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WASH RESISTANT FINISHING MEANS AND METHODS OF MANUFACTURING THEM

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This invention relates to resin precondensates and a method of preparing the same, and more particularly to polymerization of condensation products which can be applied to textile materials and impart valuable properties to the textile materials when cured.

We have found that highly effective textile finishing agents are obtained by the thermal polymerization of mixed ethers of methylol urea compounds with lower monohydric alkanols and with aliphatic saturated polyhydric alcohols in an acid aqueous medium, and subsequent neutralization of the polymerization mixture obtained. When applied to textile materials of native or regenerated cellulose, the textile treating agents of the invention provide the fabric with an excellent full hand which is not affected by laundering or dry cleaning.

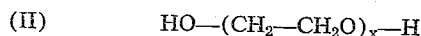
The precondensates of the invention are applied to the textile material in the usual manner by impregnation of the material with aqueous liquids which contain the precondensates and conventional acid generating curing catalysts. When these catalysts are ammonium salts of strong acids, curing may be completed by merely drying the impregnated textile material. If multivalent metal salts of strong inorganic acids are used as catalysts, drying is preferably followed by curing of the precondensate to the insoluble resin at 130 to 180° C. for a few minutes as is customary. The concentration of the precondensates of the invention in the treating bath is preferably of the order of 20 to 250 grams of a 50 percent precondensate solution per liter of the finishing bath.

The saturated aliphatic polyhydric alcohols which form mixed methylol urea ethers in conjunction with lower alkanols are of three general types. A first group of polyhydric alcohols has the formula



wherein n is an integer between two and six, and m is an integer between two and six, but not greater than n .

A second group of polyhydric alcohols has the formula



wherein x is an integer between two and fourteen.

The third group consists of the polyhydric alcohols of the formula



wherein y is either five or six.

Specific examples of polyhydric alcohols which are members of the three groups identified above, and which are suitable starting materials for synthesizing the precondensates of the invention include ethylene glycol, glycerol, erythritol, pentaerythritol, pentitols such as adonitol, arabitol, and xylitol, hexitols such as mannitol, sorbitol, and dulcitol, monosaccharides of the aldose or ketose type such as glucose, mannose, fructose, and galactose, and polyalkylene glycols having a molecular weight of less than about 600. The polyvalent alcohols may be applied solely but also jointly in mixtures.

Preferred examples of the lower alkanols with which the methylol urea compounds are also etherified include methanol and ethanol.

2

The methylol urea compounds from which the precondensates of the invention are preferably prepared are generally mixtures obtained by the reaction of 1.8 to 2.5 mols formaldehyde with one mol urea in which dimethylol urea is at least a major constituent. In the mixed ethers of the invention, the methylol urea compounds are combined with the polyhydric alcohols and the alkanols in a ratio of one mol equivalent of urea to 1.7 to 2.5 mol equivalents of hydroxyl radicals in the polyhydric alcohols and 0.6 to 2.0 mols of lower alkanol.

The etherification of the methylol urea compounds may be carried out in the presence or in the absence of water. The polymerization of the ether formed, however, must be carried out in the presence of water in an acid medium. The amount of water present has to be within the limits of 1 to 10 mols, 2 to 6 mols of water for each mol equivalent of urea have been found advantageous from a practical point of view.

The formation of the mixed ether and the polymerization may be performed in a single operation. The pH of the aqueous reaction mixture during the polymerization is held at a value of less than 3 which usually requires the presence of strong inorganic or organic acids. The polymerization is continued until the viscosity of the liquid polymerization mixture has increased at least to three times its original value while the product is still infinitely miscible with water of 20° C. even though the dilute solution may be opalescent. Optimal products are these forming opalescent solutions by diluting.

If the polymerization reaction is interrupted prematurely, that is, before the viscosity of the solution has risen to at least three times the original value, there are obtained products which do not impart optimum hand to a treated cellulosic fibrous material, and more specifically to a fabric of native or regenerated cellulose. If the polymerization is permitted to continue beyond the preferred stage, there are obtained products which are no longer infinitely soluble in water. When such products are diluted to desirable treating bath concentrations, resinous particles are precipitated from the bath, and cause serious difficulties in the processing of the textile material. Such over-polymerized products are not readily emulsified, if they can be emulsified at all.

