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3,190,716

PROCESS OF FINISHING CELLULOSIC FABRICS WITH ALDEHYDE-CONTAINING SOLUTIONS AND SAID SOLUTIONS

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This invention relates to textile finishing procedures and, more particularly, to processes of treating cellulose textiles such as cotton, rayon and viscose fabrics and yarns to impart thereto wash-and-wear characteristics, a desirable soft finish or hand, wrinkle or crease resistance, and this without impairing the tensile strength to an unsatisfactory level.

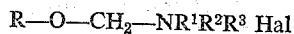
The treatment of cellulose textiles with formaldehyde is well known to effect cross-linking of the cellulose molecules and thus improve the wet strength, resistance to swelling by water, and resistance to wrinkling of such textiles. For example, United States Patent 2,108,520, granted February 15, 1938, discloses the treatment of viscose fabrics with an aqueous solution containing formaldehyde, a lower aliphatic acid or mineral acid and a metal salt such as calcium chloride. Such heretofore known procedures have been found objectionable for a number of reasons, chief of which is that they invariably result in excessive degradation of the threads with consequent production of fabrics of poor tensile strength below commercially acceptable standards. In the treatment of fabrics by such heretofore known procedures, the tensile strength of the fill or weft threads is reduced to an appreciably greater extent than the tensile strength of the warp threads, so much so that the fabrics are weakened in a crosswise direction as loomed, rendering them commercially unacceptable.

It is a principal object of the present invention to provide a process for treating cellulose textiles, i.e., fabrics or yarns, to impart thereto improved wash-and-wear properties, and this with a markedly less reduction of the tensile strength so that the finished fabrics and yarns are of good tensile strength, meeting commercially acceptable standards in this regard, and have improved wash-and-wear properties, hand and wear resistance.

Another object of this invention is to provide a novel aqueous aldehyde-containing solution for practicing the process of this invention.

Other objects and advantages of the present invention will be apparent from the following detailed description thereof.

In accordance with this invention, cellulose textiles are treated with an aqueous solution containing formaldehyde; a formaldehyde polymer (polyaldehyde) having not more than 6 carbon atoms in the chain such as dialdehyde, paraformaldehyde or trioxymethylene; glutaraldehyde; glyoxal; acrylic aldehyde (acrolein); methylacrylic aldehyde (methacrolein); or a mixture of such aldehydes, and a synergistic catalyst mixture constituted of (1) the acid salt of a primary aliphatic amine, RNH_2X , in which R is an alkyl group having not more than 6 carbon atoms, and X is a strong acid, and (2) a quaternary ammonium salt having the formula



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in which R is alkyl having from 12 to 18 carbon atoms and can be normal or branched, $NR^1R^2R^3$ is an aliphatic tertiary amine or a heterocyclic tertiary amine such as pyridine, dialkylaniline, trialkylamine, piperidine, quinoline, picoline or a homolog of any of these compounds, such as the alkyl pyridines, piperidines, quinolines or picolines, and Hal is halogen, preferably chlorine or bromine. The alkyl group of the alkyl pyridines can have from 2 to 6 carbon atoms.

The aqueous solution can also contain a third (3) catalyst constituent, namely, a halide, oxyhalide, nitrate, or sulfate of a metal of groups 2, 3 or 4 of the periodic table or an acid which imparts a pH below 7 to the treating solution. Any such water-soluble metallic salt which when added to water produces a solution having a pH below 7 can be used. Examples of such salts are the alkaline earth, e.g., calcium or magnesium metal chlorides, nitrates, bromides, chlorates, iodides; aluminum chloride or sulfate; boron fluoride; soluble zinc salts including silicofluoride; and zirconium oxychloride. Instead of or along with the metal salt an organic acid such as citric acid, acetic acid, monochloroacetic acid, or formic acid can be used.

