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CELLULOSIC TEXTILE TREATING COMPOSITION AND PROCESS

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This invention is directed to a novel composition, novel catalyst and novel process for imparting dimensional stability to cellulosic textiles. The novel composition consists of an aqueous solution of dimethylolethyleneurea or its admixture with tetramethylolurea, zinc nitrate and an alkali metal acetate. The catalyst consists of a mixture of zinc nitrate and an alkali metal acetate. The process of the present invention comprises treating the textile with a solution of the textile treating agent and the novel catalyst, and after curing, completely neutralizing the treated fabric.

Dimethylolethyleneurea and tetramethylolurea are known to impart dimensional stability, crease resistance, calendering effects, etc. to cellulosic textiles. It is also known, as set forth in U.S. Patent 2,661,312, that zinc nitrate may be used as a curing catalyst for dimethylolethyleneurea. As a curing catalyst, zinc nitrate is effective and permits good crease recovery effects to be obtained. The use of zinc nitrate also results in good resistance to damage by retaining chlorine after repeated bleaching and ironing of textiles so treated. However, zinc nitrate as a catalyst for dimethylolethyleneurea and its admixture with tetramethylolurea has disadvantages in that it (*a*) causes a yellowing of the fabric, (*b*) adversely affects the shade of many dyes on cotton, and, (*c*) adversely affects the tensile strength of the fabric.

It is an object of the present invention, therefore, to overcome these described disadvantages. It is a further object of the present invention to effect dimensional stability to cellulosic textiles by the use of a novel catalyst and process. It is also an object of the present invention to impart crease resistant, calendering properties together with other properties heretofore unattainable. These and other objects will become apparent in the following description and claims.

More specifically, the present invention is directed to a novel composition of matter significantly useful as a curing catalyst concentrate, for treating cellulosic textiles, comprising a mixture of zinc nitrate and an alkali metal acetate, the weight ratio of zinc nitrate to alkali metal acetate being between about 1:1 and 5:1; and, a process of treating cellulosic textiles with a fabric stabilizer consisting of dimethylolethyleneurea and a mixture of dimethylolethyleneurea and tetramethylolurea, said mixture comprising at least 20% by weight of the mixture of dimethylolethyleneurea, the improvement which consists of padding the textile with a pad bath containing from about 2 to about 10% by weight of the bath of the fabric stabilizer, 0.25% to 2.0% by weight of zinc nitrate and .05% to 2.0% by weight of an alkali metal acetate, and within 24 hours after curing the fabric at 300° F. to 400° F. for 0.5 to 10 minutes, neutralizing the fabric by washing it with an aqueous alkaline solution until the equilibrium pH of the washing solution containing the textile is between about 8.0 and 11.0 and finally rinsing the neutralized fabric until the equilibrium pH of the rinsing solution containing the fabric is between about 7.0 and 8.0.

An alternate embodiment of this invention is a novel composition consisting of an aqueous solution containing the textile stabilizer and the catalyst mixture of zinc nitrate and sodium acetate. In this embodiment, the composition consists of a clear aqueous solution containing 20 to 70%, by weight of the solution, of dimethylolethyleneurea or its admixture with tetramethylolurea, 3 to 10% by weight of an alkali metal acetate, the weight ratio of zinc nitrate to the alkali metal acetate being between 1:1 and 5:1.

A preferred embodiment of the novel catalyst is a concentrate which is a clear, colorless liquid consisting of an aqueous solution of zinc nitrate and an alkali metal acetate. The total amount of zinc nitrate and alkali metal acetate in the solution is between about 5% and 45% by weight of the solution. The weight ratio of the zinc nitrate to alkali metal acetate will be from about 1:1 to about 5:1.

An alternate catalyst composition consists of a mixture of solid zinc nitrate and solid alkali metal acetate, the weight ratio of these compounds being from about 1:1 to about 5:1. Zinc nitrate is usually obtained in the form of its tetra- or hexahydrate and these forms as well as other hydrates or the anhydrous salts may be used. Similarly the alkali metal acetates may be used in the anhydrous form or as hydrates. Sodium acetate, potassium acetate or other alkali metal acetates may be used. The preferred salt to make the liquid catalyst concentrate is sodium acetate trihydrate because it is low in cost and is readily available. For the solid catalyst mixture zinc nitrate tetrahydrate and anhydrous sodium acetate is preferably used.

