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PROCESS FOR TREATING TEXTILES WITH ETHYLENE UREA-FORMALDEHYDE REACTION PRODUCTS

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The present invention relates to a process for treating cellulose-containing textile materials and to the materials so treated. More particularly, it relates to a novel process for the treatment of cellulosic textile materials with ethylene urea-formaldehyde reaction products, whereby shrinkage control and wrinkle recovery of a high order are imparted thereto.

It is an object of the present invention to provide a novel process for treating cellulosic textile materials with an aqueous solution of an ethylene urea-formaldehyde reaction product, by which excellent shrinkage control and wrinkle resistance are obtained employing relatively mild conditions for drying and curing.

It is a further object to provide a novel process for treating cellulosic textile materials which is readily adaptable to conventional plant equipment, which may employ lower temperatures and shorter times for drying and curing of treated fabric, and still produce desired results.

These and other objects and advantages will become more apparent from the detailed description set forth hereinbelow.

While, generally speaking, ethylene urea-formaldehyde type resins have been employed on textile fabrics heretofore, the present invention concerns itself with a particular novel method for applying the formaldehyde reaction products of ethylene urea to cellulosic textile materials and is characterized by the treating of such materials with such reaction products while employing critical concentrations thereof, a critical type of catalyst and critical catalyst concentrations, whereby these methylol derivatives may be dried and cured at relatively low temperatures over relatively short periods of time.

According to the present invention, a process is provided which comprises treating a cellulose-containing textile material with a stable aqueous solution having a pH of between 1 and about 3.5, which comprises a substantially water-soluble ethylene urea-formaldehyde reaction product and an acid acting curing catalyst having an ionization constant of at least 10^{-5} so as to apply about 5% resin solids on the material, based on the weight of the material. Thereafter, a material so treated may be dried and cured for 3 minutes at 225° F. to a water-insoluble state to obtain a wrinkle recovery of at least 200.

By "cellulose-containing textile material" as the term is used herein, it is intended to include textile materials containing at least 50% of cellulosic materials, such as, for example, cotton, rayon, both cuprammonium and viscose, and the like. Thus, blends of these materials with synthetic fibers, such as nylon, acrylics, polyesters, and/or natural fibers such as wool, linen and the like, is contemplated.

Ethylene urea may be prepared according to the process set forth in U.S. Patent No. 2,517,750 and may thereafter subsequently be reacted with formaldehyde to produce the methylol derivatives thereof contemplated by the present invention. This may be done by reacting 1 mole of ethylene urea with from between 1.5 and 3 moles respectively of formaldehyde at a pH of from between 7 and 10 at a temperature of from between, for example, 40° C. and 100° C. until solution of reactants is achieved. Thereafter, the reaction mixture is cooled to room temperature and, if desired, the reaction product isolated.

Between 1 and 2 moles of formaldehyde are usually combined employing known procedures, and preferably between 1.5 and 2 moles and usually about 1.8 moles of formaldehyde are combined. When the number of combined moles are of the order of 1.8 moles and higher, the product is generally referred to as dimethylol ethylene urea.

The ethylene urea-formaldehyde reaction products employed in the present process are substantially water soluble and essentially monomeric in nature. However, a degree of polymerization which does not detract from the substantially water soluble nature of the reaction product is satisfactory. Additionally, mixtures of essentially monomeric and polymerized and/or partially polymerized reaction products may be employed, as long as the mixture is substantially water soluble.

It is essential that the pH of the stable aqueous solution be between 1.0 and about 3.5 and preferably from between 1.5 and 3. When pH values of 4 and above are employed, cellulosic material having inferior shrinkage control and wrinkle recovery result when concentrations and conditions similar to those of the present invention are employed. If pH values of less than 1.0 are employed, other deleterious effects on the treated fabric, such as unacceptable tensile strength, result.

The pH value of the stable aqueous treating solution is achieved by the use of acid acting catalysts such as free acid and acid salt catalysts having ionization constants of at least 10^{-5} and preferably from between 10^{-5} to 10^{-1}. Examples of such catalysts are acetic, acrylic, adipic, ammonium acid sulfate, ammonium trihydrogen pyrophosphate, chloroacetic, citric, dichloroacetic, formic, glutaric, glycolic, lactic, maleic, malic, malonic, methyl acid pyrophosphate, oxalic, phosphoric, succinic, sulfanilic, and tartaric. These acids and acid salts and others having ionization constants of at least 10^{-5} may be employed singly or in combination with one another. These catalysts are employed in amounts sufficient to adjust the pH of the resin solution to between 1.0 and about 3.5. Acids such as hydrochloric, sulfuric, nitric, or salts such as magnesium chloride are not within the contemplation of the present invention.

In employing the process of the present invention, the ethylene urea-formaldehyde reaction product is applied, as by padding, spraying, dipping, or the like, from a stable aqueous solution so as to impart about 5% resin solids and amounts up to 25% solids, and in special instances more, based on the weight of the textile fabric. Employing the process of the present invention, resin solids applications significantly below 5% do not impart acceptable wrinkle recovery to the treated fabric. Resin solids concentrations of from between 7½ to 12.5% are preferred.

