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2,804,402

TREATMENT OF CELLULOSE CONTAINING TEXTILE MATERIALS AND COMPOSITIONS THEREFOR

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The present invention relates to improvements in the art of finishing cellulose containing textile materials, particularly to provide a finish which is resistant to the absorption of chlorine, and to cellulose containing textile materials having a novel finish. The present invention also relates to novel compositions for producing such a finish.

It has been known heretofore to impregnate cellulose fabrics such as cotton and regenerated cellulose fabrics with an aqueous solution of dimethylol imidazolidone-2 (also known as dimethylol ethylene urea) and to heat the resulting fabric to about 300° F. to obtain a wrinkle or crush-resistant finish. The treated fabrics exhibit a greater tensile and tear strength loss than similar fabrics which have been treated with the commercially available water-soluble methylated melamine-formaldehyde condensation products using a catalyst such as 2-amino-2-methyl propanol - (1) hydrochloride and a curing temperature of 300° F., but the dimethylol ethylene urea treated fabrics exhibit less loss in tensile strength when treated with solutions containing available or free chlorine and dried and heated than in the case of fabrics treated with the commercially available methylated melamine-formaldehyde condensation products. On the other hand the cellulose fabrics treated with dimethylol ethylene urea have dimensional stability and a crush or wrinkle resistant finish which is substantially equivalent to that of similar cellulose fabrics treated with the commercially available methylated melamine-formaldehyde condensation products.

In accordance with the present invention, it is possible to provide a finish on cellulose fabrics or textile materials comprising cellulose fibers which is not only equivalent in respect to tensile and tear strength, crush resistance and dimensional stability to the finish produced by the use of commercially available methylated melamine-formaldehyde condensation products, but is also superior in respect to its ability to withstand chlorination followed by drying and heating without a marked loss in tensile strength than corresponding fabrics treated with either dimethylol ethylene urea or commercially available methylated melamine-formaldehyde condensation products. The present invention also provides novel compositions for providing a finish on cellulose fabrics which is resistant to the absorption of chlorine.

It is, accordingly, one object of this invention to provide a process of treating textile materials comprising cellulose fibers to provide a finished material which is suitable as to tensile and tear strength and crush resistance and which does not exhibit excessive tensile strength loss after chlorination and drying and heating of the material.

It is a further object of this invention to provide a textile material comprising cellulose fibers which is suitable as to tensile and tear strength and crush resistance and does not exhibit excessive tensile strength loss after chlorination and drying and heating of the material.

It is a further object of this invention to provide novel

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el compositions which are particularly suitable for treating textile materials comprising cellulose fibers to produce a finish which does not exhibit excessive tensile strength loss after chlorination and drying and heating of such material.

Still further objects and advantages of this invention will become apparent from the following description and the appended claims.

The processes of this invention are carried out, in general, by impregnating a textile material comprising cellulose fibers with an aqueous solution comprising (1) a water-soluble, fully methylolated heterocyclic compound having a saturated ring consisting of only carbon atoms and at least two nitrogen atoms, to which nitrogen atoms are attached only one hydrogen atom and (2) a thermosetting, water-soluble, infinitely dilutable methyl ether of polymethylol melamine, the methylolated heterocyclic compound and the methyl ether being present in the solution in a weight ratio between 4:1 and 1:2, and, preferably, a curing catalyst, and thereafter subjecting the treated material to elevated temperatures to produce a substantially water-insoluble finish. The resulting material is not only equivalent in respect to tensile and tear strength and crush resistance to a similar material treated with a corresponding amount of the corresponding methyl ether of polymethylol melamine per se, but also exhibits less tensile strength loss after chlorination and drying and heating than similar materials treated with the corresponding amounts of the methylolated heterocyclic compound per se or the corresponding methyl ether of polymethylol melamine per se or various combinations of such treating materials used in weight ratios other than those specified above.