The aqueous treating solution should contain from 1% to 10% by weight of formaldehyde (calculated as 100% HOCH) or aldehyde equivalent, and not more than 10% by weight of the synergistic mixture of catalysts with the catalyst components in the mixture present in approximately equal amounts. When treating cotton textiles, a solution containing from 1% to 5% by weight of formaldehyde (100% HCHO) or aldehyde equivalent is used. When treating rayon or viscose textiles the formaldehyde content or aldehyde equivalent content should be from 2% to 10% by weight calculated as 100% HCHO.

Paraformaldehyde, trioxymethylene and other formaldehyde polymers which decompose to form formaldehyde are considered as equivalent to formaldehyde on a weight basis. Two parts of acrolein, methacrolein and glyoxal are equivalent to 1 part formaldehyde (100% HOCH); hence the aqueous treating solution can contain from 2% to 20% of acrolein, methacrolein or glyoxal (on a 100% solids basis), i.e., not including the solvent in which these aldehydes are incorporated in the treating solution. Four parts of glutaraldehyde are equivalent to 1 part formaldehyde, and hence the treating solution can contain from 4 to 40 parts of glutaraldehyde on a 100% solids basis. Using an aqueous solution containing only catalyst components (1) and (2) above, the amount of the catalyst mixture should not exceed about 7% or 8% by weight based on the total weight of the treating solution. Preferably the solution contains from 0.5% to 2% of each of the catalyst component (1) and (2) and if component (3) is also used, as preferred, it is employed in amount of 1.5% to 2.5% by weight of the solution.

The treating solution may also contain additives such as a small amount, e.g., from 0.1% to 5% by weight, of a buffer to minimize degradation of the cellulose due to the acid catalyst. Examples of such buffers are melamine formaldehyde, triazine urea formaldehyde resin (Aerotex 23), dimethylol ethylene urea, dimethylol dihydroxy ethylene urea, dicyandiamide (DCY). The solution can also contain esters of stearyl alcohol and melamine formaldehyde (Permell B sold by American Cyanamide Company), or a mixture of two or more such buffers, and from 0.5% to 4% of glycerin, glucose or

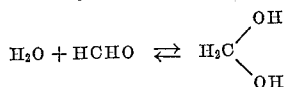
sorbitol, which protects the cellulose and aldehyde in the treating solution during the early stages of the processing, while the aldehyde is chiefly in the liquid phase.

Following application of the treating solution to the cellulosic textiles at any temperature below the boiling point of the solution, preferably at about room temperature (about 70° F.) so that the wet pick-up is from 65% to 85% by weight based on the dry weight of the textile, the textile is dried and thereafter cured at a temperature of from 220–350° F. for from 1 to 10 minutes, preferably 2 to 5 minutes. For cottons the preferred curing temperature is 300° to 310° F. and for rayons and viscose textiles the preferred curing conditions are at a temperature of about 320° F. for about 4 to 5 minutes.

Treatment of cellulose textiles as hereinabove described results in a finish having a soft, silky, lustrous hand, outstanding wash-and-wear properties, requiring little or no ironing after washing, and exceptionally good tensile properties, particularly as compared with such textiles produced by heretofore known procedures involving the treatment of the textiles with formaldehyde or a formaldehyde-containing composition. These improvements are due to the synergistic catalyst system employed in accordance with this invention.

While the explanation for the improvements effected by the synergistic catalyst system is not fully known, the following explanation, believed to be correct, is given to facilitate a better understanding of this invention. It will be appreciated, however, that this invention is not to be limited to this explanation.

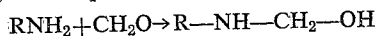
The synergistic catalyst system of this invention provides the most favorable conditions for the reaction between the aldehyde and cellulose with substantially less deterioration of the physical properties of the cellulose. The components of the catalyst mixture cooperate to promote the reaction with optimum yield and with minimum adverse effect on the cellulose. To trigger the methylene ether cellulose reactions the pH conditions on the textile must be about 2.5 and the aldehyde must be converted to a reactive form; while in the aqueous solution the aldehydes, e.g., formaldehyde, will not react with the cellulose to an appreciable extent. In the aqueous state the aldehyde is chiefly present as the hydrate, which in the case of formaldehyde is represented by the following:



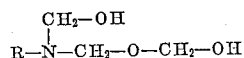
In this form, herein called the glycol form, the formaldehyde is practically non-reactive with the cellulose.

