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UREA RESIN CURING AGENTS, COMPOSITIONS, AND PROCESS FOR THE IMPROVEMENT IN THE PROPERTIES OF TEXTILES

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The present invention relates to curing agents for urea-containing resin materials, resin compositions and processes for improving the wearing properties of textiles and rendering such textiles resistant to tearing, creasing, washing action and attack by chlorine.

It is well known to improve the properties of textiles by impregnating the same with synthetic resin materials. It has always been considered foremost in this connection to obtain high magnitude dry and wet creasing angles with respect to cotton and wool staple fibers, yarns, fabrics and the like, while at the same time not sacrificing as far as possible the strength and resistance qualities of the particular staple fibers, yarns and fabrics. The properties of resistance to tearing and to the normal rubbing wear of the synthetic resin finished fabrics ought not to exhibit decreases in comparison to these properties in untreated textile materials. When employing synthetic resin finishes, obviously the utility value of the textile fabrics must be preserved.

The washing stability of such synthetic resin finishes with respect to textile fabrics, of course, is quite important and in this connection commercial requirements demand that such synthetic resin finishes be able to endure twenty or more washings at temperatures of from 80 to 90° C. without marked loss of the desired textile properties.

In many instances washing procedures contemplate treatment of cotton and wool staple fibers and/or fabrics in the course of the washing with alkali hypochlorite solutions and preparations. Inasmuch as urea resins and melamine resins as well as ethylene-urea resins which have not been completely condensed, are often used for impregnating textile materials, severe fabric damage may occur due to the fact that such resins still contain groups reactive with respect to chlorine. Chlorine is present in washing solutions as a consequence of the use of alkali hypochlorite substances, and therefore readily attacks the textiles by reacting with the incompletely condensed resin impregnants. Consequently, at high ironing temperatures the chlorine addition products of the synthetic resin impregnants decompose, whereupon the fabrics become discolored or darkened, often turning brown, and the staple fiber material hydrolyzes and loses its strength and resistance characteristics.

In order to overcome such disadvantages in view of the increased requirements for impregnated textile materials, various hardeners have been suggested for the condensation of urea-, melamine-, ethylene-urea-formaldehyde-precondensate used as textile impregnants. It was found that ammonium salts of inorganic and organic acids were unserviceable where chlorine-resistant finishes were desired. Although somewhat better, salts of organic bases with inorganic and organic acids were also considered poor in performance with respect to stability towards chlorine in the hardened or cured impregnant, and in most cases such salts exhibited insufficient resistance to washing action. Zinc salt, calcium salt and particularly magnesium salt catalysts have proved to be good as curing agents for the hardening of urea resins. Magnesium chloride is preferred in this respect since with magnesium chloride

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catalysts, good stability to chlorine of the condensed resin impregnant is obtained. While the resistance to washing action is generally good, the aforementioned metal salt catalysts unfortunately attack the cellulose staple fibers, impair the strength and resistance properties, and damage the utility effectiveness of the fabrics. With regard to these properties, zinc, calcium and magnesium salts are similar in action to that of ammonium salts of inorganic acids, such as ammonium chloride, ammonium nitrate and ammonium phosphate, all leading to the formation with urea precondensates of hard, brittle synthetic resins which result in undesired fiber damage of the finished textile.

It is an object of the present invention to overcome the foregoing drawbacks and to provide curing agents for urea-containing resin materials, resin compositions and processes for improving the wearing properties of textiles and rendering such textiles resistant to tearing, creasing, washing action and attack by chlorine.

Other and further objects of the invention will become apparent from a study of the within specification and the accompanying examples.

In accordance with the present invention, it has been found that by using salts of weak organic bases with semi-amides formed from ethylene- α,β -dicarboxylic acid and amines, as curing agents or hardening components for effecting the curing or hardening of urea resin condensates, the properties of textile fabrics, yarns, fibers and the like are substantially improved. The curing agents or hardening components in accordance with the invention produce with urea resins softer end-condensates than could be achieved heretofore. Textile materials impregnated with urea resin precondensates which are heat hardened in the presence of the salts of weak organic bases with semi-amides in accordance with the process of the invention, possess extraordinary resistance properties with respect to tearing, creasing, washing action, attack by chlorine and, in spite of slight embrittling of the fibers, excellent wet and dry creasing angles.

The effect of curing agents or hardening components in accordance with the invention is particularly noteworthy when they are used in quantities of from about 10–20% by weight based upon the initial charge of synthetic resin precondensate. Thus, all urea-, melamine-, ethylene-urea-formaldehyde-precondensates may be heat hardened at elevated temperatures, for example, at 160° C., in accordance with the invention to form final condensed resins having the desired properties. Conveniently in accordance with the invention the textile material may be impregnated with the precondensate containing the curing or hardening component and thereafter subjected to conventional heat hardening with the application of normal procedures, including imprint calendering at elevated temperatures to achieve the usual desired printing effects.

