrinkle resistance, strength and stiffness of untreated and the above treated linen fabrics:

Linen Fabric Tested	Wrinkle Resistance	Strength	Stiffness
Untreated	Poor	Very Good	Very soft and flexible.
Treated with melamine-formaldehyde condensation product only	Very Poor	Fair	Stiff and brittle.
Partially formylated and then treated with condensation product	Excellent	Good	Very soft and flexible.

Example II

A cotton fabric was pre-treated for 16 hours at room temperature in a 90% formic acid solution using about 30 parts of 90% formic acid solution to 1 part of cotton fabric. Unreacted formic acid was washed out of the fabric with water and the fabric was then padded through an aqueous solution of melamine-formaldehyde resin prepared by diluting resin solution A (prepared as described in Example I) until it contained about 15% condensation product. The solution also contained about 0.25% of zinc chloride as a catalyst and about 0.15% of the reaction product of 10 mols of ethylene oxide and 1 mol of dodecyl phenol as a penetrant. The pad pick-up was adjusted so as to deposit about 11.6% of condensation product on the dry fabric weight. The resin treated fabric was dried for 10 minutes at 200° F. and then cured at 310° F. for 4 minutes. Finally, the fabric was given a neutralizing wash with 0.01% soap solution containing about 0.6% soda ash and then dried.

A cotton fabric treated in the manner described has good wrinkle and crease resistance, is quite flexible and soft and its tensile strength is not appreciably lowered as a result of the treatment, that is, it has substantially the same tensile strength as an untreated cotton fabric from the same roll.

Example III

A linen fabric was pre-treated with formic acid as described in Example I, washed to remove unreacted acid and then air dried. The partially formylated fabric was then padded through an aqueous solution of urea-formaldehyde condensation product which solution was prepared by reacting about 1 mol of urea with about 1.5 mols of formaldehyde, adjusting to pH of 8.5 by the addition of caustic soda under refluxing conditions for approximately 7 minutes and then cooling and diluting the resulting solution until it contained about 16% resin solids. The impregnating solution also contained about 0.3% diammonium hydrogen phosphate as a catalyst and about 0.1% of sodium stearyl benzene sulfonate as a penetrant. The pad pick-up was adjusted so as to pick up about 13% condensation product based on the dry fabric weight. The fabric was framed, dried at 180° F. for about 5 minutes and then cured for 4 minutes at 315° F. Finally, the fabric was given a neutralizing wash in a 0.025% soap solution containing about 0.25% soda ash and then dried.

A linen fabric from the same roll was treated with urea-formaldehyde condensation product in substantially the same manner, but the fabric was not treated with formic acid prior to the resin treatment.

The relative wrinkle resistance, stiffness and strength of the untreated and the above treated linen fabrics compared quite closely with the corresponding fabrics treated as described in Example I.

The curing catalysts described in the foregoing examples may be replaced with other curing catalysts depending upon the particular condensation product employed. For example, latent curing catalysts such as ammonium chloride, diammonium hydrogen phosphate, zinc chloride, ethanol amine hydrochloride and 2-amino-2-methyl propanol hydrochloride are employable with urea-formaldehyde condensation products. Latent curing catalysts such as zinc chloride, 2-amino-2-methyl propanol hydrochloride or phosphate and ethanol amine hydrochloride and phosphate are suitable for curing melamine-formaldehyde condensation products in the presence of heat. Strong latent curing catalysts such as ammonium chloride, diammonium hydrogen phosphate, mineral acids and the like should not be employed with monomeric melamine-formaldehyde condensation products, however, since premature polymerization of the resin occurs before thorough impregnation of the textile materials and the resulting product has a harsher and stiffer hand than is desirable.

The present invention may be practiced or carried out on loose fibers, unwoven yarns or filaments and other forms of textile materials in addition to fabrics. Union fabrics containing natural cellulosic yarns or mixtures of natural and regenerated cellulose yarns with wool or other protein yarns, cellulose derivative yarns and the like may also be treated in accordance with the present invention.