The reaction between the aldehyde and the cellulose takes place for the most part during the curing operation, when, for split seconds the aldehyde is present in a gaseous form. Component (1) of the catalyst system provides the acidic pH simultaneously with the release of gaseous aldehyde from the glycol form at the time when the reaction takes place. The acid salt of the primary aliphatic amine starts to decompose and provides some H⁺ ions at temperatures lower than 200° F.; the major portion, however, does not decompose to form amine vapors and H⁺ ions at temperatures above 240° F., i.e., 240° to 350° F.

Moreover, the amine reacts with the formaldehyde according to the equation:



This methylol compound reacts with additional formaldehyde to replace the N hydrogen atom in the methylol group to produce compounds having the formula:



with consequent formation of a long chain oxymethylene water-soluble polymer.

From the above it is evident that the aldehyde in water

solution and in the glycol form is fugitive and the aldehyde must be kept on the textile where it can react therewith during the curing in order for the treatment to accomplish the desired results. The acid salt of the primary aliphatic amine serves as a chemical retainer for the aldehyde and at the same time provides the necessary acidic conditions when the amine is decomposed at the curing temperatures during the curing to catalyze the reaction between the aldehyde and the cellulose.

The quaternary compound in the synergistic catalyst mixture promotes autopolymerization of aldehyde to less volatile polymerizates which are more reactive with the cellulose. The quaternary compound also exercises a desired softening effect on the textile. The presence of these quaternary compounds is particularly important during the early stages of the treatment; their presence in the treating solution or bath insures maximum utilization of the aldehyde. During the curing the aliphatic amine appears to exercise the more important catalytic influence in promoting the reaction between the aldehyde and cellulose. The two together have a synergistic influence in terms of the overall effect on the cellulosic textiles particularly from the standpoint of imparting to the textiles improved wash-and-wear and tensile properties.

The water-soluble metallic salts and/or organic acids promote the formation of inter-molecular cross bonds of the cellulose molecules; the intra-molecular cross bonds are less deteriorative to the cellulose than are the intermolecular cross bonds. However, both types of cross bonds are necessary to provide good wash-and-wear performance. Employing a catalyst mixture containing components (1) and (2) above and not (3), a high dry and wet crease angle can be produced with less deterioration caused by inter-molecular cross bonds; in other words, the tensile strength is greater and while the wash-and-wear properties are good, they are not as good as is obtained when using a catalyst system containing all three components (1), (2) and (3) above. As indicated, the use of the later system results in some loss of tensile strength chiefly because of the formation of more inter-molecular cross bonds; component (3) is responsible for more deterioration of the physical properties of the cellulose than is component (1) or (2) of the synergistic catalyst mixture.

As the aldehyde reactant any of the commercial grades of formaldehyde, glutaraldehyde, glyoxal, acrylic aldehyde (acrolein), methylacrylic aldehyde (methacrolein), and formaldehyde polymers containing not more than 6 carbon atoms in the chain including dialdehyde, paraformaldehyde and trioxymethylene can be used.

During the treatment, particularly the curing, the formaldehyde polymers or aldehyde-containing compounds decompose to liberate the aldehyde.

Examples of the amine component (component (1) above) are the acid salts of monoethanol amine; butanol amine; ethylamine; 2-amino-1-butanol; 2-amino-2-methyl-1-propanol; 2-amino-2-methyl-1,3-propanediol; 2-amino-2-ethyl-1,3-propanediol; tris (hydroxymethyl)-aminomethane, particularly the hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid or citric acid salts. The amine component in combination with the other constituents of the treating solutions provides a pH of 2 to 4 on the textile during the curing. Any acid salt which gives this pH value can be used. Preferred is 2-amino-2-methyl-1-propanol hydrochloride, known commercially as Catalyst AC.