If desired, the treated material may be mechanically finished, preferably prior to insolubilization of the finish, to provide a textured material having the superior properties referred to above.

A further understanding of the processes, textile products and compositions of the present invention will be obtained from the following specific examples, which are intended to illustrate this invention, but not to limit the scope thereof, parts and percentages being by weight unless otherwise specified.

Example I

Five parts of an 80% aqueous solution of a methyl ether of polymethylol melamine containing about 3.4 mols of combined formaldehyde and 2.2 mols of combined methanol per mol of melamine and having a pH of about 10.0 (glass electrode), eight parts of a 50% aqueous solution of dimethylol ethylene urea having a pH of about 8.0 (glass electrode) and eighty-five parts of water were mixed together until a homogeneous solution was obtained. The resulting solution was stable at normal room temperature (about 75° F.) for a period of at least 3 months. The aqueous solution of methyl ether of polymethylol melamine used was further characterized in that it was infinitely dilutable with water without precipitation of any condensation product. This property was also true of the final solution obtained as a result of the mixing operation.

To the solution as obtained above were added ½ part of 55% aqueous dispersion of polyvinyl acetate (which is a water-insoluble thermoplastic vinyl resin), ½ part of a textile softener composed of mixed cationic and anionic long chain derivatives and 0.8 part of a latent curing catalyst, namely a 35% aqueous solution of 2-amino-2-methyl propanol - (1) hydrochloride adjusted to a pH of about 8.0 (glass electrode) with 2-amino-2-methyl propanol - (1).

A yarn dyed, plain woven cotton fabric (gingham)

was immersed in the above solution at room temperature padded so as to give a wet pickup of 100%, thus depositing about 4% of dimethylol ethylene urea and 4% of the methyl ether of polymethylol melamine, based on the dry fabric weight, after which the fabric was framed, dried at 180° F. and then cured for 5 minutes at 300° F. to provide a water-insoluble finish. The fabric was then given a light wash in water to remove most of the water-soluble materials such as catalyst decomposition products from the fabric.

The treated fabric was then tested for damage caused by retained chlorine using the Tentative Test Method 69-52 described on pages 96 and 97 of the 1953 Technical Manual and Year Book of the American Association of Textile Chemists and Colorists (volume XXIX) with the exception that the scorch test was carried out at 350° F. The results obtained are given in the table below opposite the fabric designated Fabric A.

A sample of gingham fabric from the same lot as referred to above was treated using the procedure given above with a solution such as that described above with the exception that the methyl ether of polymethylol melamine was omitted and the solution contained 10% of dimethyl ethylene urea and 1% of the same latent curing catalyst. The resulting fabric was then tested for damage caused by retained chlorine using the Tentative Test Method 69-52 hereinbefore referred to except that the scorch test was carried out at 350° F. The results obtained are given in the table below opposite the fabric designated Fabric B.

A sample of gingham fabric from the same lot as referred to above was treated using the procedure hereinbefore given with a solution such as described in the first two paragraphs of this example with the exception that dimethylol ethylene urea was omitted and the solution contained 9.6% of the methyl ether of polymethylol melamine and 1% of the curing catalyst. The resulting fabric was then tested for damage caused by retained chlorine using the Tentative Test Method 69-52 hereinbefore referred to except that the scorch test was carried out at 350° F. The results obtained are given in the table below opposite the fabric designated Fabric C.

Fabric Tested	Percent Loss in Tensile Strength Along Warp Direction of Fabric Due to Retained Chlorine
Fabric A.....	6
Fabric B.....	16
Fabric C.....	69

Fabric A was comparable to Fabric C in tensile and tear strength and crush resistance prior to chlorination and both of these fabrics were superior in these respects to Fabric B, but the above table shows that Fabric A is decidedly superior to Fabrics B or C in its ability to retain its tensile strength after chlorination and drying and heating.

In carrying out the above experiments comparable results are obtained by omitting the polyvinyl acetate and softener from the treating solutions. The effect of these materials is to modify the hand and body of the fabric.