In order to make the novel composition, a vessel is charged with water and the appropriate amount of alkali metal acetate added. The mixture is then agitated and, if desired, to facilitate solution, heated to about 55° to 60° C. to obtain a clear solution. Then, zinc nitrate is added and the mixture agitated (and heated to 55° to 60° C., if desired) until a clear solution is obtained. Water is added to bring the solution to the desired concentration; i.e., 5% to 45% by weight active ingredient. If the solution is not entirely clear it may be filtered before packaging for sale. Alternately, the zinc nitrate may be added first or the ingredients added simultaneously.

The process of treating textiles according to the present invention is carried out by making up, in the normal manner, a pad bath of dimethylolethyleneurea to contain between about 2% and about 10% of the textile treating agent. An amount of the novel catalyst concentrate is then added and mixed thoroughly so that the desired amount of zinc nitrate and alkali metal acetate are present. An alternate procedure is to add a textile treating agent concentrate to the novel catalyst concentrate and then dilute with water as required. In lieu of the novel catalyst composition, zinc nitrate and alkali metal acetate may be added separately to the pad bath.

Instead of using dimethylolethyleneurea as the textile treating agent, a mixture of dimethylolethyleneurea and tetramethylolurea may be used. In this case the mixture will contain at least 20% by weight of the active ingredient mixture as dimethylolethyleneurea. An advantage to the use of such a mixture is that it is more economical than the dimethylolethyleneurea alone and no sacrifice in initial tensile, whiteness and dimensional stability is observed. In carrying out the padding operation the amount of zinc nitrate employed will be about 0.25% to 2.0% based on the weight of the pad bath. The amount of alkali metal acetate in the pad bath will be 20% to 100% by weight of the zinc nitrate (i.e., a ratio of 1:5 to 1:1). Thus the amount of acetate salt present will be between about 0.05% and 2% by weight of the pad bath. If less than this amount of zinc nitrate is used (i.e., if the ratio of zinc nitrate to alkali metal

acetate is less than 1:1) the mixture does not act properly as catalyst and the desired properties of the treated fabric will not be achieved. Too little of the acetate salt however, that is, a ratio of zinc nitrate to acetate salt of over 5:1, does not give the desired improvement in tensile strength and in protecting dyed fabric against shade change.

Since zinc nitrate tends to precipitate zinc hydroxide in aqueous solution, it is expedient to add a slight quantity of acetic acid, say, .05% by weight of the pad bath, to maintain complete solution.

An alternate embodiment of this invention is to provide a composition consisting of the catalyst combined with the fabric stabilizer. In this embodiment, an aqueous solution is prepared to contain 20 to 70%, by weight of the solution, of the fabric stabilizer, 3 to 10% by weight of zinc nitrate and 1 to 4% by weight of the alkali metal acetate. To avoid precipitation of any insoluble zinc hydroxide, it is expedient to add a small amount of acid, preferably about 1 to 2% by weight of acetic acid to make the solution slightly acid. An adjustment of the pH of the solution to pH 3 to 6 is satisfactory although the higher pH is preferred. This composition is a clear, stable solution and may be utilized commercially. For use, it is diluted with water to provide a textile pad bath of the desired concentration of ingredients.

The textile fabric is treated with the pad bath solution to obtain a wet pick-up of from 50% to 150%. It is then dried at about 200° F. to 350° F. and after optionally subjecting to the desired mechanical treatment (i.e., glazing, embossing, pleating and the like) it is cured at about 300° F. to 400° F. for about 0.5 to 10 minutes, the time varying inversely with temperature. Preferred conditions are between 40 seconds and 5 minutes at 375° to 300° F. Drying and curing may be carried out in a single step providing the curing time allowed after the fabric is dried is within the above ranges.