Examples of the quaternary ammonium component (component (2) above) are stearamide methyl pyridinium chloride; octadecyl oxymethyl pyridinium chloride; oleyloxymethyl pyridinium chloride; stearamide methyl picolinium chloride; stearamide methyl quinolinium chloride. The preferred quaternary is stearamide methyl pyridinium chloride, sold commercially under the trade name Zelan AP, chiefly because it is readily available.

In preparing the padding bath employed for applying the treating solution, a portion of the water is mixed with the aldehyde, and the other constituents added in solution form to the water-aldehyde mix. The quaternary ammonium salt is dissolved in hot water (temperature 160° F.). Other constituents used, if not soluble in water at room temperature (about 70° F.), are dissolved in water at an elevated temperature below the boiling point. The temperature of the bath will depend on the particular constituents employed and should be such that all constituents remain in solution. Any temperature below the boiling point of water can be used. As a practical matter, temperatures near room temperature or a few degrees above room temperature, e.g., from 70° F. to about 110° F., can be used.

Instead of padding the textiles with the treating solution, the latter may be sprayed or otherwise applied to impregnate the textile with the treating solution. The wet pick-up is from 65% to 85% by weight based on the weight of the dry textile. After application, the treated textile is dried at a temperature of from 200° to 260° F. for from 0.5 to 2 minutes. The dried textiles are then cured at a temperature of from 220° to 350° F. for 1 to 10 minutes, the temperature and time of the curing being inversely related.

Thereafter the fabric is washed with water, or soap and water; this washing removes unreacted aldehyde and non-bound reaction products, should such products be formed.

The following examples are given to illustrate the invention. It will be appreciated the invention is not limited to these examples.

In these examples, the treating solution was at room temperature (70° F.) when the cloth was passed there-through and passed through the bite of the padding rollers, leaving the latter with a wet pick-up of about 70%.

EXAMPLE 1

	Percent
Formaldehyde	12
Aerotex	2
Glycerin	1.5
DCY	.25
Catalyst AC	.5
Calcium chloride	4
Zelan	2
Water	77.75
Total	100

EXAMPLE 2

	Percent
Formaldehyde	12
Aerotex	2
Glycerin	1.5
DCY	.25
Catalyst AC	.5
Zinc silico-fluoride	3
Zelan	2
Water	78.75
Total	100

EXAMPLE 3

	Percent
Formaldehyde	12
Aerotex	2
Glycerin	1.5
DCY	.25
Catalyst AC	.2
Zelan	2
Water	80.25
Total	100

Example No.	4	5	6	7	8	9	10	11	12
Formaldehyde	12	12	12	12	12	12	12	12	12
Aerotex	2	2	2	2	2	2	2	2	2
Glycerin	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
DCY	.25	.25	.25	.25	.25	.25	.25	.25	.25
Catalyst AC	2	2	2	2	2	2	2	2	2
Zelan	4	2	2	2	2	2	2	2	2
Citric acid		2						2	
Pyridinium hydrochloride			.5						
Ammonium chloride				.5					
Ammonium sulfate					.5		1		1
Monochloroacetic acid						1			
Permethyl B							1.5		
Water	78.25	78.25	79.75	79.75	79.75	79.25	77.75	80.25	79.25

The thus treated cotton was pre-dried at 200° F. to 260° F. and then cured at 310° F. for 3 minutes.

The fabric treated in Examples 1 to 12, inclusive, was a cotton broadcloth, 3.11 linear yards per pound, and having a count of 136 x 64.

In the examples involving formaldehyde, the commercial 37% by weight aqueous formaldehyde stabilized with methanol was used. The Aerotex was used in the form commercially available containing 48% solids in an aqueous or aqueous isopropanol medium.

