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TEXTILE FINISHING

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4 Claims. (Cl. 117—161)

This invention relates to the treating and finishing of textiles and textile-forming materials such as cotton, linen, wool, viscose, cellulose acetate, spun rayon, silk and the like. The invention includes processes for the finishing of textiles of the above and other types, textile finishing compositions for use in such processes, and textiles of improved properties finished with the compositions and by the processes of the invention.

Textiles such as cloth and other woven or knitted fabrics have heretofore been treated with finishing compositions containing urea-formaldehyde condensation products in order to impart crease-resistance, crush-resistance, a more desirable hand and other similar properties. Thus, for example, it is known to apply solutions of mono- or di-methylol urea to cotton piece goods in order to improve the stiffness and crease-resistance thereof. Alkylated or alcohol-reacted methylol ureas have also been suggested as finishing agents for imparting water-repellent properties to textiles, but the water-insoluble compounds of this type present serious difficulties in application by reason of the necessity of employing organic solvents. It is a principal object of the present invention to provide a method of applying water-insoluble urea-formaldehyde condensation products to textiles in the form of water-soluble salts which dissociate or decompose upon further treatment of the textiles and deposit a curable urea-formaldehyde resin thereon. A further object resides in the application to textiles of normally water-insoluble alkylated urea-formaldehyde condensation products, such as those obtained by reacting dimethylol urea with alcohols containing 4 or more carbon atoms, in the form of aqueous solutions or dispersions. Still further objects will become apparent from the following description of preferred modifications of the invention, when taken with the claims appended thereto.

I have found that the water-insoluble ethers of dimethylol urea in their uncured or substantially monomeric condition can be reacted with salts of tertiary ammonium bases to form a new class of quaternary nitrogen salts that are especially well suited for the finishing of textiles. These new products possess the important property of dissociating or decomposing upon heating at temperatures above about 80° C. with the deposition of water-insoluble curable resinous polymers. In practicing the process of my invention I therefore impregnate the textiles to be treated with aqueous solutions or dispersions of these new condensation products and then subject the impregnated textiles to temperatures substantially above 80° C. to decompose the quaternary salt and cure the urea-formaldehyde resin.

The water-soluble quarternary ammonium salts or condensation products used in practicing the invention are prepared from water-insoluble uncured (i. e. monomeric or only partially polymerized) diethers of dimethylol urea. In their monomeric condition these compounds are defined by the formula

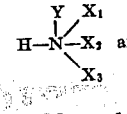
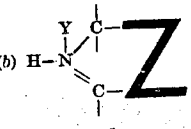
$$ROCH_2.NH.CO.NH.CH_2OR'$$

wherein R' is any suitable alcohol-forming radical but is preferably the radical of a lower aliphatic alcohol such as methyl, ethyl or propyl alcohol and R is the radical of an alcohol containing 4 or more carbon atoms, which forms a water-insoluble dimethylol urea ether. The most important starting materials are those in which R is the radical of an aliphatic alcohol such as butyl, amyl, n-octyl, n-decyl, n-dodecyl or n-tetradecyl, octadecyl or other higher alcohols obtainable by the reduction of coconut fatty acid mixtures or other higher aliphatic acids. Branched-chain higher aliphatic alcohols may also be used, such as isobutyl and isoamyl alcohols; 2-, 3-, and 4-methyl pentanol-1; 2-ethylhexanol-1; 5-ethylnonanol-2; and 3,9-diethyl tridecanol-6.

In addition to the aliphatic alcohols exemplified by those enumerated above alcohols of the cycloaliphatic, aromatic or heterocyclic series may also be used. Thus, for example, cyclohexanol and cycloaliphatic alcohols of 4–8 or more carbon atoms obtainable by the catalytic reduction of naphthenic acids may be employed, or such aromatic alcohols as benzyl alcohol and its homologs. These and other alcohols may be reacted with dimethylol urea itself, or with lower dialkyl ethers of dimethylol urea, by any suitable method. The preferred starting materials, however, are mixed ethers which are most advantageously prepared by ester or ether interchange between lower dialkyl diethers of dimethylol urea and alcohols of relatively high molecular weight by the process illustrated in detail in the following specific examples.

