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TEXTILE PROCESS WHICH USES CONCENTRATED

SULFURIC ACID AFTER RESIN TREATMENT

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No Drawing. Continuation-in-part of application Ser. No. 470,895, July 9, 1965. This application Dec. 14, 1965, Ser. No. 513,812

Claims priority, application Switzerland, July 10, 1964, 9,094/64

Int. Cl. D06m 13/12

U.S. Cl. 8—116.3

16 Claims

ABSTRACT OF THE DISCLOSURE

The instant invention is concerned with a process in which textile materials are treated with resin precondensate, dried below the curing temperature, and then treated with an aqueous solution of concentrated sulfuric acid to fix the precondensate and removing the acid.

This is a continuation-in-part of our copending application Ser. No. 470,895, now abandoned, filed July 9, 1965.

This invention relates to a textile process and the products produced by the process, and more particularly, it relates to a process which imparts crease-resistance to fabrics and further it relates to fabrics which can be treated to make them crease-resistant after they have been manufactured into articles of apparel and the like.

The processes for finishing cellulosic textile materials with resins are well-known. In one process a resin precondensate and a catalyst are applied to a textile material and subsequently cured under the influence of heat. Another known process for resin-finishing cellulosic textile material involves applying a solution of a polymerizable synthetic resin and a catalyst to the textile material, predrying the material at a temperature below the curing temperature, manufacturing articles of apparel and the like from the predried material and changing the form of the material, such as for example by adding folds or pleats, and subsequently polymerizing the synthetic resin under the influence of temperatures above about 100° C. to produce a crease-resistant finished article. This type of process has become known in the textile industry as "deferred curing."

It is also known to condense resin precondensates on cellulosic textiles under the influence of sulfuric acid, as for example by treating the material in strongly acidified baths, to produce a finished crease-resistant cellulosic textile. This operation is carried out with a comparatively weak sulfuric acid concentration and after treatment in the acidified precondensate bath the material is subsequently stored for a comparatively long reaction period. This prior art process produces a completely cured textile by means of the one-bath treatment and subsequent storage.

It would be desirable to provide a process in which cellulosic materials can be made crease-resistant after they have been formed into the finished article. In such a process the desired pleating, folding, and forming could be performed directly on the article made from the textile. It is of course possible to make articles from a cellulose-containing textile which is already crease-resistant, but it is frequently difficult or inconvenient to put permanent folds, pleats and creases into these articles at the desired place after the resin treatment. It would be possible to treat the finished article with conventional resin precondensates after manufacture, but this would

require that clothing manufacturers have chemical treating equipment, and would generally only be satisfactory for very large users. Moreover, there would be a limited range of treatment available, and many finishing agents could not be utilized.

This invention provides a method for producing cellulosic textile materials which can be made crease-resistant after fabrication into finished goods.

This invention also provides a method by which the manufacturer can produce crease-resistant cellulosic fabrics solely by the application of heat so that such materials can be formed into finished articles and then rendered crease-resistant.

Further and more specific objects, features, and advantages will clearly appear from the detailed description given below.

Briefly, the process of this invention for finishing textiles involves, first, the application of a resin precondensate to a cellulosic textile material and then drying the material, treating the dried material with aqueous sulfuric acid to fix the resin precondensate to the textile material and produce a material which can be cured in the presence of a catalyst to provide a crease-resistant textile.

In some embodiments of this invention the process includes the further steps of drying the sulfuric acid treated textile and subsequently curing it, generally at temperatures in excess of 100° C.

For purposes of this application, the terms "textile material" or "fabric" shall both be understood to include fabrics and textile materials of all kinds, including any manner of woven or knit fabrics. Further, for purposes of this application the term "cellulosic textile material" will be understood to apply to any kind of fabrics containing cellulosic fiber material, and includes fabrics in which cellulosic materials constitute a significant proportion. This term includes mixed fabrics consisting of cellulose in admixture with other natural or synthetic fibers. Especially preferred cellulosic textile materials are those made from natural cellulose such as cotton, regenerated cellulose such as viscose rayon, or chemical derivatives of cellulose such as acetate rayon. Additionally, mixtures of natural cellulose with regenerated cellulose or chemical derivatives of cellulose are comprehended by cellulosic textile materials.