Example II

An aqueous solution was prepared containing 6.5% of dimethylol ethylene urea, 3.2% of a water-soluble methyl ether of polymethylol melamine containing about 3.4 mols of combined formaldehyde and 2.2 mols of combined methanol per mol of melamine, 1.5% of a 55% aqueous dispersion of polyvinyl acetate, 1% of a 35% aqueous solution of 2-amino-2-methyl propanol-(1) hydrochloride adjusted to a pH of 8.0 with an excess of the amine and 1.5% of "Ahcovel G" which is a tradename for a cationic fatty carbamide softener of the type described in U. S. Patents No. 2,304,113 and No. 2,304,369.

A woven cotton fabric which had been bleached, mercerized and given a mild acid sour was given a long dip in the above solution to wet out the fabric, after which the fabric was padded in a single nip at 12 tons pressure per width of fabric, and finally dried in a three tenter section at 150° F., 175° F. and 200° F., respectively, to less than 2% moisture content. The dried fabric was roll calendered cold, and cured at 310° F. until a water-insoluble finish was obtained. The fabric was then given a 10 minute refinish wash at 160° F. with an aqueous solution of soda ash and a water-dispersible ethylene oxide condensate of octyl phenol, rinsed with water at 140° F. for 8 minutes and dried. This fabric was then tested for damage caused by retained chlorine using the Tentative Test Method 69-52 hereinbefore referred to in Example I. The resulting fabric showed a tensile strength loss of 26% in the warp direction and 35% in the filling direction.

A woven cotton fabric of the same lot as treated above was treated by the procedure given in the preceding paragraph using a similar solution with the exception that the methyl ether of polymethylol melamine and polyvinyl acetate were omitted and the solution contained 7.5% of dimethylol ethylene urea and 1.5% of polyvinyl alcohol. This fabric was then tested for damage caused by retained chlorine using the Tentative Test Method 69-52 hereinbefore referred to in Example I. The resulting fabric showed a tensile strength loss of 50% in the warp direction and 45% in the filling direction.

The fabric treated with dimethylol ethylene urea and the methyl ether of polymethylol melamine was at least equivalent in crush resistance to a similar fabric treated with dimethylol ethylene urea and was superior thereto in respect to tear and tensile strength prior to chlorination and decidedly superior thereto in its ability to retain its tensile strength after chlorination and drying and heating. The fabric treated with dimethylol ethylene urea and the methyl ether of polymethylol melamine was also at least equivalent in crush resistance, tensile and tear strength, prior to chlorination, to a similar fabric treated with the methyl ether of polymethylol melamine and was vastly superior thereto in respect to non-yellowing and its ability to retain its tensile strength after chlorination and drying and heating.

As in the case of Example I, the polyvinyl acetate, the polyvinyl alcohol and softener may be omitted from the treating solution, without affecting the above results, as these ingredients merely serve to alter the hand and/or body of the fabric.

Example III

A regenerated cellulose (viscose rayon) challis fabric was impregnated in an aqueous solution of 16 pounds of a 50% aqueous solution of dimethylol ethylene urea having a pH of about 8.0, 12 pounds of a 60% aqueous solution of a methyl ether of polymethylol melamine containing about 3.4 mols of combined formaldehyde and 2.2 mols of combined methanol per mol of melamine and having a pH of about 10, 1.1 pounds of a 35% aqueous solution of 2-amino-2-methyl propanol-(1) hydrochloride adjusted to a pH of about 8.5 with an excess of the amine, 0.5 pound of "Avcosol" which is the tradename for a water-dispersible softener composed of a synthetic waxy derivative of a sorbitol ester, and sufficient water to make 20 gallons of solution, which solution was infinitely dilutable with water without precipitation of any ingredient. After the fabric was completely wetted out in the above solution, it was padded to obtain a solution pick up of about 75% and then dried at 275° F. to a final moisture content of 5% within about 75 seconds. This fabric was then cured for 2.5 minutes at 330° F. and washed in a dilute aqueous solution of Igepon T



for 15 minutes, after which the fabric was rinsed with

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cold water, dried on a pin tenter using 10% overfeed and steam framed on a clip tenter.