The percentage values given in the examples are not based on 100% HCHO, but on the amount of commercial formaldehyde solution actually added to produce the treating solution.

Component (1) in the examples was Catalyst AC but any other acid salt of a primary aliphatic amine having 6 or less carbon atoms such as the hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, or citric acid salt can be used with the same results.

Component (2) was Zelan (the compound used was stearamide methyl pyridinium chloride) but any other quaternary ammonium salt as hereinabove disclosed can be used with equal results. All percentage values given are by weight, based on the weight of the total solution.

Examples 13 and 14 involved a pilot plant run. The fabric used in this run was a 136 x 64 cotton broadcloth having a weight of 2.85 square yards per pound.

	Example 13	Example 14
Formaldehyde	12	12
Aerotex	2	2
Glycerin	1.5	1.5
DCY	.25	.25
Catalyst AC	2	2.5
Zelan	2	2
Citric acid		1
Formic acid	.2	
Water	80.05	78.75

In Examples 15 to 38, inclusive, a cotton broadcloth 47" wide, 2.72 linear yards per pound, and having a count of 136 x 64 was treated as hereinabove described with the indicated solutions. The acrolein values in Examples 15 to 30, inclusive, and the glutaraldehyde values in Examples 31 to 38, inclusive, are on a basis of 100% acrolein and glutaraldehyde, respectively. The dimethylol ethylene urea was in the form of a water or water isopropanol solution containing 48% resin solids. The dimethylol

dihydroxy ethylene urea was in the form of a 50% aqueous solution containing 50% resin solids.

Example No.	15	16	17	18	19	20	21	22
Formaldehyde	5	8	12	16	4	6	10	14
Dimethylol Ethylene urea	5				6			
Dimethylol dihydroxy ethylene urea		2	8			6		4
Glycerin	1		1			2		1
DCY	.2		.25	.5	1	1	1	
Catalyst AC	.5	.5	.5	.5				1
M. ethanol amine HCl								
Zelan	2	2	2	2			2	
Magnesium chloride	2	2	2	2			.5	
Zirconium oxychloride								
Mono-magnesium phosphate								3
Pyridinium methylene bis oxymethyl chloride					1	1		1.5
Water	84.3	85.5	74.25	79	78	84	86.5	75.5

Example No.	23	24	25	26	27	28	29	30
Acrolein	5	8	12	16	4	6	10	14
Dimethylol ethylene urea	5				6			
Dimethylol dihydroxy ethylene urea		2	8			6		4
Glycerin	1		1			2		1
DCY	.2		.25	.5	1	1	1	
Catalyst AC	.5	.5	.5	.5				
M. ethanol amine HCl								1
Zelan	2	2	2	2			2	
Magnesium chloride	2	2	2	2				
Zirconium oxychloride							.5	
Mono-magnesium phosphate								3
Bis pyridinium methylene bis oxymethyl chloride					1	1		1.5
Water	84.5	85.5	74.25	79	78	84	86.5	75.5

Example No.	31	32	33	34	35	36	37	38
Glutaraldehyde	5	8	12	16	4	6	10	14
Dimethylol ethylene urea	5				6			
Dimethylol dihydroxy ethylene urea		2	8			6		4
Glycerin	1		1			2		1
DCY	.2		.25	.5	1	1	1	
Catalyst AC	.5	.5	.5	.5				
M. ethanol amine HCl								1
Zelan	2	2	2	2			2	
Magnesium chloride	2	2	2	2				
Zirconium oxychloride							.5	
Mono-magnesium phosphate								3
Bis pyridinium ethylene bis oxymethyl chloride					1	1		1.5
Water	84.3	85.5	74.25	79	88	84	86.5	75.5

In Examples 39 to 42, inclusive, a rayon challis (0.24 pound per square yard) was treated as hereinabove described in the case of the treatment of cotton broadcloth with the indicated treating solutions. As in the case of the cotton examples, the formaldehyde used was a 37% solution and the values given for the formaldehyde in those examples involving the use of formaldehyde represent the percentage of a 37% formaldehyde solution. The 15% glutaraldehyde in Example 40 is the percentage of glutaraldehyde on a 100% basis in the treating solution.

