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3,576,591

METHYLOLATED CYCLIC UREA COMPOSITIONS CONTAINING SODIUM FORMATE OR SODIUM TETRABORATE

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10 Claims

ABSTRACT OF THE DISCLOSURE

The conventional treatment of cellulosic fabrics with cyclic urea cellulose reactive crease-proofing agents to produce durable press or wash-and-wear properties is improved by the addition of a minor amount of sodium formate or sodium tetraborate. This salt addition to the crease-proofing composition reduces adverse yellowing or color changes caused by the conventional treatments.

BACKGROUND OF THE INVENTION

The treatment of cellulosic fabrics to impart crease-proofing properties has become a highly developed art. A wide variety of useable nitrogen containing organic crease-proofing agents have been developed and various general procedures for successfully treating fabrics with such materials are now available to the textile industry. Such operations include the so-called pre-cure finishes in which flat fabric is treated in a textile processing plant to obtain a crease-proofed material which can then be converted by apparel manufacturers or other users into garments or the like. More recently, the so-called "post-cure" technique has been developed in which fabrics treated with crease-proofing agent but left in an uncured state are fabricated into garments which are then heated in an oven or given an equivalent treatment to cross-link or otherwise cure the treating agent upon the cellulosic fabric and fix pleats, creases, or other mechanical finishes placed in the garment into a relatively durable form. Textiles prepared by the pre-cure technique are commonly referred to as "wash-and-wear fabrics" while the garments and other articles produced by the so-called post-cure technique are normally now referred to as "durable press" garments or articles.

Literally thousands of different materials have been investigated as crease-proofing agents in these operations. In the early stages, urea-formaldehyde resins were employed, but these agents involved numerous deficiencies, e.g., poor shelf life, tendency to absorb chlorine from chlorine containing bleaching agents resulting in degradation of the cloth upon hot pressing or ironing, undue loss in tensile strength and other properties of the treated fabric and the like. There followed the development of other agents such as melamine-formaldehyde resins and similar amino-plasts as the active crease-proofing agents. More recently, cellulose reactive materials which are not in themselves resin forming have become conventional in the textile trade as the crease-proofing agents. Such cellulose reactive materials include the aldehyde condensation products of cyclic ureas such as ethylene urea, propylene urea and their hydroxy, alkyl and aryl substituted derivatives.

Dihydroxy ethylene urea crease-proofing agents made by condensation of glyoxal, urea and formaldehyde are one class of the cellulose reactive materials in widespread commercial use today for the treatment of cotton fiber containing fabrics. However, use of the dihydroxy ethylene urea agents have been mostly restricted to dyed goods. There are agents on the market suitable for white goods,

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but are higher priced. It would be desirable for DHEU agents to be useable in crease-proofing of white goods.

The conventional methods of treating cellulosic fabrics with crease-proofing agents as generally discussed above are well known to involve production of adverse color characteristics in the treated product. This has resulted, for the most part, in having such procedures be restricted to the crease-proofing of dyed goods. This is true both for the so-called pre-cure as well as post-cure finishes. The discoloration problem is particularly apparent in the resin finishes which are employed in post-cure techniques when applied to dyed goods using zinc nitrate catalysts. Thus, most colors undergo a shade change to some degree, particularly with the severe cure conditions, e.g., 325° F. for 15 minutes, employed in some of these operations to attain a high degree of durable press properties. Also, the use of these finishing methods has not found wide acceptance on white goods because of yellowing of the goods. Attempts have been made to remedy this discoloring phenomena by use of modified catalysts, e.g., use of magnesium chloride type catalysts in place of zinc nitrate. In addition, select bluing and optical brightening agents have been tried to mitigate the yellowing. However, these attempts to avoid the undesired color changes caused by the conventional crease-proofing treatments have not been completely satisfactory.

The textile trade is in the need of improved products and/or methods by which cellulosic fabrics may be treated with known and readily available crease-proofing agents while avoiding the discoloring or yellowing effects which have been associated with the crease-proofing treatments available heretofore.