The fabric was then tested for damage caused by retained chlorine using the Tentative Test Method 69-52 hereinbefore referred to in Example I with the exception that the fabric was rinsed until a negative reaction to starch-iodide reagent was obtained. The fabric showed no loss in tensile strength resulting from averaging the tensile strengths in the warp and filling directions. On the other hand, a fabric from the same lot treated with a substantially equal weight amount of the dimethylol ethylene urea or the methyl ether of polymethylol melamine using the same procedure and using the same test showed at least 68% tensile strength loss. From this it is obvious that the two methylol compounds used in the weight ratio specified given an unusual synergistic effect in respect to resistance to loss in tensile strength due to chlorination and drying and heating.

Example IV

Three pieces of 96 x 96 cotton cloth from the same lot were treated using the treating solutions and procedures set forth in Example I, with the exception that the wet padded fabrics were dried to a moisture content of 55% and were then embossed or given an ornamental texture by pressing each fabric individually between two platens having an engraved pattern thereon. The top platen was at a temperature of 350° F. and was forced against the bottom platen at a pressure of 280 pounds per square inch for a period of 5 seconds. The pressure was then released and the fabric was removed from the platens and cured for 5 minutes at 300° F. After chlorination and scorching as set forth in Tentative Test Method 69-52 results comparable to those given in Example I were obtained.

Although the foregoing examples illustrate the use of dimethylol ethylene urea, it is possible to replace part or all of this compound with a water-soluble, fully methylolated heterocyclic compound having a ring consisting of carbon atoms and at least two nitrogen atoms, preferably a ring having 3 carbon and 2 nitrogen atoms, in which the nitrogen atoms have only one hydrogen atom attached thereto and the remaining valences of the nitrogen are taken up by carbon atoms. Preferred heterocyclic compounds of this type are those having from 3 to 4 carbon atoms having oxygen or sulfur atoms attached to from 1 to 2 carbon atoms in the ring and from 2 to 4 nitrogen atoms having only one hydrogen atom attached to any one nitrogen atom, the remaining valences of the carbon atoms being satisfied by hydrogen atoms. As examples of fully methylolated heterocyclic compounds which may be used may be mentioned dimethylol ethylene thiourea, dimethylol 1-2 propylene urea, dimethylol 1-2 propylene thiourea, dimethylol 1-3 propylene urea, dimethylol 1-3 propylene thiourea, dimethylol 1-3 butylene urea, dimethylol 2-3 butylene urea, tetramethylol acetylene diureine, dimethylol hydantoin and the like. However, from the standpoint of availability and the results obtained, it is preferred to employ dimethylol ethylene urea as this compound does give a result which is superior, for the purposes of this invention, to that of the other fully methylolated heterocyclic compounds of the type described.

Various thermosetting, water-soluble methyl ethers of polymethylol melamine, aqueous solutions of which are infinitely dilutable with water without precipitation of condensation product, may be used instead of the specific product illustrated in the examples. Thus, such ether may contain varying amounts of combined formaldehyde and combined methanol as long as the product is thermosetting and water-soluble and aqueous solutions thereof are infinitely dilutable with water in the sense described above. For convenience in description such products may be referred to as thermosetting, water-soluble, infinitely dilutable methyl ethers of polymethylol melamines. A particularly suitable class of such condensation products are

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those which are essentially monomeric and contain from about 2.5 to 5 mols of combined formaldehyde and from about 2 to 4 mols of combined methanol per mol of melamine and which are further characterized in having from about 0.5 to 1.5 unetherified methylol groups per mol of melamine, that is, have from 0.5 to 1.5 mols of combined formaldehyde in excess of the combined methanol per mol of melamine. A particularly preferred class of products of this type are those which are essentially monomeric and contain from about 3 to 4 mols of combined formaldehyde and from about 2 to 3 mols of combined methanol per mol of melamine, the amount of combined formaldehyde being about 1.0 to 1.5 mols in excess of the combined methanol per mol of melamine. The products described above are readily prepared by the processes described in the Bonzagni Patent No. 2,645,625.