Suitable resin precondensates for use in the process of this invention are all the precondensates used in the textile-finishing art. For example, precondensates consisting of formaldehyde and a nitrogenous material can be used in this invention. Desirable nitrogenous materials are, for example, urea or thiourea and their derivatives, especially the cyclic derivatives of urea in the form of heterocyclic five- or six-membered ring compounds, and also bicyclic compositions such as the so-called acetylene-diurea. Moreover the nitrogenous material can be a carbamate derivative or a triazine derivative, and particularly melamine derivatives and the like or, generally, amino methylol compounds.

In one aspect of this invention, it is especially preferred to use substances which react at acid pH with the cellulose, or with themselves and the cellulose, to cross-link the cellulose. Examples of desirable compounds are acetals, epoxides, polyepoxides, halohydrins, and methylol compounds, for example precondensates of formaldehyde and a compound having interchangeable hydrogen atoms, as for example the methylol compounds of ketones and of urea, thiourea, and their derivatives. It is especially preferred to use cyclical urea derivatives in the form of heterocyclic five- or six-membered ring compounds and their hydroxy or oxo derivatives. It is also advantageous to use bicyclic hetero compounds such as the so-called acetylene-diurea, dicyandiamide, guanidine, or carbamates and

the like. Moreover, triazine derivatives such as derivatives of melamine and their etherification products can be used. Also useable are mixtures of such products commonly used in the textile finishing art.

The resin precondensates can be applied to the cellulosic textile materials in various forms and by various techniques. For example, the resin precondensates can be applied to the cellulosic textile material from aqueous solutions, suspensions, or dispersions or from solutions, suspensions, or dispersions of the precondensate in other solvents or vehicles. The precondensate can be applied to the cellulosic textile material by dipping, padding, spraying, and other means of impregnating the material uniformly with the precondensate.

The cellulosic textile material is subsequently dried after impregnation with the precondensate. It will be understood that the term "drying" includes the removal of a substantial portion of the solvent or vehicle from the material. It will be further understood that the drying takes place at a temperature which is sufficiently low to obviate any significant amount of curing of the precondensate. The cellulosic textile material is treated with the amount of precondensate customarily used in the production of crease-resistant textiles. The drying is ordinarily carried out at temperatures below 100° C. to a final moisture content no greater than the equilibrium moisture of the textile in ambient air.

The step subsequent to this drying step is the one which partially fixes the precondensate onto the cellulosic textile material to provide the outstanding advantages of this invention. This partial fixing or prefixing of the resin precondensate by means of the sulfuric acid apparently binds a number of the reactive groups of the resin to the cellulose, while sufficient reaction groups remain free, so that the resin can be completely cured by heating in the presence of a catalyst having a potential acid reaction. Such curing may take place after the material has been changed in form, for example, by manufacture of apparel or other articles from the fabric.

In distinction to the prior art processes above mentioned, this invention partially binds the precondensate to the cellulosic material under the influence of the sulfuric acid. This partial fixation is readily detectable among other criteria, by the fact that it is impossible to wash out the prefixed resin from the textile material. Moreover, a material, for example, a cotton fabric, already shows even in this intermediate stage a very high wet crease-angle. However, it has been surprisingly found that the sulfuric acid treatment of this process permits the retention of sufficient free reactive groups in the resin precondensate to allow a complete cure of the resin merely by heating it in the presence of a condensation catalyst.

Thus contrary to expectations from consideration of prior art sulfuric acid treatments, the process of this invention does not result directly in the final crease-resistant product, but rather an intermediate product is first obtained in which the resin is bound to the cellulose, but still retains sufficient free reactive groups to be cured completely in a later reaction step. Thus, this invention provides textile materials which can be changed in form and then subsequently permanently fixed during final curing of the textile. For example, between the treatment with the precondensate and the final curing step folds and creases can be set into the finished article after fabrication.

The textile materials of this invention are capable of being readily worked and formed into finished articles without the necessity for special care to cut the fabric along such lines as to maintain the creases previously permanently set into the fabric and without the necessity to attempt to impregnate finished articles evenly with precondensates and then to fix them. Indeed, this latter procedure would be impractical because the treatment with the precondensate has a tendency to take out any creases or folds which have formed in the article.