Example No.	39	40	41	42
Glutaraldehyde		15		
Formaldehyde	26		18	16
Zirconium oxychloride	37		.5	
Glycerin	1		1.5	
Dimethylol dihydroxy ethylene urea				8
DCY	1	.5	.5	
Magnesium chloride		2.5		2
Catalyst AC	1.5	1	1	1
Zelan		2	1	2
Water	33.5	79	77.5	71

The above values for the constituents in the respective examples are percentage values.

The table which follows gives the test results on the fabrics of some of the above examples. In this table the values for tensile strength were obtained by the Scott Tester ASTM Standard D39-49. The Crease Recovery values were obtained by the Monsanto Method, ASTM Standards D1295-53T American Society for Testing Materials, Philadelphia, Pa. Wash-and-Wear or No-Iron Rating was determined by AATCC Tentative Test method, 38-1960, AATCC Technical Manual 1960, volume 36, page 148. According to this test procedure a value of 5 is perfect and a value of 4 is excellent.

Table

Example	Tensile		Crease recovery		No-iron rating		Bound HCHO, percent
	Warp	Fill	Warp	Fill	Spin and drip	Spin and tumble	
13	64	32	115	120	4.5	4	
14	50	29	131	122	4.5	3.8	
15	48	36	116	115	2.5	3.5	0.65
17	36	25	138	140	4.5	5	1.36
20	42	32	120	125	4	4	0.82
22	36	28	130	128	4	4.5	1.15

These fabrics when tested for shrinkage upon repeated washings showed exceptionally good dimensional stability. They had a pleasing soft hand and showed good wear resistance, rendering them particularly useful for shirts and other apparel of the better grades.

It will be noted that the present invention provides a process for treating cellulosic textiles, particularly cotton, rayon and viscose fabrics having markedly improved wash and wear properties, good dimensional stability upon washing, a soft pleasing hand and good wear resistance. The finish imparted to the textiles withstands repeated washings and dry cleanings. This invention also provides a treating solution for use in treating cellulosic textiles to obtain the desirable wash and wear finish requiring little or no ironing and retaining a non-wrinkled flat crisp appearance upon drying.

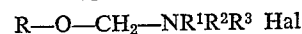
The expression "formaldehyde" is used in the claims to include formaldehyde polymers and compounds which release formaldehyde in aqueous solutions.

The invention includes the treatment of textiles containing cellulosic fibers blended with other fibers, such, for example, as polyester and other synthetic fibers. Preferably the textile contains at least 50% cellulosic fibers.

It will be appreciated that this invention is not to be limited to the disclosure herein except as indicated by the appended claims.

What is claimed is:

1. The process of finishing cellulosic textiles which comprises applying to the textile an aqueous solution containing an aldehyde from the group consisting of formaldehyde, formaldehyde polymers containing not more than 6 carbon atoms, glutaraldehyde, glyoxal, acrylic aldehyde and methylacrylic aldehyde, in amount of from 1% to 10% by weight, calculated as 100% formaldehyde, in the case of formaldehyde and formaldehyde polymers, in amount of from 2% to 20% by weight in the case of acrylic aldehyde and methylacrylic aldehyde, and in amount of from 4% to 40% by weight in the case of glutaraldehyde, and from about 2% to 10% by weight of a synergistic catalyst mixture, the components of said mixture being present in approximately equal amounts and containing an acid salt of a primary aliphatic amine having no more than 6 carbon atoms and a quaternary ammonium salt having the formula

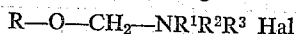


in which R is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the

aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen, and heating the thus treated textile to a temperature of from 220° to 350° F.