Although salts of any tertiary nitrogen base can be condensed with the dimethylurea diethers described above, the most important classes of compounds for this purpose are the salts of tertiary amines and the salts of pyridine and pyridine homologs. The salts of these two classes

of compounds correspond respectively to the formulas

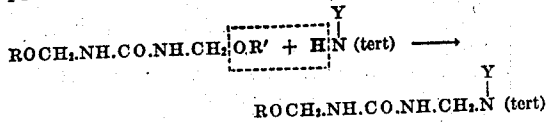
(a)  and (b) 

wherein X_1, X_2 and X_3 in Formula *a* are preferably alkyl radicals such as methyl or ethyl and Z in Formula *b* is the residue of a pyridine base. In either formula Y is the anion of the acid that forms a salt with the tertiary nitrogen base and is preferably a halogen such as chlorine, bromine or iodine, although any acid sufficiently strong to form a salt with a tertiary nitrogen base may be employed. These salts are defined as a class by the formula

H—N(tert)—Y

wherein N(tert) is the tertiary nitrogen base used and Y is as defined above. Suitable tertiary amines are trimethylamine, triethylamine and the like, while any pyridine base may be employed such as pyridine, the alkyl substituted pyridines or picolines and pyridine bases containing condensed aromatic nuclei such as the quinolines.

The quaternary ammonium condensation products are prepared by reacting water-insoluble dimethylol urea ethers with the tertiary nitrogen base salts described above. Upon heating these two classes of compounds at temperatures of 30–80° C. and preferably on the order to 40–60° C. alcohol is liberated and the new condensation products are formed by the following reaction



wherein R, Y and N (tert) are as defined above. The salts of pyridine bases are much more easily condensed with the dimethylol urea ethers by this method and form quaternary compounds which are much more readily soluble in water, and therefore the condensation products of these pyridinium salts constitute a preferred class of the compounds of the present invention. The corresponding quaternary ammonium compounds derived from trialkylammonium salts are much more difficult to prepare and are more difficultly soluble in water, but these products can be dispersed in water and are therefore included within the scope of the invention in its broader aspects. I have also found that the salts of tertiary nitrogen bases formed with inorganic acids will react much more readily with the dimethylol urea ethers described above than will the corresponding salts of organic acids, and therefore I prefer to employ strong inorganic acids such as hydrochloric, hydrobromic and nitric acids or even weaker inorganic acids such as sulfurous acid in preference to the organic acids such as acetic and chloracetic acids.

The above described quarternary ammonium salts may be applied to the textiles in aqueous solution either alone or in admixture with other materials, and any suitable application procedure may be employed. Thus, for example, quaternary ammonium salts of water-insoluble dimethylol urea ethers may be applied in admixture with water-soluble monomeric methylol melamines or with their water-soluble methyl ethers. Similarly, these products may be applied in admixture with water-soluble methylol ureas such as mono- and dimethylol ureas. The solution may also contain suitable curing accelerators such as salts of phosphoric acid having an acid reaction, hexamethylene tetramine, or mixtures thereof, starches, gums, sulfonated oils and other conventional water-dispersible finishing agents.

One method of application which has given excellent results in practice is the following: A finishing bath is prepared by dissolving a quaternary ammonium salt of one or more of the dimethylol urea ethers in water to a 5–15% solution to which methylol ureas, methylated methylol melamines or other auxiliary finishing agents may be added if desired. The textiles are impregnated with this solution by immersion, spraying or any other suitable mechanical means after which the textiles are suspended on tenter frames in a drying oven, heated substantially above 80° C. and preferably at temperatures of about 240–300° F. Heating is continued at these temperatures for a period of time sufficient to decompose the quaternary nitrogen salt and set the resulting dimethylurea monoether on the fiber. The cloth is then preferably washed in an aqueous soap solution, which may also contain a small amount of sodium carbonate, in order to remove the pyridine or other tertiary nitrogen base from the fibers.

The invention will be illustrated in greater detail by the following specific examples. It should be understood, however, that these examples are given primarily for purposes of illustration and that the invention in its broader aspects is not limited thereto.