OBJECTS

A principal object of this invention is the provision of new improvements in fabric treating compositions and methods for imparting crease-proof properties to cellulosic fabrics. Further objects include the provision of:

(1) Methods by which conventional treatment of cellulosic fabrics with cellulose reactive crease-proofing agents to produce durable press properties may be improved to eliminate undesirable color changes or yellowing in the final treated fabric.

(2) New crease-proofing compositions employing conventional cellulose reactive crease-proofing agents which are relatively free from the tendency to discolor dyed goods or to yellow white goods treated with the crease-proofing agents.

(3) Knowledge concerning ways to improve conventional cellulose fabric crease-proofing agents and compositions to eliminate discoloration or yellowing after treatment and curing of cellulosic fabrics to generate wash-and-wear or durable press properties in the fabric.

Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description. It should also be understood the foregoing abstract of the disclosure is for the purpose of providing a non-legal brief statement to serve as a searching-scanning tool for scientists, engineers and researchers and is not intended to limit the scope of the invention as disclosed herein nor is it intended it should be used in interpreting or in any way limiting the scope or fair meaning of the appended claims.

SUMMARY OF THE INVENTION

These objects are accomplished according to the pres-

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ent invention by a method for modifying cyclic urea cellulose fabric crease-proofing compositions to improve color characteristics in cellulosic fabrics treated with the compositions which comprises adding a minor amount of a salt selected from the group consisting of sodium formate and sodium tetraborate to the compositions.

The objects are further accomplished by the provision of improved compositions for use in the treatment of cellulosic fabrics to impart crease-proof properties thereto with minimal effect upon the color characteristics of the treated fabric which comprises:

- a cyclic urea cellulosic fabric crease-proofing agent,
- a salt selected from the group consisting of sodium formate and sodium tetraborate, and
- the proportion of said salt to said agent in the composition being between 1:100 and 1:4.

Advantageously, the new crease-proofing compositions contain an acidic aminoplast curing catalyst. Further, the preferred compositions contain these active ingredients dissolved in water to form a solution which has a pH between about 3 and 7.

In further explanation of the invention, a preferred composition for treatment of cellulosic fabrics according to the invention would be formed of the following ingredients in the parts by weight indicated:

- Cyclic urea cellulosic fabric crease-proofing agent ----- 100
- Sodium formate or sodium tetraborate ----- 1-25
- Acidic aminoplast curing agent ----- 1-5

DISCLOSURE OF PREFERRED EMBODIMENTS

The following details of operations in accordance with the invention and reported data illustrate the further principles and practice of the invention to those skilled in the art. In these examples and throughout the remaining specification and claims, all parts and percentages are by weight and all temperatures are in degrees Fahrenheit unless otherwise specified.

EXAMPLE 1

The example concerns the treatment of cotton fabric with a glyoxal/urea/formaldehyde condensation product prepared from the following ingredients in the parts indicated:

- Glyoxal (40% aqueous) ----- 395
- Urea ----- 163
- Formaldehyde (37% aqueous) ----- 442
- Sodium hydroxide 50% ----- 10

The procedure used was to:

- Charge #1 and adjust pH to 5.5 with a small amount of 50% NaOH.
- Add #2 and heat to 60° C.
- Hold at 60° C. for 30 minutes.
- Remove heat and charge #3.
- Add #4 bringing pH to 7.5.
- Allow to exotherm to 80° C. Hold at 80° C. for two hours.
- Cool and adjust pH to 5 with HCl.

Analysis of the resulting product gave the following data:

	Percent
Solids -----	44
Free HCHO -----	<1/2

The above product was designated as composition A and was divided into three parts. Into two of these was dissolved the following salts:

(B)

	Percent
Composition A -----	90
Borax -----	10

(C)

	Percent
Composition A -----	95
Anhy. sodium formate -----	5

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In the preparation of composition B, a sharp pH drop was noted on slow addition of borax followed by a gradual rise to pH 5.5 on complete dissolving of the borax in the liquid. Samples B and C were padded on white 136 x 64 broadcloth as well as dyed 100% cotton using product A as a comparison of what a commercial finish would do on the same cloth. The products were padded on as follows:

	1, per- cent	2, per- cent	3, per- cent
Product:			
A -----	20	-----	-----
B -----	-----	20	-----
C -----	-----	-----	20
50% Zn(NO ₃) ₂ -----	2	2	2

The fabrics were immersed in the bath solutions, squeezed between pad rollers to about 70% wet pickup and dried at 250° F. They were then cured at 340° F. for 90 seconds in an oven. The physical results obtained were: Fabric—136 x 64 white broadcloth; 100% cotton blue dyed fabric.