The threefold increase in viscosity which at least has to be reached by the polymerization reaction is measured from the intermediate ether stage. By carrying out the etherification of the methylol urea and the polymerization reaction in one single stage, the viscosity of the ether is measured of a trial lot which is taken as soon as etherification has finished and is neutralized.

The precondensates of the invention which are based on urea have important advantages over the known textile finishing agents which are prepared from aminotriazines by reaction with formaldehyde and polyhydric alcohols. In equally effective amounts, the urea derivatives of the invention which are more readily available, are very much less costly than aminotriazine compounds. The precondensates formed from urea as well as the treating baths obtained from the precondensates are more stable and therefore capable of longer storage than equally effective baths prepared from aminotriazine derivatives. The treating baths of the invention are also insensitive to relatively high temperatures and permit textile finishing operations to be performed under a relatively wide range of conditions.

Contrary to the known textile finishing agents based on ethers of methylol melamine compounds and related aminotriazine derivatives, the textile finishing agents of the invention do remarkably less impair the light fastness of textile materials dyed with substantive and with reactive dyes. Even where the inexpensive and convenient ammonium salts are employed as curing catalysts,

no fish odor is generated in storage under unfavorable atmospheric conditions.

The textile finishing agents of the invention are also superior to finishing agents that can be prepared from methylol urea compounds by etherification of the methylol radicals with monohydric or polyhydric alcohols. The polymerization of the mixed ethers in an acid aqueous medium according to the invention substantially improves the hand of fabrics treated with the agents produced, and makes the finish resistant to laundering and dry cleaning.

The invention will be further illustrated by examples of specific embodiments thereof, but it will be understood that it is not limited thereto but is to be construed broadly within the scope of the appended claims.

Example 1

1200 grams (12 mols) of a 30 percent formaldehyde solution are adjusted with triethanolamine to a pH of 7.5, and 300 grams (5 mols) urea are added. The mixture is heated until 560 grams water are distilled off at ambient pressure. The urea and formaldehyde are present in the concentrated residue in the form of methylol urea compounds, 400 grams of an 80 percent aqueous glucose solution and 160 grams methanol are added, and the pH is adjusted to approximately 2 by the addition of 7 grams of a 36 percent aqueous hydrochloric acid. The temperature is raised to 60° C. and etherification is completed within 8 to 10 minutes.

The temperature of the solution is then raised to 70° C. while the pH value is kept at the same level, whereby the mixed ether is polymerized. The degree of polymerization is carefully controlled by periodically withdrawing samples, neutralizing them, and diluting them with water. The end point of the desired polymerization is reached when a sample upon dilution forms a strongly opalescent solution, but not a precipitate. The time required to reach this stage is 30 to 50 minutes. The polymerization mixture itself has a viscosity of 8 P at 65° C. Polymerization is stopped at this stage by the addition of sodium hydroxide until the pH value of the mixture rises to 7.8 to 8.0, and the mixture is diluted somewhat by the addition of 200 grams of water. The resulting precondensate solution contains about 50 percent solids.

A textile finishing bath is prepared from 100 grams per liter of the precondensate solution and 3 grams per liter ammonium chloride. Pieces of staple rayon fabric and of cotton fabric are impregnated with the bath in the usual manner, passed between squeeze rolls, and dried. The cotton fabric is additionally glazed. Both types of fabric have a good, full hand which is maintained after repeated laundry and drying cycles. The rayon fabric shows good wrinkle resistance when wet, and the laundry resistance of the glaze finish of the cotton fabric is greatly improved.

Comparative tests are performed with pieces of the same materials treated in an analogous manner with finishing solutions prepared under comparable conditions from dimethylol urea etherified with methanol and glucose, but not polymerized. The results obtained are tabulated below.

Finishing Agent	Staple Rayon Recovery angle, wet, degrees	"No Iron" Picture ¹	Cotton, Laundry resistance of glaze finish
Polymerized.....	132	Note 4.....	good.
Not polymerized.....	98	Note 2.....	mediocre.

¹ According to Monsanto Chemical Co. wash-and-wear standards

Example 2

600 grams spray dried dimethylol urea are dispersed in a mixture of 350 ml. water, 350 grams sorbitol, and 160 grams methanol. 4 grams 36 percent hydrochloric acid are added, and the resulting mixture is heated six

minutes to 60° C. whereupon a clear solution of the mixed ether is formed. The solution is heated further to 70° C. and held at that temperature while a portion of the methanol evaporates and the viscosity increases fourfold. A sample of the product formed dissolves in water, but the solution is opalescent. The polymerization mixture is neutralized at once and is cooled. It is employed as a textile finishing agent as described in Example 1.