The weight ratio of the fully methylolated heterocyclic compound to the methyl ether of polymethylol melamine in the textile treating composition is critical and should be between 4:1 and 1:2 as hereinbefore described. If the weight ratio employed falls outside of these limits, the treated textile material shows a loss in tensile strength, after chlorination, which is substantially the same as that obtained by the use of the fully methylolated heterocyclic compound per se or the methyl ether of the polymethylol melamine per se either of which gives decidedly inferior results. In general, best results from an over all standpoint in physical properties of the textile material are obtained by using a weight ratio between 2:1 and 1:2 and such a weight ratio is preferred over the wider range referred to above. Optimum results in the treatment of the textile materials, particularly from the standpoint of minimum loss in tensile strength after chlorination, are obtained with a weight ratio of about 1:1 and this particular weight ratio is preferred above all others.

The compositions of this invention comprise an aqueous solution of the fully methylolated heterocyclic compound and the methyl ether of polymethylol melamine, which materials are present in the solution in the weight ratios referred to above. The concentration of these materials in the solution is relatively unimportant and depends in large measure on whether the solution is to be used directly for textile treatment or shipped to a point of use where the solution is to be diluted prior to use with a suitable liquid such as water. In general, the compositions may contain from about 2 to 80% by weight of the fully methylolated heterocyclic compound and the methyl ether of polymethylol melamine. In those instances when the composition is to be shipped, the composition may contain about 40 to 80% by weight of such materials. In those instances where the composition is to be used directly in textile treatments, the concentration of such materials therein will depend on the amount of such material which is desired to be deposited in the textile material and the mode of application of the composition to the textile material. In general, compositions of the latter type may comprise from about 2 to 15% by weight of such materials.

As is illustrated in the examples, the compositions may also contain conventional textile auxiliaries such as stiffening or bodying agents, softening agents, curing catalysts, wetting agents, antifoaming agents and the like, but such agents are not essential. When such agents are used it is preferred, for best results, to use textile auxiliaries which are free of nitrogen atoms.

As examples of stiffening or bodying agents which may be employed may be mentioned aqueous dispersions of water-insoluble thermoplastic vinyl resins such as polyvinyl acetate, polyvinyl chloride, polystyrene, polyalkyl acrylates, polyalkyl methacrylates, vinyl chloride, vinyl acetate copolymers and the like and/or water-soluble thermoplastic resins such as polyvinyl alcohol; water-soluble partially hydrolyzed polyvinyl acetates; water-soluble ammonium salts of styrene-maleic anhydride copolymers, styrene-alkyl acid maleate copolymers, vinyl

acetate-maleic anhydride copolymers, vinyl acetate-crotonic acid copolymers, vinyl acetate-alkyl acid maleate copolymers; or the like. Generally such agents are employed in amounts of about 0.05 to 5% by weight of the composition.

As examples of softening agents, in addition to those referred to in the examples, may be mentioned water-soluble alkali metal and ammonium salts of sulfonated mineral oils, sulfonated fatty alcohols such as sulfonated cetyl and stearyl alcohol, sulfonated castor oil and the like; water-soluble or water-dispersible polyethylene oxides of high molecular weight; the water-soluble reaction products of ethylene oxide or propylene oxide with aryl and aralkyl alcohols or with esters of a fatty acid and sorbitan and the like; cationic type softeners such as cetyl dimethyl benzyl ammonium chloride and the quaternary ammonium salts of diethyl amino-ethyl oleyl amide hydro acetate, or the like. Generally such agents are employed in amounts of 0.05 to 5% by weight of the composition.