Example 1

Dimethoxy dimethylurea was prepared by dissolving 1 part by weight of freshly prepared dimethylol urea in 2 parts of methanol containing .0025 part of oxalic acid, adding sufficient NaOH solution to raise the pH to 8.0 or slightly higher and concentrating under reduced pressure to remove excess alcohol and the water of condensation. The product was crystallized and dried at 45° C. to constant weight.

148 parts by weight of dimethoxy dimethylurea were charged into a flask fitted with an agitator and distillation column together with 270 parts of n-octadecanol and 0.1 part of phthalic acid. The flask was heated to about 85° C. during 30–45 minutes to dissolve the contents after which the pressure was reduced to about 435 mm. of mercury and the distillation of methanol was begun. After about 30 minutes the pressure had risen to 700 mm. and the temperature to 100° C., and the distillation of methanol was completed under these conditions in about 15 minutes. 33 parts of methanol were removed in this manner. The product was the stearyl methyl ether of dimethylol urea of the formula

$C_{18}H_{37}OCH_2.NH.CO.NH.CH_2OCH_3$

It was a white solid of waxy consistency, insoluble and immiscibile with water but soluble in acetone.

The lauryl methyl ether of dimethylol urea was prepared by the same method, substituting 186 parts by weight of lauryl alcohol for the stearyl alcohol used in the above procedure.

Example 2

Pyridinium hydrochloride was prepared by dissolving pyridine in benzene, passing in dry gase-

ous HCl, and filtering off and drying the precipitated salt.

A mixture containing 38.6 parts by weight of the stearyl methyl ether of dimethylol urea of Example 1, 40 parts of 95% ethyl alcohol and 11.5 parts of pyridine hydrochloride were reacted at 70° C. for 30 minutes, giving a clear solution. The solution was dried at 40–50° C. to a water-soluble powder which was identified as the pyridinium salt of monostearyl ether of dimethylurea.

Upon heating a sample of the dried powder at 80–100° C. fumes of pyridine were given off and an amorphous, water-insoluble and water-repellent solid was obtained. An aqueous solution was even more easily and rapidly dissociated when heated above 80° C. and deposited a water-repellent film on the bottom of a shallow dish containing the solution. Upon baking the dish at 130° C. this film was further converted to an infusible, water-repellent resin.

10 parts by weight of the dried powder were dissolved in 30 parts of hot denatured ethyl alcohol and diluted with 100 parts of warm water. 80 x 80 cotton cloth and spun rayon challis were padded in the solution, passed between rollers set to retain a weight of solution equal to the weight of the cloth, dried and cured by heating in an oven for 7 minutes at 290° F., washed 15 minutes in a 1% soap solution, dried and ironed. Both samples of treated cloth were then very soft and had excellent water-repellency.

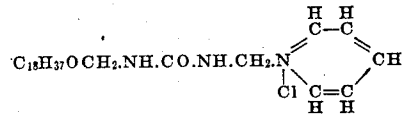
Example 3

A mixture containing 80 parts by weight of stearyl methyl ether of dimethylurea, 28 parts of pyridine hydrochloride, 40 parts of ethyl alcohol and 5 parts of pyridine was reacted at 70° C. for 30 minutes and then poured into 600 parts of acetone. The resulting precipitate was filtered off, washed with acetone and dried at 40° C. The dry powder was readily soluble in water.

An analysis of a sample for carbon, hydrogen, nitrogen, chlorine and formaldehyde gave the following molar ratios:

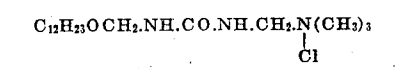
Pyridine: urea=0.98:1
HCHO: urea=2:1
Octadecanol: urea=1:1
Chlorine: urea=1:1

This corresponds to a compound of the formula



Example 4

30.2 parts by weight of the lauryl methyl ether of dimethylol urea were suspended in 40 parts of ethyl alcohol containing 10.5 parts of trimethylamine hydrochloride and heated at 60° C. for 15–17 hours, or until a clear solution was obtained. This solution was poured into 300 cc. of acetone and the resulting precipitate was filtered off, washed with acetone and dried at 40° C. The product was the quaternary ammonium salt of monolauryl ether of dimethylurea of the formula



This product was obtained as a white powder which was dispersible in water to a 10% colloidal solution or suspension having a milky appearance. A piece of cotton cloth was soaked in this dispersion, wrung out to 10% solids on the weight of the cloth, dried and cured by heating at 280° F. for 3 minutes, and washed, rinsed and ironed. The treated cloth was highly water-repellent.