Example 3

1200 grams of a 30 percent formaldehyde solution are neutralized with triethanolamine, and 300 grams urea are added. The mixture is heated and a portion of the water is distilled off to form a 70 percent solution of dimethylol urea. 400 grams ethylene glycol, 150 grams ethanol, and 4 grams of concentrated hydrochloric acid (36%) are added to the dimethylol urea solution. The mixture is heated first to 60° and then to 70° C. in order to achieve etherification and limited polymerization of the ether in a manner analogous to Examples 1 and 2. When the desired degree of polymerization is reached, the reaction is stopped by neutralization and cooling. The product obtained is liquid, and remains liquid in extended storage. It is readily diluted with cold water to form opalescent solutions which are excellent textile finishing baths when combined with conventional acid generating catalysts.

Example 4

200 cc. water, 420 grams glycerol, and 6.5 grams concentrated hydrochloric acid (35%) are added to 980 grams of an etherification mixture consisting of 72 percent dimethylol urea dimethyl ether, 27.5 percent water, and 0.5 percent sodium chloride. The resulting mixture is kept about 90 minutes at a temperature of about 65 to 70° C. The methyl ether of methylol urea is partly transformed into the glycerol ether by alcoholysis, and the resultant mixed ether is polymerized to the desired extent so that a viscous polymerization mixture is obtained which is capable of being diluted with water to form an opalescent solution free of any palpable precipitate. The polymerization is stopped by the addition of sodium hydroxide until the pH is raised to a value between 7.6 and 7.8.

Example 5

1800 grams of a 30 percent aqueous formaldehyde solution are neutralized with triethanolamine and mixed with 600 grams urea. The mixture is heated by distilling off water in a vacuum until the residue contains 68 percent solids consisting essentially of methylol urea compounds. 440 grams of an approximately 80 percent aqueous glucose solution, 380 grams ethylene glycol, 300 grams methanol, and 4 grams concentrated hydrochloric acid (36%) are added. The mixture obtained is rapidly heated to 55° C. and complete etherification is achieved within 12 minutes at that temperature. 5 grams of concentrated hydrochloric acid are added and the temperature is raised to 70° C. After 40 minutes the polymerization mixture has greatly increased in viscosity and forms an opalescent solution without precipitation when diluted with water. It is neutralized to pH 7.8.

It is readily diluted to form a textile treating bath. Its ability of ready solution with water, and the finish obtained from the bath so formed are not impaired by eight months' storage at 20° C.

Example 6

800 grams of a product consisting of 85 percent of the monoethyl ether of dimethylol urea, 9 percent ethanol, 6.5 percent water, and 0.5 percent sodium chloride are mixed with 600 grams of a 70 percent aqueous solution of pentaerythritol and with 5 grams concentrated hydrochloric acid. A polymerized mixed ether of the invention is prepared from the mixture by heating to a temperature of 75 to 80° C. for approximately one hour, whereupon the mixture is neutralized and is ready for use

as a textile finishing agent either at once or after a period of storage.

An equal product is obtained by using 500 gr. of an aqueous 60% solution of pentaerythritol and 300 gr. of a polyethylene glycol having an average molecular weight of 320 instead of the above mentioned 600 gr. of pentaerythritol solution.

Although the products formed according to the specific embodiments of the invention set forth in Examples 1 to 6 differ not only in certain details of their preparation, but also in their composition, they produce textile finishes which are substantially equivalent. Textile finishing agents of equal quality can be produced in an analogous manner by replacing the reactants by their homologs, and by analogous compounds as defined in the appended claims.

More specifically, the procedures of Examples 1 and 5 lead to textile treating agents of closely similar properties when the glucose of those examples is replaced by equal amounts of other monosaccharides such as mannose, fructose, and galactose. Glucose, however, is preferred over all other hexoses because of its ready availability and low cost.

No advantage is achieved by replacing methanol or ethanol in Examples 2 and 3 respectively by propanol or isopropanol. The lower alkanols of one to three carbon atoms are fully operative in the procedures described in Examples 2 and 3 although their somewhat different boiling points and rates of etherification will introduce minor variations in processing conditions for which those skilled in the art will readily make the necessary allowances.