Weak organic bases which may be used to form the curing component salts in accordance with the invention include aliphatic and aromatic amines, and in particular dicyanide diamide, melamine, triazine, imidazoles, pyroles, pyridines and the like. The semi-amides may include any ethylene- α,β -dicarboxylic acid such as substituted and unsubstituted maleic acid, with an aliphatic amine or cyclic amine polyamine such as morpholine, N-cyclohexylamine, N-alkoxy amines such as N- β -ethoxy amine, and generally any primary, secondary or tertiary amine. Thus, any N-substituted ethylene- α,β -dicarboxylic acid semi-amide may be used with the weak organic base to form the desired salt.

In accordance with the invention, the curing component may comprise the following salts: maleamic acid melamine salt; N- β -ethoxy maleamic acid melamine salt; melamido-maleamic acid melamine salt; the melamine salt of 1,2-bis(maleamic acid)ethylene; N-cyclohexyl

maleamic acid melamine salt; semi-substituted morpholino maleic acid melamine salt, and the like.

The end-condensates or finished or hardened resins obtained in accordance with the invention exhibit only very slight or no chlorine binding capacity, which proves that all reactive groups in the hardened synthetic resins are blocked and that practically a quantitative condensation has been attained. By means of the curing salts of the invention, modern day requirements are satisfactorily fulfilled with respect to urea resin finishes on cellulose fibers. Textile materials impregnated with urea-containing hardenable resins having incorporated therein the salts of the present invention possess high crease-free properties and extensive fiber protection and resistance to tearing and washing action. The stability of the finished resin-impregnated textile with respect to chlorine, as for example may be present in a chlorine cleaning solution, is excellent. Moreover, in most cases it has been found unnecessary to after-treat the finished fabrics by washing since the finished condensed impregnants are neutral in effect. In contrast thereto, where metal salt catalysts, such as zinc, calcium and magnesium salts, are used in effecting the hardening of the impregnants on textiles, subsequent washing must be carried out to render the finished textiles commercially acceptable.

The following examples are set forth for the purpose of illustrating the invention, and it is to be understood that the invention is not to be limited thereto.

Example 1

An impregnating solution for the finishing of cotton print goods contains 80 grams of dimethylol-urea per liter of liquor as resin, and the solution is separately treated with the various catalysts indicated below. After impregnating the cotton print goods on a pad in the usual manner using a different catalyst (a to e) in each instance, the fabric is preliminarily dried in the normal way and subsequently after-condensed for 3 minutes at 160° C. Separate samples of the impregnated cotton print goods (each sample containing a different catalyst, a to e), are thereafter subjected to washing action for 15 minutes in a boiling solution of 2 grams of soap and 3 grams of soda. The results obtained are set forth below:

Catalyst	Synthetic resin loss after boiling-washing for 15 minutes with 2 g. soap and 3 g. soda, percent by weight
(a) 4 g. ammonium chloride.....	33
(b) 4 g. ammonium phosphate.....	41
(c) 5 g. monoethanolamine phosphate.....	45
(d) 7 g. magnesium chloride.....	51
(e) 8 g. maleamic acid melamine salt.....	18

Example 2

Poplin shirt material is finished with 80 g. of dimethylol-ethylene-urea per liter of liquor as resin in the same manner as carried out in Example 1. The poplin fabric is treated in the usual way with the synthetic resin precondensate solution on a pad, thereafter preliminarily dried and then condensed for 3 minutes at 160° C. The following results are obtained:

Catalyst	Synthetic resin loss after the boiling-washing, percent by weight	Decrease in tear resistance (mean value from chain and weft), percent	Decrease in tear resistance of finished goods after boiling-washing, treatment with chlorine liquor and ironing at up to 220° C., percent
(a) 4 g. ammonium phosphate.....	17.5	-32.0	32
(b) 15 g. magnesium chloride.....	14.0	-26.7	17
(c) 16 g. N- β -ethoxymaleamic acid melamine salt.....	4.5	-14.2	7

Example 3

A wool staple fiber fabric is impregnated on a pad in the usual manner with 100 grams of a dimethylol compound of ethylene-urea and 20 grams of the dimethylol compound of diethylene-triurea, per liter of liquor, in the presence of the various catalysts set forth below, in the same way as carried out in accordance with Example 1. The resin material impregnated textile is then carefully pre-dried such that the fabric still contains 10% residual moisture. The fabric is then imprinted on an imprint calender under a pressure of 5 to 6 kg./cm.² and at a roller temperature of 190° C., and subsequently condensed for 3 minutes at 160° C.

Catalyst	Synthetic resin loss after boiling-washing for 15 minutes with 2 g. soap and 3 g. soda, percent by weight
(a) 5 g. ammonium chloride.....	17.8
(b) 8 g. zinc chloride.....	17.3
(c) 16 g. magnesium chloride (with 2 mols water).....	14.5
(d) 15 g. melamido-maleamic acid melamine salt.....	6.8

What is claimed is:

1. In the process for improving the properties of textile materials including fabrics, yarns, fibers and the like by treatment with urea-containing hardenable resins selected from the group consisting of urea-, melamine- and ethylene-urea-formaldehyde-precondensates, the improvement which comprises effecting the hardening of the urea-containing hardenable resin material by heating with a salt of a weak organic base with a semi-amide formed from an ethylene- α,β -dicarboxylic acid and an amine.