	Percent light reflectance, photovolt	Wash/ wear, Eastman OH		Tensile		Elmen- dorf tear		Crease angle, °	
		1-W	5-W	W	F	W	F	W	F
Finish:									
1.-----	78.5	4.5	4.0	40	26	550	450	139	134
2.-----	82.5	4.0	3.8	49	35	620	560	147	141
3.-----	81.0	4.0	4.0	56	35	620	560	140	138
Standard plate.-----	80.5	-----	-----	-----	-----	-----	-----	-----	-----

On the blue dyed fabric finished as above, finish #1 changed shade from a blue to a greenish blue, while finishes 2 and 3 retained the original blue color. On white cloth, there was a large improvement in whiteness as judged by the light reflectance between finishes 2 and 3 as compared to 1.

The foregoing data show some slight lowering of the wash-wear performance, but large improvement in tensile strength in the modifications.

EXAMPLE 2

The example concerns the treatment of 100% khaki dyed cotton twill fabric using the products A, B and C of Example 1 under the following post-cure conditions:

	5, per- cent	6, per- cent	7, per- cent
Product:			
A -----	25	-----	-----
B -----	-----	25	-----
C -----	-----	-----	25
50% Zn(NO ₃) ₂ -----	3	3	3

The fabrics were immersed and squeezed as before, then dried at 250° F. The fabrics were cured at 325° F. for 15 minutes, such as would be done under conventional delayed cure conditions. Test results:

	Wash/wear, Eastman OH		Tensile		Elmendorf tears (g.)		Crease angle, °	
	1-W	5-W	W	F	W	F	W	F
Finish:								
5.-----	4.2	4.5	91	61	1,088	1,594	127	160
6.-----	4.2	4.2	112	78	1,542	2,182	123	155
7.-----	4.2	4.2	115	77	1,651	2,470	122	155

Finish #5 changed shade noticeably while 6 and 7 retained the original color of the unfinished.

DISCUSSION OF DETAILS

The success of the present invention is due in part to the discovery that sodium tetraborate and sodium formate when added in small amounts to conventional cellulose fabric crease-proofing agents are unique in their bene-

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ficial effects upon the color characteristics produced in cotton or other cellulosic fabrics treated with these modified crease-proofing compositions. A variety of other salts have been investigated, but have been found not to provide the unique results attainable through the use of sodium tetraborate or sodium formate as described above. The other salts which have been unsuccessfully tried include:

sodium bicarbonate
disodium phosphate
sodium sulfate
sodium citrate
barium chloride
sodium polyphosphate
1% sodium polyphosphate/1% citric acid
zinc acetate
potassium acid phthalate
sodium glycolate
urea hydroxide.

It has been further found that the addition of sodium tetraborate or sodium formate improves the color of glyoxal-urea-formaldehyde condensation products as well as the whiteness of white goods treated with this crease-proofing agent. In addition, cotton fabrics treated with conventional cyclic urea crease-proofing agents modified by the addition of small amounts of sodium formate or sodium tetraborate exhibit improved tensile strength, resistance to scorching and less shade change on dyed goods.