The sulfuric acid treatment of this invention is carried out by contacting the dried textile material which has previously been impregnated with the precondensate with sulfuric acid having a concentration of from about 40 to about 60% H_2SO_4 . The treatment period desirably ranges from about half a minute to about thirty minutes. Since the process of this invention is particularly adapted to continuous operation, it is preferred to contact the material with the sulfuric acid for a time of from about one to about ten minutes. It is especially preferred to utilize sulfuric acid strengths in the range of from about 50 to about 60% H_2SO_4 . Unless otherwise indicated, all parts, percentages, and proportions herein are by weight.

After the sulfuric acid treatment step, the acid is completely removed from the material by washing and/or neutralization, as with aqueous alkali, and the material is dried. At this stage it will be found that the resin is already fixed on the cellulose, but only partially so that sufficient active groups remain to allow cross-linking under the influence of later treatment. After this sulfuric acid treatment the textile material of this invention is ready for further processing, as for example by the manufacture of clothing and articles of apparel therefrom.

Before or after the garment or other artifact has been formed, a curing catalyst is applied to the fabric. This can readily be accomplished by padding, spraying, and the like. All catalysts customarily used for resin curing, and especially ordinary acid catalysts and those having a potential acid reaction, can be utilized. Combined catalysts offered by the trade can also be used. Especially suitable for use in this process are salts which have a neutral reaction at ordinary temperatures, but possess an acid reaction at curing temperatures, as disclosed below. Examples of suitable catalysts are magnesium chloride, ammonium chloride, monoammonium phosphate, zinc chloride, zinc nitrate, magnesium perchlorate, zinc fluoborate and the like.

After treatment with the catalyst, the resin cure is completed by heat treatment at temperatures in excess of 100° C. It is preferred to carry out the curing at temperatures in the range of from about 120° to about 180° C., desirably over a period of from about one to about ten minutes. This curing can be carried out in any desired manner, such as by heating in an oven or in a press. It will be found that any changes in form which have been made on the finished article, such as folds or pleats, will be permanently fixed into the finished article, whereas the remainder of the fabric exhibits little or no creasing and dries smoothly.

During the treatment with catalyst and curing, the cellulose is in a non-swollen condition, as opposed to its swollen condition during treatment with the sulfuric acid. Thus, this second treatment especially improves the dry-crease angles. This behavior confirms the fact that reactive groups remain even after treatment with the sulfuric acid.

In another aspect of this invention a resin precondensate is added to the catalyst solution further to enhance the crease resistance of material onto which a precondensate has already been fixed by means of sulfuric acid. Relatively small quantities of these materials which are capable of reacting with cellulose or with themselves and cellulose are added in this stage of the process. The resin precondensates as set forth above are suitable for use in this aspect of the invention.

The following examples are given to illustrate the practice of this invention, but it will be understood that these examples do not limit the scope of the invention, the scope being determined by the claims appended hereto.

EXAMPLE I

A cotton poplin fabric is padded with a solution of 140 g./l. of "Lyofix CH" melamine-formaldehyde precondensate manufactured by Ciba Ltd. of Basel, Swit-

zerland. The fabric is then predried and treated in a bath of 57% sulfuric acid for three minutes, briefly rinsed in water, neutralized with a dilute soda solution, and thoroughly rinsed.

After any desired time interval and treatment a solution containing 20 g./l. of "Catalyst PR" curing catalyst is sprayed onto the fabric so that about 1.0–1.5% by weight (based on the dry fabric) of the catalyst is deposited as uniformly as possible on the fabric. This fabric can be subjected to garment finishing operations and then rendered creas-resistant by a high-temperature treatment to cure it.

EXAMPLE II

A cotton poplin fabric is padded with a solution of 150 g./l. of 50% 4,5-dihydroxy-1,3-dimethylolethylene urea so as to deposit approximately 5% of the urea on the fabric. After predrying, the fabric is treated with a 57.0% sulfuric acid solution for three minutes and thoroughly rinsed with water. Subsequently, the fabric is padded with a catalyst solution consisting of 15 g./l. of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and dried to a final moisture content of 8–10%.

Thereupon the fabric is manufactured into finished clothing and folds or pleats are applied as desired to the treated fabric. The treated fabric is then rendered wash-proof by curing for five minutes at 145–150° C. while the remainder of the fabric is wash-and-wear finished, that is, it is smooth-drying.