2. Improvement according to claim 1 wherein the weak organic base is melamine.

3. Improvement according to claim 1 wherein the amine used to form the semi-amide is selected from the group consisting of aliphatic amines and cyclic amines.

4. Improvement according to claim 1 wherein the semi-amide is an N-substituted ethylene- α,β -dicarboxylic acid semi-amide.

5. Improvement according to claim 1 wherein the salt is maleamic acid melamine salt.

6. Improvement according to claim 1 wherein the salt is N- β -ethoxy maleamic acid melamine salt.

7. Improvement according to claim 1 wherein the salt is melamido-maleamic acid melamine salt.

8. Improvement according to claim 1 wherein the salt is the melamine salt of 1,2-bis(maleamic acid)-ethylene.

9. Improvement according to claim 1 wherein the salt is N-cyclohexyl maleamic acid melamine salt.

10. Improvement according to claim 1 wherein the salt is semi-substituted morpholino maleic acid melamine salt.

11. Improvement according to claim 1 wherein the salt is used in an amount of from about 10-20% by weight of the urea-containing hardenable resin material under the application of heat.

12. Process for curing urea-containing hardenable resin material selected from the group consisting of urea-, melamine- and ethylene-urea-formaldehyde-precondensates which comprises effecting the curing by heating in the presence of a salt of a weak organic base with a semi-amide formed from an ethylene- α,β -dicarboxylic acid and an amine.

13. Hardened urea-containing resin on a substrate produced by heating on the substrate a hardenable urea-containing resin precondensate selected from the group consisting of urea-, melamine- and ethylene-urea-formaldehyde-precondensates with a salt of a weak organic base with a semi-amide formed from an ethylene- α,β -dicarboxylic acid and an amine in an amount of from about 10-20% by weight of the precondensate.

14. Textile material having impregnated therein a hardened urea-containing resin resistant to tearing, creas-

ing, washing action and attack by chlorine, produced by heat hardening a hardenable urea-containing resin precondensate selected from the group consisting of urea-, melamine- and ethylene-urea-formaldehyde-precondensates impregnated in the textile material, with a salt of a weak organic base with a semi-amide formed from an ethylene- α,β -dicarboxylic acid and an amine in an amount of from about 10–20% by weight of the precondensate.

15. Hardened urea-containing resin composition containing a heat hardened member selected from the group consisting of urea-, melamine- and ethylene-urea-formaldehyde-precondensates, impregnated on a substrate and having incorporated therein a salt of a weak organic base with a semi-amide formed from an ethylene- α,β -dicarboxylic acid and an amine, in an amount of from about 10–20% by weight of the resin precondensate.

16. Composition according to claim 15 wherein the weak organic base is melamine.

17. Composition according to claim 15 wherein the amine used to form the semi-amide is selected from the group consisting of aliphatic amines and cyclic amines.

18. Composition according to claim 15 wherein the semi-amide is an N-substituted ethylene- α,β -dicarboxylic acid semi-amide.

19. Hardened urea-containing resin composition containing a heat hardened member selected from the group consisting of urea-, melamine- and ethylene-urea-formaldehyde-precondensates, impregnated on a substrate and having incorporated therein maleamic acid melamine salt, in an amount of from about 10–20% by weight of the resin precondensate.

20. Hardened urea-containing resin composition containing a heat hardened member selected from the group consisting of urea-, melamine- and ethylene-urea-formaldehyde-precondensates, impregnated on a substrate and having incorporated therein N- β -ethoxy maleamic acid

melamine salt, in an amount of from about 10–20% by weight of the resin precondensate.

21. Hardened urea-containing resin composition containing a heat hardened member selected from the group consisting of urea-, melamine- and ethylene-urea-formaldehyde-precondensates, impregnated on a substrate and having incorporated therein melamido-maleamic acid melamine salt, in an amount of from about 10–20% by weight of the resin precondensate.

22. Hardened urea-containing resin composition containing a heat hardened member selected from the group consisting of urea-, melamine- and ethylene-urea-formaldehyde-precondensates, impregnated on a substrate and having incorporated therein the melamine salt of 1,2-bis(maleamic acid)-ethylene, in an amount of from about 10–20% by weight of the resin precondensate.

23. Hardened urea-containing resin composition containing a heat hardened member selected from the group consisting of urea-, melamine- and ethylene-urea-formaldehyde-precondensates, impregnated on a substrate and having incorporated therein N-cyclohexyl maleamic acid melamine salt, in an amount of from about 10–20% by weight of the resin precondensate.

24. Hardened urea-containing resin composition containing a heat hardened member selected from the group consisting of urea-, melamine- and ethylene-urea-formaldehyde-precondensates, impregnated on a substrate and having incorporated therein semi-substituted morpholino maleic acid, in an amount of from about 10–20% by weight of the resin precondensate melamine salt.

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