After the textile material has been treated with the ethylene urea-formaldehyde reaction product (preferably dimethylol ethylene urea) according to the present invention, it may be dried and cured for 3 minutes at 225° F. to a water-insoluble state whereby a material having a wrinkle recovery of at least 200 is obtained. Wrinkle recovery values of less than 200 are, for the most part, of little commercial significance.

While, according to the present invention, drying and curing in a single step for 3 minutes at 225° F. will produce acceptable wrinkle recovery, acceptable wrinkle recovery may be obtained by employing higher temperatures for simultaneous drying and curing, i.e. 250° F.–400° F. and the like, for shorter periods of time. In addition, lower temperatures, for example, 200° F., may be employed for longer periods of time and still produce acceptable results.

Thus, for the most part, the length of time of cure is inversely proportional to the temperature employed, as is well known to those in the art. However, it will be noted that none of the conventional textile resins, for example, melamine-formaldehyde resins, urea-formaldehyde resins, and even ethylene urea-formaldehyde resins, when employed according to conventional finishing processes, will impart a wrinkle recovery of 200 when dried and cured simultaneously for but 3 minutes at 225° F. Because by the employment of the present process, drying and curing can be effected in relatively short periods of time at relatively low temperatures, these times and temperature, as a matter of economy, are significant.

While the above remarks concern themselves principally with a single step operation (dry and cure) it will, of course, be apparent that a fabric treated according to the present process may be first dried and then cured, though this is unnecessary in the practice of the present process. In the event that such a procedure is followed, drying is usually carried out at temperatures of from about 100 to 225° F. until the fabric is dry to the touch, and thereafter the ethylene urea-formaldehyde reaction product is cured at from about 225° F. to 400° F. for from about 1 minute to a few seconds, i.e., less than 5, respectively.

By the practice of our invention, we are able to simultaneously dry and cure ethylene urea-formaldehyde reaction products on cellulose-containing fabrics in less time than is normally required at conventional curing temperatures to cure previously dried fabric. As an example, we are able to obtain a wrinkle recovery of 250° on 80 x 80 cotton percale, using the conditions of our invention when the fabric is simultaneously dried and cured for only 2 minutes at 275° F. Using conventional catalysts under conventional conditions, it would be substantially impossible to get wrinkle recoveries this high at this temperature. If values this high are obtained at all, curing times alone much in excess of 2 minutes would be required.

In order than the present invention may be more fully understood, the following examples are given primarily by way of illustration. No details therein should be construed as limitations except as they appear in the appended claims. All parts and percentages are by weight unless otherwise designated.

EXAMPLE 1

80 x 80 cotton was padded through an aqueous pad bath solution containing 10% solids of a substantially water-soluble, essentially monomeric, dimethylol ethylene urea, and sufficient phosphoric acid (H_3PO_4) to adjust the bath pH to 2.9. The treated fabric was then run through squeeze rollers adjusted to provide a 100% wet pick-up. The fabric was then dried and cured at 225° F. for 3 minutes.

In addition to the dimethylol ethylene urea, a melamine formaldehyde resin having approximately three methylated methylol groups thereon and dimethylol urea were applied to 80 x 80 cotton in a manner similar to that set forth in Example 1 above, from a bath having a pH of 2.9, after which the fabric was dried and cured for a total time of 3 minutes at 225° F. Like fabric samples were treated in a similar manner with the mentioned resins, but were dried and cured for 5 minutes at 225° F. The following table indicates the effect of low temperature drying and curing on wrinkle recovery of the various resins.

Table I.—Low temperature curing of various resins

Resin	Total Wrinkle Recovery	
	3′	5′
Methylated melamine formaldehyde	175	177
Dimethlol urea	180	187
Dimethylol ethylene urea	241	238
Untreated	147	147

It will be evident that low temperature curing of the melamine formaldehyde and the dimethylol urea when practiced according to the present invention produces an unacceptable wrinkle recovery when compared with the dimethylol ethylene urea in each instance. All wrinkle recovery values reported in this case are determined on a Monsanto crease-angle tester and the values are in degrees.

In the following table, the effect of low temperature drying and curing is further illustrated. In each instance, in the chart hereinbelow, the resin was applied to 80 x 80 cotton as set forth in Example 1. The resin solids on the cloth was 10%, the pH of the pad bath was 3, adjusted thereto with phosphoric acid, and the drying and curing time and temperature were varied as indicated therein.