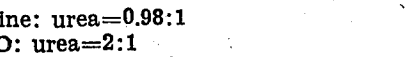
Example 5

66 parts by weight of SO_2 were absorbed in 79 parts of pyridine to form pyridinium sulfite. 386 parts of stearyl methyl ether of dimethylol urea were then added and the mixture was heated at 60° C. for about 20–30 minutes until solution occurred. The product was then poured into ethyl ether and the precipitated pyridinium salt of monostearyl ether of dimethylurea was recovered by filtration, washing and drying. The dried material was easily soluble in water to a soap-like solution that foamed on shaking.

50 parts by volume of a 10% aqueous solution of trimethoxy trimethylmelamine, prepared by condensing trimethylol melamine with methanol by the method described in the first paragraph of Example 1, were mixed with an equal quantity of a 10% solution of the above described pyridinium salt and 0.5 part of a diammonium phosphate curing accelerator were added. Cotton cloth and spun rayon challis were impregnated with the resulting solution, squeezed out to retain 10% solids on the dry weight of the cloth, and dried and cured by heating in an oven for 8 minutes at 280° F. The treated cloth was found to possess excellent water repellency.

Example 6

400 parts by weight of dimethylol urea, 920 parts of n-butanol and 1.4 parts of phthalic acid were heated together at 80° C. until solution was complete and then distilled at atmospheric pressure until the temperature of the liquid reached 115° C. 350 parts of 2-ethyl-hexanol-1 were then added and the mixture was distilled under reduced pressure at 90° C. to replace one butyl radical by an octyl radical. The product was the symmetrical butyl octyl diether of dimethylol urea of the formula



29 parts by weight of this compound were dissolved in an equal weight of alcohol and mixed with 11.5 parts of pyridine hydrochloride. The mixture was heated at 70° C. for 5–10 minutes and the resulting solution was poured into acetone. A white precipitate was obtained which was washed with acetone and dried to a white powder which was easily soluble in water.

5 parts by weight of this material were dissolved in 100 parts of water and printed chintz piece goods were impregnated in the solution, squeezed to retain 5% resin solids on the weight of the dry cloth, and cured for 6–8 minutes in an oven at 260–270° F. The cloth was then washed 15 minutes in a 1% soap solution, rinsed, dried and ironed. A stiff fabric having excellent resistance to creasing was obtained.

The quaternary ammonium salts of urea-formaldehyde condensation products are not claimed as such, since they are described and claimed in my copending application Serial No. 475,671, filed February 12, 1943.

What I claim is:

1. A method of finishing textiles which comprises impregnating them with an aqueous solution of a quaternary ammonium salt of a water-insoluble ether of dimethylol urea and then subjecting the textiles to heating at temperatures above 80° C. to decompose the quaternary am-

monium salt and cure the dimethylol urea ether to a resin.

2. A method of finishing textiles which comprises impregnating them with an aqueous solution of a quaternary ammonium salt of a monoalkyl ether of dimethylol urea wherein the alkyl radical contains at least 4 carbon atoms and then subjecting the textiles to heating at temperatures above 80° C. to decompose the quaternary ammonium salt and cure the dimethylol urea ether to a resin.

3. A method of finishing textiles which comprises impregnating them with an aqueous solution of a quaternary pyridine salt of a water-insoluble ether of dimethylol urea and then subjecting the textiles to heating at temperatures above 80° C. to decompose the quaternary pyridine salt and cure the dimethylol urea ether to a resin.

4. A method of finishing textiles which comprises impregnating them with an aqueous solution of a quaternary pyridine salt of a monoalkyl ether of dimethylol urea wherein the alkyl radical contains at least 4 carbon atoms and then subjecting the textiles to heating at temperatures above 80° C. to decompose the quaternary pyridine salt and cure the dimethylol urea ether to a resin.

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