As examples of curing catalysts may be mentioned the salts of an amino or substituted amino-aliphatic alcohol and phosphoric or hydrochloric acid, for example, salts such as 2-amino butanol-(1) phosphate, 2-amino butanol-(1) hydrochloride, 2-amino-2-methyl propanol-(1) phosphate, 2-amino-2-methyl propanol-(1) hydrochloride, 1-amino-2-methyl butanol-(2) phosphate, 1-amino-2-methyl butanol-(1) hydrochloride, 3-amino-2-methyl butanol-(1) hydrochloride, diethanolamine hydrochloride or phosphate, monoethanolamine hydrochloride or phosphate, triethanolamine hydrochloride or phosphate, and the like, and ammonium chloride of diammonium phosphate. While it is not desirable to use curing catalysts in the compositions of this invention because such catalysts markedly decrease the useful life of the composition it is desirable to incorporate such catalysts in the compositions just prior to the treatment of the textile materials with the composition in order to bring the cure time within practical limits. The amount of curing catalyst employed is not critical, but is preferably about 1 to 10% by weight, based on the combined weight of the fully methylolated heterocyclic compound and the methyl ether of polymethylol melamine in the composition.

As examples of wetting agents which may be used may be mentioned sodium salts of alkylated benzene sulfonates such as sodium decyl benzene sulfonate, sodium dodecyl benzene sulfonate; sodium lauryl sulfate; the sodium salt of methyl stearamide ethionic acid; dioctyl sodium sulfosuccinate; and the like. In general, such agents are employed in amounts of about 0.05 to 3% by weight of the composition.

As examples of anti-foaming agents may be mentioned water-insoluble silicone compounds, water-insoluble oils, water-insoluble alcohols and the like. The amount of such agent used varies with its effectiveness in minimizing foaming, but, in general, amounts of about 0.1 to 5% by weight of the composition may be employed.

The compositions may be applied to the textile materials in various ways so long as impregnation of the textile materials is obtained. For example, the textile materials may be dipped or immersed in the composition or the composition may be dripped or sprayed on the textile material until the textile material is wetted out with the composition. In order to facilitate the control of deposition of the methylol compounds on the textile material and reduce the drying time, it is desirable to extract the textile material to remove excess solution therefrom. This is suitably accomplished by padding, wringing, squeezing or hydroextracting the textile material. The amount of fully methylolated heterocyclic compound and methyl ether of polymethylol melamine applied to the textile material is controlled by the degree of extraction used and/or the concentration of these materials in the composition, and may be varied widely depending on the amount of crush resistance and dimensional stability de-

sired in the textile material. In general, the amount of such ingredients applied is between about 2 and 15% by weight, based on the dry textile material, but in order to obtain practical crush resistant effects, it is preferred to apply from about 5 to 12% by weight, based on the dry textile material.

After the composition has been applied, the textile material may then be dried at normal drying temperatures and finally heated at elevated temperatures of about 250 to 360° F. to obtain a water-insoluble finish or the textile material may be dried and cured to provide a water-insoluble finish in one heating operation at temperatures of about 250 to 360° F. The temperature may be higher than 360° F. depending on the particular textile material, the type and amount of catalyst and the duration of heating without adversely affecting the textile material. The duration of heating may vary widely depending primarily on the moisture content and the temperature used but is generally between about 1 and 15 minutes with the longer times corresponding to the lower temperatures. The textile material thus obtained may be given the usual finishing operations such as a refinish wash to remove water-soluble materials, steam framing and the like. Such operations may be desirable, but are not essential.