Sorbitol in Example 2 and pentaerythritol in Example 6 may be replaced by equivalent amounts of other polyhydric alcohols of which erythritol, adonitol, arabitol, xylitol, mannitol, and dulcitol are merely representative examples. At this time, sorbitol and pentaerythritol are the only members of this group of alcohols which are produced commercially on a large scale, and are therefore available at reasonable cost. Since the textile finishing agents prepared from sorbitol and pentaerythritol do not lack any desirable properties that are found in the corresponding methylol urea derivatives synthesized with the use of the rarer polyhydric alcohols, sorbitol and pentaerythritol are preferred starting materials.

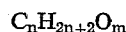
Polyethylene glycol may be substituted for ethylene glycol in the procedures of Examples 3 and 5. If these polyethers have a molecular weight of less than about 600, the textile finishes produced by the modified procedures have the same general properties as those prepared with ethylene glycol. There is some difference in the hand produced, and the wet wrinkle resistance of a rayon fabric treated is slightly reduced.

It should be understood, of course, that the foregoing disclosure relates to only preferred embodiments of the invention, and that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of the disclosure which do not constitute departures from the spirit and scope of the invention set forth in the appended claims.

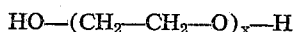
What we claim is:

1. A method of preparing a polymerized water-soluble curable precondensate, which comprises heating a mixed ether of a methylol urea compound in an aqueous acid medium having a pH of less than 3 and containing 1 to 10 mols of water for each mol equivalent of urea to a temperature of 60° C. to 100° C. until the viscosity of said medium has been increased to at least three times the original viscosity of said medium containing the original quantity of water, and continuing the heating until said solution after neutralisation is miscible with an excess of cold water to form a liquid free of precipitates, said mixed ether being an ether of methylol urea compound with a lower monohydric alkanol and with a polyhydric alkanol selected from the group con-

sisting of compounds having the formula



wherein n is an integer between two and six, and m is an integer between two and six and is not greater than n ; of compounds having the formula



wherein x is an integer between two and fourteen; and of compounds having the formula



wherein y is an integer between five and six.

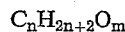
2. A method according to claim 1, wherein said medium is heated until upon dilution with water it forms an opalescent solution.

3. A method according to claim 1, wherein said methylol urea compound is dimethylol urea.

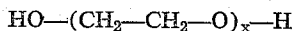
4. A method according to claim 1, wherein said lower alkanol is selected from the group consisting of methanol and ethanol.

5. A method according to claim 1, wherein said aqueous acid medium contains 2 to 6 mols of water for each mol equivalent of urea.

6. A method of preparing curable precondensates, which comprises heating jointly a methylol urea compound, a monohydric lower alkanol and a polyhydric alkanol selected from the group consisting of compounds having the formula



wherein n is an integer between two and six, and m is an integer between two and six and is not greater than n ; of compounds having the formula

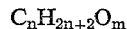


wherein x is an integer between two and fourteen; and of compounds of the formula

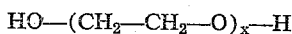


wherein y is an integer between five and six, to an elevated temperature in an aqueous medium in the presence of an acid until a mixed ether of said methylol urea compound with said monohydric alkanol and said polyhydric alkanol is formed, adjusting said resulting solution of said mixed ether to a pH lower than 3 and to a water content 1 to 10 mols of water for each mol equivalent of urea and further heating said acid solution to a temperature of 60° C. to 100° C. until the viscosity of said solution, containing the same quantity of water as the solution of the intermediate formed mixed ether of methylol urea, has been increased to at least three times, and until said solution after neutralisation is miscible with an excess of cold water to form a liquid free of precipitates.

7. A textile treating agent consisting essentially of an aqueous, substantially neutral solution of a polymer of a mixed ether of a methylol urea compound with a lower monohydric alkanol and with a polyhydric alkanol selected from the group consisting of compounds having the formula



wherein n is an integer between two and six, and m is an integer between two and six and is not greater than n ; of compounds having the formula



wherein x is an integer between two and fourteen; and of compounds having the formula



wherein y is an integer between five and six; said aqueous solution being miscible with an excess of cold water to form a liquid free of precipitates, the viscosity of said aqueous solution being higher than three times the viscosity of an aqueous solution of said unpolymersized mixed ether in equal concentration.

8. A textile treating agent according to claim 7, wherein the degree of polymerization of said polymer is such that said aqueous neutral solution upon dilution with an excess of cold water forms an opalescent solution free of precipitates.

5

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