After curing it is essential to give the treated fabric an alkaline neutralizing wash. This must be done within 24 hours after the curing operation. If it is not done within this time, the resistance of the treated fabric to chlorine retention is adversely affected. This step involves working the fabric in an aqueous alkaline treating bath until the finish on the fabric is neutralized and the equilibrium pH of the solution containing the fabric is between 8 and 11. Normally, a 0.1 to 0.5% sodium carbonate solution will be used for this step. In lieu of working in a carbonate solution, the carbonate solution may be padded on the textile to effect neutralization. The fabric is then rinsed until the equilibrium pH of the rinsing solution containing the rinsed fabric is between 7 and 8; i.e., neutral or only very slightly alkaline. The completely neutralized fabric is then dried.

It will be understood that other diverse agents may be present in the pad bath as for example, softeners, water repellents, oil repellents, anti-microbial agents, and the like.

It will be observed from the examples which follow that the present invention produces a cellulosic fabric, dimensionally stabilized with dimethylolethyleneurea or its admixture with tetramethylolurea which has unexpected and improved initial tensile strength over the zinc nitrate catalyst above, improved whiteness of undyed fabric and which imparts a negligible shade change on vat dyed fabric. In addition, the present invention results in a treated fabric which has excellent resistance to the adverse effects of bleaching; that is, the fabrics obtained by this process may be laundered, bleached with hypochlorite and ironed repeatedly and little or no scorching and subsequent loss of tensile strength of the fabric will be experienced.

Representative examples illustrating the present invention are as follows.

EXAMPLE 1

A. *Preparation of product (approx. 10% sodium acetate, approx. 21% zinc nitrate)*

A vessel is charged with 1000 parts of water and 333 parts of sodium acetate trihydrate (201 parts of sodium acetate) and the mixture is agitated at 55° to 60° C. until a clear solution is obtained. Then 586 parts of zinc nitrate tetrahydrate (425 parts of zinc nitrate) is added and the mixture agitated further at 55° to 60° C. until a clear solution is obtained. Finally, 81 parts of water is added. A small amount of insoluble material is filtered off and the solution is ready for use.

B. *Application to textile fabric*

A textile treating solution is prepared by thoroughly mixing 8 parts of a 50% by weight aqueous solution of dimethylolethyleneurea, 3 parts of the above concentrate and water to make 100 parts. This results in a textile pad bath containing on a weight basis: 4% dimethylolethyleneurea, 0.6% zinc nitrate, and 0.3% sodium acetate.

A piece of cotton sheeting is then padded through the bath, squeezed to obtain a 100% wet pick-up and the treated fabric is dried by hanging on a line. The dried fabric is cured for 90 seconds at 350° F. Immediately after curing, the fabric is immersed in an aqueous solution containing on the weight of the solution, 0.2% of soda ash. The fabric is agitated gently in this solution for 3 minutes, at the end of which time the pH of the solution is constant at 10.0. Then, the fabric is removed, washed free of alkali and after the pH of the washing solution remains constant at 7.5, the fabric is squeezed to remove excess liquid and is ironed dry.

The treated fabric is then subjected to the following tests:

Tensile strength.—Carried out by means of the standard "Scott tester." In general, tensile strength improvements of 10% to 20% are considered worthwhile.

Crease resistance.—The standard crease angle recovery method (Monsanto) is used. Initial recovery values of 250° and above are excellent results. After washing, the value should be no less than about 220° to indicate durability.

Whiteness.—Percent reflectivity of the fabric is obtained as measured with a General Electric spectrophotometer at a wavelength of 400 millimicrons. The reflectivity of MgO is taken as 100% for a standard control. A difference in 1% to 2% reflectivity is noticeable to the eye.

Chlorine retention.—A fresh sodium hypochlorite bath is prepared by diluting a commercially available 5% sodium hypochlorite solution with distilled water to obtain 0.25% of available chlorine. The pH of the solution is adjusted to between 9 and 10 with sodium bicarbonate.

The fabric sample is first pre-wetted in distilled water at 160° F., then cooled and transferred to the above hypochlorite bath, which is maintained at about 77° F. After impregnation, the sample is wrung out, rinsed, dried, adjusted to normal moisture re-gain (about 8%). Then, it is submitted to a scorching test at 365° F. for 30 seconds after which the fabric is readjusted to normal moisture re-gain. Tensile strength measurements are made on a piece of resin treated and cured fabric which is given the bleach treatment but not scorched. The tensile strength measurements are carried out according to standard procedure and are accurate to within ±10%. The results of tensile strength (TS) measurements are calculated as follows:

$$\frac{(\text{TS of bleached}) - (\text{TS of bleached and scorched})}{(\text{TS of bleached})} \times 100$$

=percent damage due to chlorine retention.