As is illustrated in Example IV, the textile material may be given a textured finish. This is suitably accomplished by first applying the composition, partially drying the textile material, preferably to a moisture content of about 5 to 20% by weight, based on the dry textile material, and then subjecting the textile material to a mechanical finishing operation such as calendering, glazing, pleating, crimping, embossing or Schreiner or the like to change the form and relative disposition of the textile fibers or yarns in the textile material and thus alter the surface texture of the textile material. The textile material is then subjected to elevated temperatures, for example, the curing temperatures referred to above, to provide a water-insoluble finish which retains the surface texture imparted by mechanical finishing despite numerous hand launderings. Chlorination of the textured textile materials followed by drying and heating does not materially reduce the tensile strength of the material.

A large variety of textile materials comprising cellulose fibers may be treated in accordance with the processes of this invention, but the textile material should contain at least 40% by weight of cellulose fibers, and preferably 60% by weight or more of cellulose fibers. The textile materials treated may be woven or knitted fabrics, referred to generally as fabrics, or yarns or fibers, but it is preferred to treat fabrics. The cellulose fibers may be natural cellulose fibers such as cotton, linen, flax or ramie fibers or regenerated cellulose staple fibers or filaments produced by the viscose or cuprammonium processes. It is preferred, however, to treat cotton fibers or viscose rayon staple fibers or filaments. The preferred textile materials are 100% cotton woven fabrics or 100% viscose rayon woven fabrics or woven fabrics composed entirely of cotton and viscose rayon.

What is claimed is:

1. A composition of matter consisting essentially of a stable aqueous solution of (1) a water-soluble, fully methylolated heterocyclic compound and (2) a thermosetting, water-soluble, infinitely dilutable methyl ether of polymethylol melamine, said fully methylolated heterocyclic compound and said methyl ether being present in the solution in a weight ratio between 4:1 and 1:2, said heterocyclic compound having a saturated ring consisting of from 2 to 4 nitrogen atoms having only one hydrogen atom attached to each nitrogen atom and from 3 to 4 carbon atoms having a chalcogen of the group consisting of oxygen and sulfur attached to at least one such carbon atom.

2. A process of finishing textile materials to provide crush resistant materials which resist loss in tensile strength due to chlorination followed by drying and heat-

ing, which comprises impregnating a textile material comprising at least 40% by weight of cellulose fibers with an aqueous solution of (1) a water-soluble, fully methylolated heterocyclic compound, (2) a thermosetting, water-soluble, infinitely dilutable methyl ether of polymethylol melamine, said fully methylolated heterocyclic compound and said methyl ether being present in the solution in a weight ratio between 4:1 and 1:2, and (3) a curing catalyst, and thereafter subjecting the textile material to elevated temperatures to dry the textile material and to provide a water-insoluble finish, said heterocyclic compound having a saturated ring consisting of from 2 to 4 nitrogen atoms having only one hydrogen atom attached to each nitrogen atom and from 3 to 4 carbon atoms having a chalcogen of the group consisting of oxygen and sulfur attached to at least one such carbon atom.

3. A process of finishing textile fabrics to provide crush resistant materials which resist loss in tensile strength due to chlorination followed by drying and heating, which comprises impregnating a woven textile fabric comprising at least 40% by weight of cellulose fibers with an aqueous solution of (1) a water-soluble, fully methylolated heterocyclic compound, (2) a thermosetting, water-soluble, infinitely dilutable methyl ether of polymethylol melamine and (3) a curing catalyst, said fully methylolated heterocyclic compound and said methyl ether being present in the solution in a weight ratio between 4:1 and 1:2, partially drying said fabric, altering the surface texture of the fabric and thereafter heating the fabric at elevated temperatures to fully dry the fabric and provide a water-insoluble textured finish, said heterocyclic compound having a saturated ring consisting of from 2 to 4 nitrogen atoms having only one hydrogen atom attached to each nitrogen atom and from 3 to 4 carbon atoms having a chalcogen of the group consisting of oxygen and sulfur attached to at least one such carbon atom.