EXAMPLE III

A cotton fabric is padded with a solution of 300 g./l. of 50% dimethylol methylcarbamate and dried. Subsequently the padded and dried fabric is brought into contact with a dilute sulfuric acid solution containing 54% sulfuric acid for ten minutes. The sulfuric acid is then completely washed out of the fabric, first by neutralization with an alkali and then by thoroughly rinsing. Subsequently a solution containing 10 g./l. of zinc nitrate and 30 g./l. of a conventional 50% ethyleneureaformaldehyde precondensate is padded onto the fabric and dried again.

Fabrics pretreated in this manner can be processed at a subsequent time to obtain articles of apparel and folds can be made in the fabric if desired. The articles of apparel are cured in an ironing press at a temperature of 160–170° C. for approximately five minutes by which means washproof folds are permanently fixed in the fabric and improved crease-resistance achieved.

EXAMPLE IV

A cotton fabric is padded with 150 g./l. of "Fixapret CP" dimethylol dihydroxyethylneurea, manufactured by Badische Anilin & Sodafabrik AG of Ludwigshafen, Germany, and predried. This precondensate is fixed by treatment for eight minutes in a sulfuric acid bath containing 55% sulfuric acid.

After having been thoroughly washed out and dried the fabric is padded with an aqueous solution containing 75 g./l. of "Fixapret PH" dimethylol propylene urea and 7.5 g./l. of zinc nitrate, and dried to a residual moisture of about 15%. This fabric is processed to articles of apparel and press-in folds are permanently fixed by subsequent heat treatment at 140° C. for six minutes. Improved crease angles are also obtained.

EXAMPLE V

A spun-rayon imitation linen fabric is padded with a solution of 150 g./l. of a conventional tetramethylol acetylene diurea resin and predried. The resin is fixed by treating the fabric in a 52% H_2SO_4 bath for two minutes. The fabric is thoroughly rinsed and dried.

To produce articles of apparel at a later time, a solution containing a mixture of a propylene urea formaldehyde precondensate and magnesium chloride in a proportion of 5:2 is sprayed onto the fabric until 1.4% of magnesium chloride (based on the weight of the fabric) is applied. After the manufacture of articles of apparel

and possibly pressing-in of folds, curing is completed by heating at 125–140° C. for ten minutes.

This treatment produces pressed-in folds that are fixed at the same time as the crease resistance of the fabric is improved.

EXAMPLE VI

A blended fiber fabric consisting of 65% cotton and 35% polyester staple fibers is padded with 140 g./l. of a precondensate produced from urea and glyoxal by methylolizing and then dried. The fixing is effected by treatment in a 56.0% H_2SO_4 bath for three minutes. The acid treated material is then washed until a neutral reaction is obtained.

After an intermediate drying the fabric is immersed in aqueous solution containing 80 g./l. of ethylene urea-formaldehyde precondensate (50% strength) and 8 g./l. of zinc nitrate and squeezed to an add-on of 65%. Subsequently the fabric is dried to a residual moisture of approximately 12% and in this condition the fabric is prepared for the manufacture of garments. If creases are applied, a final treatment by heating at 150° C. for five minutes is sufficient to render the fabric wash-proof and simultaneously improve the dry crease-angles. In this process the wet crease angles have already been considerably increased after the sulfuric acid treatment.

The treatment with precondensate and sulfuric acid produces very high wet-crease angles with only slight losses in tensile strength. The dry-crease angle, as disclosed above, is materially improved by the subsequent curing in the presence of catalyst and (optionally) additional precondensate. Accordingly, the treatment with precondensate and sulfuric acid as set forth above followed by treatment with the catalyst (and optional precondensate) and curing produces very high wet-crease angles and improved dry-crease angles with relatively low losses in tensile strength. This is further illustrated in the following examples.

EXAMPLE VII

Part A

Cotton poplin is padded with an aqueous solution of 140 g./l. "Lyofix CH" melamine-formaldehyde precondensate. The squeezing effect amounts of 70%. After predrying the textile fabric is immersed in a 58.0% solution of sulfuric acid at 20° C. for 4 minutes.

The textile fabric is then rinsed, neutralized with a 2% sodium carbonate solution and washed in running water until free from salt. The treated textile fabric shows a wet-crease angle of 150° (average value from warp and weft) and a remaining tensile strength of 71%, whereas the dry-crease angle remains unchanged.