2. The process as defined in claim 1, in which the catalyst mixture also contains from 1.5% to 2.5% by weight of a compound selected from the group consisting of the halides, oxyhalides, nitrates, and sulfates of a metal from groups 2, 3 and 4 of the periodic table and an acid from the group consisting of citric acid, acetic acid, monochloroacetic acid and formic acid.

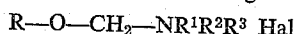
3. The process of finishing cellulosic fabrics which comprises padding the fabrics through a bath containing from 1% to 10% of formaldehyde, from 0.5% to 2% of an acid salt of a primary aliphatic amine containing no more than 6 carbon atoms, from 0.5% to 2% by weight of a quaternary ammonium salt having the formula



in which R is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen, and from 1.5% to 2.5% by weight of a compound selected from the group consisting of the halides, oxyhalides, nitrates, and sulfates, of a metal from groups 2, 3 and 4 of the periodic table and an acid from the group consisting of citric acid, acetic acid, monochloroacetic acid and formic acid to apply to the fabric from 65% to 85% of said solution based on the dry weight of the fabric, drying the fabric at a temperature of from 200° to 260° F., then curing the dried fabric at a temperature within the range of from 220° to 350° F. for from 1 to 10 minutes and washing the cured fabric to remove unreacted formaldehyde therefrom.

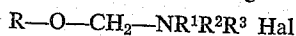
4. The process as defined in claim 3, in which the amine compound is 2 amino, 2 methyl, 1 propanol hydrochloride and the quaternary ammonium compound is stearamide methyl pyridinium chloride.

5. The process of finishing cellulosic fabrics which comprises padding the fabrics through a bath containing from 1% to 10% of formaldehyde, from 0.5% to 2% of the acid salt of a primary aliphatic amine containing no more than 6 carbon atoms, from 0.5% to 2% by weight of a quaternary ammonium salt having the formula



in which R is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen, and from 1.5% to 2.5% by weight of a compound selected from the group consisting of the halides, oxyhalides, nitrates, and sulfates of a metal from groups 2 and 3 of the periodic table and an acid from the group consisting of citric acid, acetic acid, monochloroacetic acid and formic acid, from 1% to 5% by weight of a triazine urea formaldehyde resin, and from 0.5% to 4% by weight of glycerin, to apply to the fabric from 65% to 85% of said solution based on the dry weight of the fabric, drying the fabric at a temperature of from 200° to 260° F., then curing the dried fabric at a temperature within the range of from 220° to 350° F. for from 1 to 10 minutes and washing the cured fabric to remove unreacted formaldehyde therefrom.

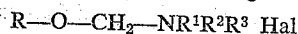
6. The process of finishing cellulosic fabrics which comprises padding the fabrics through a bath containing from 1% to 10% of formaldehyde, from 0.5% to 2% of an acid salt of a primary aliphatic amine containing no more than 6 carbon atoms, from 0.5% to 2% by weight of a quaternary ammonium salt having the formula



in which R is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the

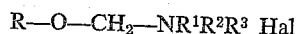
aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen, from 1% to 5% by weight of a triazine urea formaldehyde, and from 0.5% to 4% by weight of glycerin, to apply to the fabric from 65% to 85% of said solution based on the dry weight of the fabric, drying the fabric at a temperature of from 200° to 260° F., then curing the dried fabric at a temperature within the range of from 240° to 350° F. for from 1 to 10 minutes and washing the cured fabric to remove unreacted formaldehyde therefrom.