Crease-proofing compositions of the invention advantageously include an acidic aminoplast curing catalyst and have a pH between about 3 and 7. The initial addition of a small amount of sodium tetraborate in accordance with the invention to the conventional crease-proofing agent made from glyoxal, urea and formaldehyde results in a drastic reduction of pH from about 5.5 to 1.8 or 2.0. The addition of more of the sodium tetraborate results in gradual pH increase back up toward neutral and with excessive amounts of such addition may rise as high as 8.5. Raising the pH to above about 5.0, however, causes precipitation of zinc salts when zinc catalyst is added to the crease-proofing composition bath. Accordingly, it is preferred to adjust the pH of the aqueous treating composition to between about 3 and 5. In the case of sodium tetraborate, this has been accomplished by the addition of about 11% sodium tetraborate to a conventional dimethylol dihydroxy ethylene urea crease-proofing agent. The resulting composition then has a sodium tetraborate content of about 10%. Analysis of a typical sodium tetraborate containing composition of this type would produce the following data:

pH -----	Percent
Ash -----	5.0
Ash as borax -----	5.65
	10.75

Since pure sodium borate has an ash (known as fused sodium borate) of 52.77%, a solution containing 9.9% borax should give an ash of about 5.2%.

The initial reduction of pH on addition of borax to the cyclic urea derivative can be explained by complex ion formation between borate ions and hydroxy functional groups present in the resin.

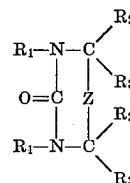
Zinc nitrate and magnesium chloride may advantageously be used as the acidic aminoplast curing catalyst. However, other materials known in the art as useful for this purpose may be employed. In addition to mineral acids such as hydrochloric acid, free organic acids may be used as well as organic and inorganic salts having an acidic reaction. Mixtures of salts and acids may also be employed. A brief test of the acidic material will quickly reveal the effectiveness of the substance for the contemplated operation. Specific examples of usable acidic catalyst materials include: sulfuric, pyrophosphoric, oxalic and chloroacetic acids; zinc chloride, aluminum chloride, sodium acid fluoride and sodium bisulfate.

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The new color improvement techniques of the invention are applicable to a wide variety of cellulosic crease-proofing agents of the cyclic urea type. Specific examples of such polymethylol heterocyclic compounds which may be used in accordance with the invention include:

dimethylol dihydroxy ethylene urea
dimethylol ethylene urea
3,5-dimethylol-2,6-dihydrotriazine-4-one
dimethylol propylene urea
dimethylol hexyl ethylene urea
3,5-dimethylol-2,3-dibromopropyl-2,6-dihydrotriazine-4-one

and equivalent cyclic urea derivatives of the general formula:



wherein:

Z is the group



or a single bond between the adjacent carbon atoms,

R₁ is a methylol group or equivalent cellulose reactive group,

R₂ and R₃ are C1 to C12 alkyl, C1 to C12 aryl, hydrogen, halogen or hydroxy.

Mixtures of two or more of these crease-proofing agents may be used.

The formulation of the crease-proofing compositions of the invention may be varied and proportions of ingredients can depend, in part, upon the particular crease-proofing agent and catalyst used, the amount of wet pickup employed in the treating procedure and similar variables as is known to those skilled in the art of textile treatment with crease-proofing agents. Advantageously, crease-proofing compositions will contain between about 25 to 75% by weight of active cyclic urea cellulosic fabric crease-proofing agent. Other ingredients in turn are usually controlled in proportion to the content of the crease-proofing agent. The proportion of the sodium tetraborate or sodium formate relative to the crease-proofing agent may be in a weight ratio of between 1 to 100 and 1 to 4 although best results appear to be obtained with use of 1 to 20 parts of sodium formate or sodium tetraborate for each 100 parts of the crease-proofing agent. The acidic catalyst in turn is advantageously used in an amount between about 1 to 5 parts for each 100 parts of the crease-proofing agent.

The aqueous crease-proofing compositions are advantageously applied to the fabric to give a pickup of about 60 to 100% of the aqueous treating solution based upon the dry weight of the fabric. Such fluid pickup can be accomplished by known padding operations, by saturating the fabrics and then rolling, by brushing or spraying the treated solution onto the fabric or in any other suitable manner. Curing or equivalent heat treatment of the impregnated fabric to cause cross-linking of the cellulosic fibers by the treating agent may be accomplished at any suitable stage. Thus, the new techniques are applicable both to the so-called pre-cure as well as post-cure operations which are now conventional in this art. Partial drying of the fabric may be involved so that the fabric can be pressed, pleated, embossed or otherwise handled to create a pattern mechanical effect and suitable apparatus may be used for this purpose.