Part B

A cotton poplin fabric is treated as described in Part A. Subsequently a solution of 2 g./l. "Catalyst AC" aliphatic amine hydrochloride, produced by Monsanto Chemical Company, is padded on the fabric, predried and cured at 145 to 150° during 5 minutes. The dry-crease angle of the so treated fabric increases to 100° (average value of warp and weft), the wet-crease angle is 145°, and the remaining tensile strength is 65%.

EXAMPLE VIII

Cotton poplin fabric is treated as described in Part A of Example VII. Subsequently a solution containing 20 g./l. commercial dimethylol-ethylene urea precondensate and 1 g./l. zinc nitrate is padded onto the fabric. The fabric is predried and cured during 5 minutes at 145 to 150°. The dry-crease angle of the so treated fabric increases to 120°, the remaining tensile strength amounts to 55%, and the wet-crease angle is 145°.

EXAMPLE IX

Cotton poplin is padded with an aqueous solution of 70 g./l. tetramethylol-acetylene diurea and predried. The

fabric is then passed through 57.0% sulfuric acid for three minutes and subsequently washed until completely free of acid. This finishing results in a wet-crease angle of the fabric of 165° (average value from warp and weft) and a remaining tensile strength of approximately 75%. The dry-crease angle is practically unchanged.

In the second stage the fabric is padded with an aqueous solution of 20 g./l. tetramethylol-acetylene diurea and 10 g./l. of a commercial zinc nitrate catalyst, dried, and cured at 150° C. The dry-crease angle is now increased from 55° to 100°. The flat-drying properties of this fabric are extremely good.

EXAMPLE X

A cotton poplin fabric is padded with an aqueous solution of carbamate precondensate containing 100 g./l. dimethylol methyl carbamate. The precondensate is produced according to known methods from technical methyl carbamate and formaldehyde at pH 11. After predrying the fabric is subjected to a treatment with 60% sulfuric acid for 30 seconds. After having washed the fabric free from acid and drying it, an aqueous solution of 10 g./l. "Catalyst PR" zinc nitrate made by Ciba is padded onto it. The fabric is then dried and cured for 5½ minutes. Subsequently the fabric is washed out and finished in the usual way. The fabric shows considerably greater wet-crease angle of 170° (average warp and weft), a moderately increased dry-crease angle, and favorable flat drying properties.

EXAMPLE XI

A cotton poplin fabric is impregnated with an aqueous solution of 70 g./l. tetramethylol acetylene diurea and picked up solution to a 70% weight increase. After predrying the fabric is immersed in sulfuric acid containing 45.0% H₂SO₄ for 20 minutes and subsequently washed to the neutral point. By this treatment the cotton fabric achieves a wet-crease angle of 156° at a minimum loss in tensile strength of approximately 10%. The dry-crease angle is increased by an after-treatment described in Example VIII, which also provides extremely good flat-drying properties of the fabric.

EXAMPLE XII

A solution of 150 g./l. "Knittex Everfit CR" triazine mixed resin made by Pfersee G.m.b.H., Augsburg, Germany, is padded onto a cotton poplin fabric. After drying the fabric is immersed in 56% sulfuric acid for eight minutes, rinsed, and washed free of acid. After redrying, the fabric is padded with a solution of 100 g./l. dimethylol-propylene urea and 5 g./l. ammonium chloride, cured at 120° for 20 minutes, and washed out as usual. Samples of this fabric show the following values as compared to the untreated materials:

	Dry-crease angle (deg.)	Wet-crease angle (deg.)	Tensile strength (kg.)	Monsanto values
Untreated (control)-----	58	90	21.0	1-2
Treated-----	117	154	12.1	4-5

EXAMPLE XIII

An aqueous solution containing 15% commercial polyglycolic acetal ("Quaker Reactant 16" of Quaker Chemical Products Corp., U.S.A.) is padded onto cotton poplin and after predrying the fabric is immersed in a 57.0% sulfuric acid bath, rinsed, washed free of acid, and dried. By subsequent padding with a solution containing 10 g./l. MgCl₂·6H₂O and 100 m./l. "Quaker Reactant 16" followed by curing at 160° C. for 3½ minutes, the dry-crease angles can also be increased, whereas the wet-crease angles are increased to 150° in the intermediate stage.