7. A finishing solution for the treatment of cellulosic textiles consisting essentially of an aldehyde from the group consisting of formaldehyde, formaldehyde polymers containing not more than 6 carbon atoms, glutaraldehyde, glyoxal, acrylic aldehyde and methylacrylic aldehyde, in amount of from 1% to 10% by weight, calculated as 100% formaldehyde, in the case of formaldehyde and formaldehyde polymers, in amount of from 2% to 20% by weight in the case of acrylic aldehyde and methylacrylic aldehyde, and in amount of from 4% to 40% by weight in the case of glutaraldehyde, from 0.5% to 2% of an acid salt of a primary aliphatic amine containing no more than 6 carbon atoms, from 0.5% to 2% by weight of a quaternary ammonium salt having the formula



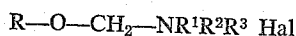
in which R is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen, and from 1.5% to 2.5% by weight of a compound selected from the group consisting of the halides, oxyhalides, nitrates, and sulfates of a metal from groups 2, 3 and 4 of the periodic table and an acid from the group consisting of citric acid, acetic acid, monochloroacetic acid and formic acid.

8. A finishing solution for the treatment of cellulosic textiles consisting essentially of from 1% to 10% of formaldehyde, calculated as 100% formaldehyde, from 0.5% to 2% of an acid salt of a primary aliphatic amine containing no more than 6 carbon atoms, from 0.5% to 2% by weight of a quaternary ammonium salt having the formula



in which R is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, and Hal is a halogen from the group consisting of chlorine and bromine.

9. A finishing solution for the treatment of cellulosic textiles consisting essentially of from 1% to 10% of formaldehyde, calculated as 100% formaldehyde, from 0.5% to 2% of an acid salt of a primary aliphatic amine containing no more than 6 carbon atoms, from 0.5% to 2% by weight of a quaternary ammonium salt having the formula

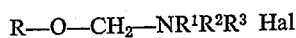


in which R is alkyl having from 12 to 18 carbon atoms, $NR^1R^2R^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen, and from 1.5% to 2.5% by weight of a compound selected from the group consisting of the halides, oxyhalides, nitrates, and sulfates of a metal from groups 2, 3 and 4 of the periodic table and an acid from the group consisting of citric acid, acetic acid, monochloroacetic acid and formic acid, from 1% to 5% by weight of a triazine urea formaldehyde resin, and from 0.5% to 4% by weight of glycerin.

10. A finishing solution for the treatment of cellulosic textiles consisting essentially of from 1% to 10% of formaldehyde, calculated as 100% formaldehyde, from 0.5% to 2% of an acid salt of a primary aliphatic amine containing no more than 6 carbon atoms, from 0.5% to 2%

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by weight of a quaternary ammonium salt having the formula

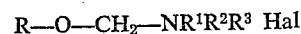


in which R is alkyl having from 12 to 18 carbon atoms, $\text{NR}^1\text{R}^2\text{R}^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, and Hal is a halogen from the group consisting of chlorine and bromine, from 0.1 to 5% by weight of a buffer which minimizes degradation of the cellulose from the group consisting of melamine formaldehyde, triazine urea formaldehyde, dimethylol ethylene urea, dimethylol dihydroxy ethylene urea, and dicyandiamide, and from 0.5% to 4% by weight of glycerin.

11. A finishing solution for the treatment of cellulosic textiles consisting essentially of an aldehyde from the group consisting of formaldehyde, formaldehyde polymers containing not more than 6 carbon atoms, glutaraldehyde, glyoxal, acrylic aldehyde and methylacrylic aldehyde, in amount of from 1% to 10% by weight, calculated as 100% formaldehyde, in the case of formaldehyde and formaldehyde polymers, in amount of from 2% to 20% by weight in the case of acrylic aldehyde and methylacrylic aldehyde, and in amount of from 4% to 40% by weight in the case of glutaraldehyde, from 0.5 to 2% of an acid salt of a primary aliphatic amine contain-

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ing no more than 6 carbon atoms, from 0.5% to 2% by weight of a quaternary ammonium salt having the formula



5 in which R is alkyl having from 12 to 18 carbon atoms, $\text{NR}^1\text{R}^2\text{R}^3$ is selected from the group consisting of heterocyclic tertiary amines and aliphatic tertiary amines, the aliphatic chain containing from 2 to 6 carbon atoms, and Hal is halogen.

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