Table II.—Low temperature curing of dimethylol ethylene urea effect of curing temperature

Dry and Cure (One Operation)		Warp (Percent) Shrinkage, 1 Hr.	Total Wrinkle Recovery, 1 Hr.	Total Tensile Strength, 1 Hr.
Time, minutes	Temp., ° F.			
3	225	1.1	241	64
4	225	1.1	239	63
5	225	1.2	238	65
2	250	1.1	249	63
3	250	1.2	242	61
4	250	1.1	232	62
2	275	1.1	250	57
3	275	1.1	250	56
4	275	0.8	249	61
1	300	1.2	232	65
2	300	1.0	255	60
3	300	0.8	259	55
Untreated		4.2	147	93

By studying Table II it is readily evident that temperatures as low as 225° F. for 3 minutes are satisfactory for drying and curing dimethylol ethylene urea under the conditions stated. Increasing the time of drying and curing does not have any deleterious effect on the properties of the fabric. When temperatures as high as 300° F. are used, that is more conventional curing temperatures, then the drying and curing cycle can be appreciably reduced. Only 1 minute is required at 300° F. The data in the above table also show the excellent shrinkage control that is obtained under these conditions.

One might think that the use of a strong acid, such as phosphoric acid, would result in severe degradation of the fabric. That this does not occur is shown by the high tensile strength of the treated fabric. The tensile strength given in pound units is of the order of magnitude obtained by normal curing conditions.

Dimethylol ethylene urea was applied in a manner similar to that set forth in Example 1 in five different instances except that the pad bath pH was varied from between 2 and 4, and all fabric was dried and cured for 5′ at 225° F. The results of varying the pH of the pad bath are recorded in Table III hereinbelow.

Table III.—Low temperature curing of dimethylol ethylene urea effect of pad bath pH

Bath pH	Warp (Percent) Shrinkage, 1 Hr.	Total Wrinkle Recovery		Total Tensile Strength	
		Init.	1 Hr.	Init.	1 Hr.
1.0	1.5	210	205	50	58
2.0	1.7	221	217	58	67
2.5	1.1	240	214	56	64
3.0	0.8	227	221	62	60
3.5	1.7	216	211	69	67
4.0	2.2	186	175	81	86
Untreated	4.7	147	--------	104	--------

It will be observed that pH values from between 1 and 3.5 result in a fabric having good shrinkage control, wrinkle resistance and tensile strength and that when the pad bath pH is a value of 4 the wrinkle recovery is unacceptably low.

Resin solids were applied to 80" x 80" cotton generally as in Example 1 so as to add four different resin solids concentrations thereto, ranging from 3.5% to 10%. The pad bath solution had a pH of 3.0, having been adjusted thereto with phosphoric acid, and the treated fabric was dried and cured for 3 minutes at 225° F. The results are indicated in the table set forth hereinbelow.

Table IV.—Low temperature curing of dimethylol ethylene urea effect of resin solids

Resin Solids	Warp (Percent) Shrinkage, 1 Hr.	Total Wrinkle Recovery		Total Tensile Strength	
		Init.	1 Hr.	Init.	1 Hr.
10%	0.8	235	229	62	60
7.5%	0.8	225	212	62	64
5.0%	1.4	215	200	77	80
3.5%	2.2	175	170	81	81
Untreated	4.7	147	--------	104	--------

It will be observed that resin solids concentrations of the order of 3.5% result in unacceptable wrinkle recovery when compared with cellulosic textile fabrics having a resin solids concentration of 5% and above based on the weight of the fabric.

While the process of the present invention has been described in conjunction with ethylene urea-formaldehyde reaction products, it is also applicable to other alkylene urea-formaldehyde reaction products, such as those 1,2-propylene urea, 1,3-propylene urea, and/or mixtures of the three types of formaldehyde reaction products and/or their alkylated derivatives, such as methylated dimethylol alkylene ureas. Regardless of the reaction product employed, it should be substantially water soluble and essentially monomeric, subject to the limitations on these terms set forth hereinabove.

Other additives may be employed in the pad bath if desired as known to those skilled in the art, including stiffeners, softeners, lubricants, and the like.

We claim:

1. A process comprising treating a textile material containing at least 50% of cellulosic material with a stable, aqueous solution having a pH of between 1.0 and about 3.5, consisting essentially of an ethylene urea-formaldehyde reaction product and an acid-acting curing catalyst, having an ionization constant of at least 10^{-5}, so as to apply thereto between about 5% and about 25% resin solids, based on the weight of the textile material, and thereafter curing said ethylene urea-formaldehyde reaction product to a water-insoluble state on said material by the application of heat.

2. A process according to claim 1 in which the textile material contains at least 50% cotton.

3. A process according to claim 1 in which the textile material contains at least 50% rayon.

4. A cellulosic material characterized by a high order of shrinkage control and wrinkle recovery produced according to the process of claim 1.

5. A process comprising treating a cellulosic textile material with a stable, aqueous solution having a pH of 1.5 to 3.0, consisting essentially of a substantially water-soluble, essentially monomeric dimethylol ethylene urea and an acid-acting curing catalyst having an ionization constant between 10^{-5} and 10^{-1}, so as to apply thereto from between 7.5 and 12.5% resin solids, based on the weight of the material, and thereafter curing said dimethylol ethylene urea to a water-insoluble state on said material by the application of heat.

6. A process according to claim 5 in which the cellulose textile material is cotton.

7. A process according to claim 5 in which the cellulose textile material is rayon.

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