Washing procedure.—Fabrics are laundered, bleached, rinsed, and ironed under home laundering conditions.

Test results.—The treated test fabric has excellent properties as can be seen from the following table where comparison with a control is made. The control fabric is treated by the same process except that no sodium acetate is in the pad bath.

Fabric	Crease Recovery Angle		Initial Tensile Strength (lbs./in.)	Percent Whiteness	Percent Loss of Tensile Strength Due to Chlorine Retention	
	Initial degrees	After 10 Washes, degrees			Initial	After 10 Washes
Test	270	262	59	80	None	None
No sodium acetate	272	270	50	73	None	None

It is readily seen that the test fabric has excellent crease resistance, an improvement of 18% in initial tensile strength, an improvement of 9.6% in whiteness and has excellent resistance to chlorine retention damage.

EXAMPLE 2

Example 1 is repeated with different amounts of zinc nitrate and sodium acetate in the pad bath. The following table illustrates the results obtained.

CATALYST SYSTEM

	Percent in Pad Bath		Weight Ratio of $Zn(NO_3)_2$ to $NaC_2H_3O_2$
	$Zn(NO_3)_2$	$NaC_2H_3O_2$	
(a)	0.77		
(b)	0.77	0.19	4:1
(c)	0.77	0.74	1:1
(d)	1.14	0.56	2:1
(e)	0.38	0.19	2:1

	Crease Recovery Angle		Initial Tensile Strength (lbs./in.)	Percent Whiteness	Percent Loss of Tensile Strength Due to Chlorine Retention	
	Initial degrees	After 10 Washes, degrees			Initial	After 10 Washes
(a)	272	270	50	73	None	None
(b)	269	263	56	78	None	None
(c)	265	260	63	81	None	None
(d)	250	240	66	81	None	None
(e)	260	220	68	81	None	None

EXAMPLE 3

Example 1 is repeated, but with a piece of cotton broadcloth dyed a deep blue shade with a vat dye of Color Index #1113. The control piece, padded without sodium acetate in the pad bath was changed to a pale green. The test piece padded in the presence of sodium acetate showed no shade change.

EXAMPLE 4

Mixtures of tetramethylolurea and dimethylolethyleneurea are prepared to contain 50% by weight of textile treating agent and having a weight proportion of tetramethylolurea to dimethylolethyleneurea of 75:25, 50:50 and 25:75. Each of these solutions is then used to make up a pad bath containing 4% by weight of the textile agents and 3% by weight of the catalyst concentrate prepared in Example 1A. Cotton sheeting is then padded at 100% wet pick-up as in Example 1. After air drying and curing at 350° F. for 1.5 minutes, the fabrics are neutralized as in Example 1 with a 0.2% by weight sodium carbonate solution, an equilibrium pH of 8.0 being obtained. Then the neutralized fabric is rinsed until the pH of the rinsing solution containing the fabric

is constant at 7.0 After drying, the fabrics have the following properties:

Weight Ratio of TMU [1] to DMEU [2]	Crease Recovery Angle		Initial Tensile Strength (lbs./in.)	Percent Whiteness	Percent Loss of Tensile Strength Due to Chlorine Retention	
	Initial	After 10 Washes			Initial	After 10 Washes
75:25	259	253	31	81	9	27
50:50	261	264	31	79	11	3
25:75	266	266	28	79	+7	10

[1] TMU=tetramethylolurea.
[2] DMEU=dimethylolethyleneurea

EXAMPLE 5

An aqueous pad bath is prepared to contain, on a weight basis, 10% dimethylolethyleneurea, 0.85% zinc nitrate and 0.38% sodium acetate. Rayon challis fabric is padded to obtain a 100% wet pick-up and after drying on a line the fabric is cured in one case at 325° F. and in a second case at 350° F. per 1½ minutes. The cured fabrics are then washed for 5 minutes at 110° to 120° F. in a solution containing 0.2% by weight of sodium carbonate and 0.05% of a fatty alcohol sulfate detergent; the fabrics are then rinsed and ironed dry.