EXAMPLE XIV

Cotton poplin is padded with an aqueous solution of 140 g./l. "Lyofix CH" and predried. It is then contacted

with 57% sulfuric acid for four minutes and thoroughly washed out. The dry fabric is then padded with a solution consisting of 100 g./l. "Fixapret AH" dimethylol ethylene urea precondensate made by BASF, Ludwigshafen, Germany, 10 g./l. "Catalyst PR," 6 g./l. of "Cerol WB," a stearyl-methylamidomethylene pyridinium chloride made by Sandoz A. G., Basel, Switzerland, and 1 g./l. "Triton X 100" surface active agent produced by Rohm & Hass, Philadelphia, Pa., predried, cured at 145° for five minutes, and washed out. The textile is found to have a dry crease angle of 145°, a wet crease angle of 155°, and extremely good flat-drying properties.

EXAMPLE XV

A spun rayon linen imitation fabric (or spun rayon cretonne) is padded with an aqueous solution containing 250 g./l. "Lyofix CH" and dried. The fabric is then brought into contact with 50% sulfuric acid for two minutes and is then thoroughly washed out and dried. The dry fabric is padded with an aqueous solution consisting of 100 g./l. of a urea formaldehyde precondensate (50%), 10 g./l. MgCl₂·6H₂O, and 5 g./l. polyvinyl alcohol, predried, cured at 145 to 150° for 5 minutes, and subsequently washed out. This treatment results in remarkably good flat-drying properties.

What is claimed is:

1. A process for finishing textiles which comprises first applying a resin precondensate to a cellulosic textile material, drying the material at a temperature below 100° C., treating the dried material with an aqueous solution consisting essentially of sulfuric acid having a concentration of from about 40% to about 60% H₂SO₄ to fix the resin precondensate to the textile material and produce a material which can be cured in the presence of a catalyst to provide a crease-resistant material, and removing the sulfuric acid from the material.

2. The process of claim 1 wherein a condensation catalyst is applied to the material, after the sulfuric acid has been removed.

3. The process of claim 2 wherein the fixed precondensate is cured by heating to temperatures in excess of 100° C.

4. The process of claim 1 wherein the dried material is treated with an aqueous solution containing from about 40 to about 60% of sulfuric acid for a period of from about 0.5 to about 30 minutes.

5. The process of claim 1 wherein the sulfuric acid is subsequently removed from the material by neutralizing with an alkali.

6. The process of claim 1 wherein the precondensate consists essentially of formaldehyde and a nitrogenous compound.

7. The process of claim 6 wherein the nitrogenous compound is a cyclic urea selected from the group consisting of heterocyclic five- and six-membered rings.

8. The process of claim 6 wherein the nitrogenous compound is a carbamate.

9. The process of claim 6 wherein the nitrogenous compound is a triazine derivative.

10. A process for preparing finished artifacts which comprises first applying a resin precondensate to a cellulosic textile material, drying the material at a temperature below 100° C., treating the dried material with an aqueous solution consisting essentially of sulfuric acid having a concentration of from about 40% to about 60% H₂SO₄ to fix the resin precondensate to the textile material and produce a material which can be cured in the presence of a catalyst to provide a crease-resistant textile, removing the sulfuric acid from the material, forming an artifact, and curing the formed artifact by heating to temperatures in excess of 100° C. in the presence of a condensation catalyst.

11. A process for finishing textiles which comprises first applying a resin precondensate to a cellulosic textile material, drying the material at a temperature below

100° C., treating the dried material with an aqueous solution consisting essentially of sulfuric acid having a concentration of from about 40% to about 60% H₂SO₄ to fix the resin precondensate in the textile material and produce a material which can be cured in the presence of a catalyst to provide a crease-resistant textile, removing the sulfuric acid from the material, treating the material with a condensation catalyst, and finally curing the material by heating at temperature above about 100° C.

12. The process of claim 11 wherein the treatment with sulfuric acid is carried out for from about 0.5 to about 30 minutes in acid from about 40% to about 60% H₂SO₄.

13. The process of claim 12 wherein the curing temperature is from 120° to 180° C.

14. The process of claim 12 wherein the precondensate is an acetal.

15. The process of claim 12 wherein the precondensate

is selected from the group consisting of epoxides and polyepoxides.

16. The process of claim 13 wherein precondensates of formaldehyde with compounds having interchangeable hydrogen atoms are added to the catalyst.

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U.S. Cl. X.R.

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