What is claimed is:

1. The method of preparing improved wrinkle or crease resistant cellulosic textile materials which comprises treating a natural cellulose textile material with an 80 to 100% formic acid solution until from 1 to 10% of the hydroxyl groups of the cellulose are esterified; removing substantially all of the unreacted formic acid from said material; impregnating said material with an

aqueous solution comprising a latent curing catalyst and from about 6 to 20% by weight of a substantially unpolymerized urea-formaldehyde condensation product; extracting said material to deposit from about 6 to 16% by weight, based on the dry material, of said condensation product; and then insolubilizing said condensation product by heating said material at a temperature between about 275 and 350° F.

2. The method according to claim 1, but further characterized in that a substantially unpolymerized melamine-formaldehyde condensation product is employed instead of a urea-formaldehyde condensation product.

3. The method of preparing an improved wrinkle or crush resistant cellulosic textile material which comprises reacting a natural cellulose textile material with an organic esterifying agent selected from the group consisting of formic acid, acetic acid, acetic anhydride, propionic acid and propionic anhydride until from 1 to 10% of the hydroxyl groups of the cellulose have been reacted with said agent; removing substantially all of the unreacted agent from said material; impregnating the resulting material with an aqueous solution comprising a latent curing catalyst and from about 6 to 20% by weight of a substantially unpolymerized condensation product selected from the group consisting of urea-formaldehyde, melamine-formaldehyde, methylated urea-formaldehyde and methylated melamine-formaldehyde condensation products and mixtures thereof; extracting said material to deposit from about 6 to 16% by weight, based on the dry material, of said condensation product; and then insolubilizing said condensation product by heating said material at a temperature between about 275 and 350° F.

4. The method of preparing improved wrinkle or crease resistant cellulosic textile materials which comprises treating a natural cellulose textile material with a solution containing from 80 to 100% by weight of formic acid until from 1 to 10% of the hydroxyl groups of the cellulose are esterified; removing substantially all of the unreacted formic acid from said material; impregnating said material with an aqueous solution comprising a latent curing catalyst and from about 6 to 20% by weight of a substantially unpolymerized condensation product selected from the group consisting of urea-formaldehyde, melamine-formaldehyde, methylated urea-formaldehyde and methylated melamine-formaldehyde condensation products and mixtures thereof; extracting said material to deposit from about 6 to 16% by weight, based on the dry material, of said condensation product; and then insolubilizing said condensation product by heating said material at a temperature between about 275 and 350° F.

5. A wrinkle and crease resistant cellulosic textile material consisting of partially esterified natural cellulose textile fibers selected from the group consisting of partial formyl, partial acetyl and partial propionyl esters of natural cellulose, in which from 1 to 10% of the hydroxyl groups of the natural cellulose have been esterified, impregnated with from about 6 to 16% by weight, based on the dry material, of an insolubilized condensation product selected from the group consisting of urea-formaldehyde, melamine-formaldehyde, methylated urea-formaldehyde and methylated melamine-formaldehyde condensation products and mixtures thereof, said fibers being characterized by a tensile strength which

is substantially the same as the untreated natural cellulose textile fibers from which they were prepared.

6. A wrinkle and crease resistant cellulosic textile material consisting of partially formylated natural cellulose textile fibers, in which from 1 to 10% of the cellulose hydroxyl groups have been formylated, impregnated with from about 6 to 16% by weight, based on the dry material, of an insolubilized urea-formaldehyde condensation product, said fibers being characterized by a tensile strength which is substantially the same as the untreated cellulosic textile fibers from which they were prepared.

7. A wrinkle and crease resistant cellulosic textile material consisting of partially formylated native cellulose textile fibers, in which from 1 to 10% of the cellulose hydroxyl groups have been formylated, impregnated with from about 6 to 16% by weight, based on the dry material, of an insolubilized melamine-formaldehyde condensation product, said fibers being characterized by a tensile strength which is substantially the same as the untreated cellulosic textile fibers from which they were prepared.

8. A wrinkle and crease resistant cellulosic textile material consisting of partially formylated natural cellulose textile fibers, in which from 1 to

10% of the cellulose hydroxyl groups have been formylated, impregnated with from about 6 to 16% by weight, based on the dry material, of an insolubilized condensation product selected from the group consisting of urea-formaldehyde, melamine-formaldehyde, methylated urea-formaldehyde and methylated melamine-formaldehyde condensation products and mixtures thereof, said fibers being characterized by a tensile strength which is substantially the same as the untreated cellulosic textile fibers from which they were prepared.

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