For comparative purposes, a control is run with 1% zinc nitrate as catalyst, no sodium acetate being used.

The following table indicates the results of tests made on the treated fabrics:

	Curing Temperature			
	325° F.		350° C.	
	Control	Test Sample	Control	Test Sample
Tensile Strength (lbs.)	56	63	51	59
Crease Recovery Angle	289	283	296	291

EXAMPLE 6

An aqueous solution is prepared by mixing on a parts by weight basis, 200 parts of a 70% acqueous solution of dimethylolethyleneurea, 100 parts of an aqueous solution containing 21.2% zinc nitrate and 10% sodium acetate, and 0.8 part of glacial acetic acid. The clear solution had a pH of 5.7 and contained 46.6% by weight dimethylolethyleneurea, 7.1% zinc nitrate, and 3.3% sodium acetate.

This composition is used as a pad bath by diluting it to a dimethylolethyleneurea concentration of 4% by weight. Cotton sheeting is then padded at 100% wet pick-up and is dried, cured at 325° F. and neutralized for 5 minutes in 0.2% soda ash and 0.05% alcohol sulfate detergent. After rinsing and drying the treated fabric is tested.

The following table indicates the excellent properties of treated fabric:

Percent reflectance [1]	81
Tensile strength (lbs.)	67
Crease recovery angle	245
Percent chlorine retention damage	3

[1] A control fabric treated with water only has a reflectance of 81.5.

EXAMPLE 7

A roller mill is used to mix 17.7 parts by weight of zinc nitrate tetrahydrate (12.8 parts $Zn(NO_3)_2$) and 6.0 parts of anhydrous sodium acetate. The resulting white product forms lumps which are readily handled.

A pad bath of 1000 parts by weight containing 10% by weight of dimethylolethyleneurea is prepared and 15 parts of the above solid mixture of zinc nitrate and sodium acetate is added. This results in a pad bath solution essentially the same as that Example 5.

When rayon challis fabric was padded and treated, as in Example 5, essentially the same results are obtained.

Combinations of zinc nitrate with other salts do not give the unexpected results achieved by the present invention; for example, zinc nitrate with sodium citrate, zinc nitrate with sodium salicylate and zinc nitrate with potassium thiocyanate when utilized according to the present invention adversely affect the initial tensile strength of the cellulosic materials treated therewith.

Although the theory of the present invention is not fully understood, it is believed that the alkali-metal acetate modifies the adverse effects of zinc nitrate by buffering its acid properties during curing; then during the process of the neutralization step, the zinc ion is precipitated as hydroxide and is deposited within the textile fibers. Thus, basic zinc hydroxide is considered to be present in the textile to offset the adverse effects of acid arising from retained chlorine after bleaching and ironing.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A cellulosic textile treating curing catalyst comprising a mixture of zinc nitrate and an alkali metal acetate, the weight ratio of zinc nitrate to said alkali metal acetate being between 1:1 and 5:1.

2. A cellulosic textile treating curing catalyst composition comprising a mixture of (1) a fabric stabilizer taken from the group consisting of dimethylolethyleneurea and a mixture of dimethylolethyleneurea and tetramethylolurea, said mixture comprising at least 20% by weight of the mixture of dimethylolethyleneurea, and, (2) a mixture of zinc nitrate and sodium acetate, the weight ratio of zinc nitrate to said sodium acetate being between 1:1 and 5:1.

3. In the process of treating cellulosic textiles with a fabric stabilizer taken from the group consisting of dimethylolethyleneurea and a mixture of dimethylolethyleneurea and tetramethylolurea, said mixture comprising at least 20% by weight of the mixture of dimethylolethyleneurea, the improvement which consists of padding the textile with a pad bath containing from about 2 to about 10% by weight of the bath of the fabric stabilizer, 0.25% to 2.0% by weight of zinc nitrate and .05% to 2.0% by weight of sodium acetate, and within 24 hours after curing the fabric at 300° F. to 400° F. for 0.5 to 10 minutes, neutralizing the fabric by washing it with an aqueous alkaline solution until the equilibrium pH of the washing solution containing the textile is between about 8.0 and 11.0 followed by rinsing the neutralized fabric until the equilibrium pH of the rinsing solution containing the fabric is between about 7.0 and 8.0.

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