4. A textile material comprising at least 40% by weight of cellulose fibers and having a water-insoluble finish comprising a heat-set, fully methylolated heterocyclic compound and a thermoset methyl ether of polymethylol melamine, said heat-set heterocyclic compound and thermoset methyl ether being present in a weight ratio between 4:1 and 1:2, said heterocyclic compound having a saturated ring consisting of from 2 to 4 nitrogen atoms having only one hydrogen atom attached to each nitrogen atom and from 3 to 4 carbon atoms having a chalcogen of the group consisting of oxygen and sulfur attached to at least one such carbon atom.

5. A composition of matter according to claim 1, but further characterized in that said fully methylolated heterocyclic compound is dimethylol ethylene urea.

6. A composition of matter consisting essentially of a stable aqueous solution of dimethylol ethylene urea and a thermosetting, water-soluble, infinitely dilutable methyl ether of polymethylol melamine containing from about 2.5 to 5 mols of combined formaldehyde and about 2 to 4 mols of combined methanol per mol of melamine and further characterized in that it contains from about 0.5 to 1.5 unetherified methylol groups per mol of melamine, said dimethylol ethylene urea and said methyl ether being present in the solution in a weight ratio between 2:1 and 1:2.

7. A composition of matter consisting essentially of a stable aqueous solution of dimethylol ethylene urea and a thermosetting water-soluble, infinitely dilutable

methyl ether of polymethylol melamine, said materials being present in the solution in a weight ratio of about 1:1.

8. A composition of matter as in claim 7, but further characterized in that said methyl ether contains from about 3 to 4 mols of combined formaldehyde and from about 2 to 3 mols of combined methanol per mol of melamine and has about 1.0 to 1.5 unetherified methylol groups per mol of melamine.

9. A process as in claim 2, but further characterized in that the fully methylolated heterocyclic compound is dimethylol ethylene urea.

10. A process as in claim 9, but further characterized in that the textile material is a woven textile fabric.

11. A process of finishing textile fabrics to provide a crush resistant fabric which resists loss in tensile strength due to chlorination followed by drying and heating which comprises impregnating a woven textile fabric comprising at least 60% by weight of cellulose fibers with an aqueous solution of (1) dimethylol ethylene urea, (2) a thermosetting, water-soluble, infinitely dilutable methyl ether of polymethylol melamine, said dimethylol ethylene urea and said methyl ether being present in the solution in a weight ratio between 2:1 and 1:2, and (3) a curing catalyst, and thereafter heating the fabric at elevated temperatures to dry the fabric and provide a water-insoluble finish.

12. A process as in claim 11, but further characterized in that the methyl ether contains from about 2.5 to 5 mols of combined formaldehyde and from about 2 to 4 mols of combined methanol per mol of melamine and has from about 0.5 to 1.5 unetherified methylol groups per mol of melamine.

13. A process as in claim 11, but further characterized in that the fibers are cotton fibers.

14. A process as in claim 11, but further characterized in that the fibers are viscose rayon fibers.

15. A process of finishing an all cellulose textile fabric to provide a crush resistant fabric which resists loss in tensile strength due to chlorination followed by drying and heating which comprises impregnating said fabric with an aqueous solution of (1) dimethylol ethylene urea, (2) a thermosetting, water-soluble, infinitely dilutable methyl ether of polymethylol melamine and (3) a curing catalyst, said dimethylol ethylene urea and said methyl ether being present in said solution in a weight ratio of about 1:1, said solution being supplied in an amount sufficient to deposit from about 5 to 12% by weight of said dimethylol ethylene urea and said methyl ether, based on the dry weight of said fabric, and thereafter heating the fabric at elevated temperatures to dry the fabric and provide a water-insoluble finish.

16. A process as in claim 15, but further characterized in that the methyl ether contains from about 3 to 4 mols of combined formaldehyde and from about 2 to 3 mols of combined methanol per mol of melamine and has about 1.0 to 1.5 unetherified methylol groups per mol of melamine.

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