The ultimate desired crease resistant properties are imparted to the impregnated cellulosic fabric by heat treating the textile at elevated temperatures without removal of the cross-linking agent. This operation can be carried out at various temperatures and times which are conventional in the art and known to be useful in conjunction with the particular crease-proofing agent which might be selected for use in accordance with the new techniques. Typical curing or heat treating operations would be from 150 to 325° F. for 1 to 30 minutes, longer times generally being used for lower temperatures and vice versa. These curing or heat treatment operations can be accomplished in any suitable equipment such as hot air ovens, by use of infrared lights, induction heating or the like. Following the heat treatment, the unfinished fabric or completed garment may be washed or otherwise cleansed to remove unreacted treating agent, neutralize acidic catalyst or the like. Such after treatment may involve washing with dilute alkaline solutions, with water and the like and drying in any convenient manner.

The new operations as described above can be used in conjunction with other textile processing procedures if this appears desirable or vital because of the end use of the fabric. Such conjunctive operations include application of sizing agents, softeners, lubricating materials, water-repellent agents, moth-proofing agent, mildew-proofing agents, dyes, pigments and the like.

The new operations may be used with any form of textile made of cotton, linen, viscose rayon or mixtures of these as well as fabrics containing such cellulosic fibers along with non-cellulosic fibers. Where the non-cellulosic fibers are inert to the reactant substances used in the operations, reaction will only take place with the cellulose and by improving the crease recovery properties of the cellulosic fibers, the blended yarn fabric can be improved in crease recovery properties up to and even beyond those of the pure non-cellulosic fiber. Fabrics treated may be in the form of non-woven fabrics, woven fabrics, knitted fabrics or the like.

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

1. A method of modifying methylolated cyclic urea cellulose fabric crease-proofing compositions to improve color characteristics in cellulose fabrics treated with such compositions which comprises adding a minor amount of a salt selected from the group consisting of sodium formate and sodium tetraborate to said composition.

2. A method as claimed in claim 1 wherein between 1 and 25% by weight of said salt based upon the dry weight of the active crease-proofing agent in said composition.

3. A method as claimed in claim 1 wherein the active crease-proofing agent in said composition is a glyoxal-urea-formaldehyde reaction product.

4. A method as claimed in claim 3 wherein said composition contains between 1 to 20 parts of said salt for each 100 parts of said reaction product.

5. A composition for use in the treatment of cellulosic fabrics to impart crease-proof properties thereto with minimal effect upon the color characteristics of the treated fabric which comprises:

- (a) a methylolated cyclic urea cellulosic fabric crease-proofing agent;
- (b) a salt selected from the group consisting of sodium formate and sodium tetraborate, and
- (c) the proportion of said salt to said agent in the composition being between 1:100 and 1:4.

6. A composition as claimed in claim 5 wherein said agent and salt are dissolved in water and the solution has a pH between about 3 and 7.

7. A composition as claimed in claim 5 containing an acidic aminoplast curing catalyst.

8. A composition as claimed in claim 5 consisting essentially of the following ingredients in the parts by weight indicated:

(a) Methylolated cyclic urea cellulosic fabric crease-proofing agent	100
(b) Sodium formate or sodium tetraborate	1-25
(c) Acidic aminoplast curing agent	1-5
(d) Water	50-200

9. A composition as claimed in claim 5 consisting essentially of the following ingredients in the parts by weight indicated:

(a) Dimethylol dihydroxy ethylene urea	100
(b) Sodium formate or sodium tetraborate	1-20
(c) Zinc nitrate	1-5
(d) Water	50-200

10. A cellulosic fabric having therein the heat-cured residue of a crease-proofing composition as claimed in claim 5, said fabric being characterized by improved crease-proof properties as compared with the untreated fabric and improved color characteristics as compared with a fabric treated with a crease-proofing composition that is identical except that it does not contain said salt.

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