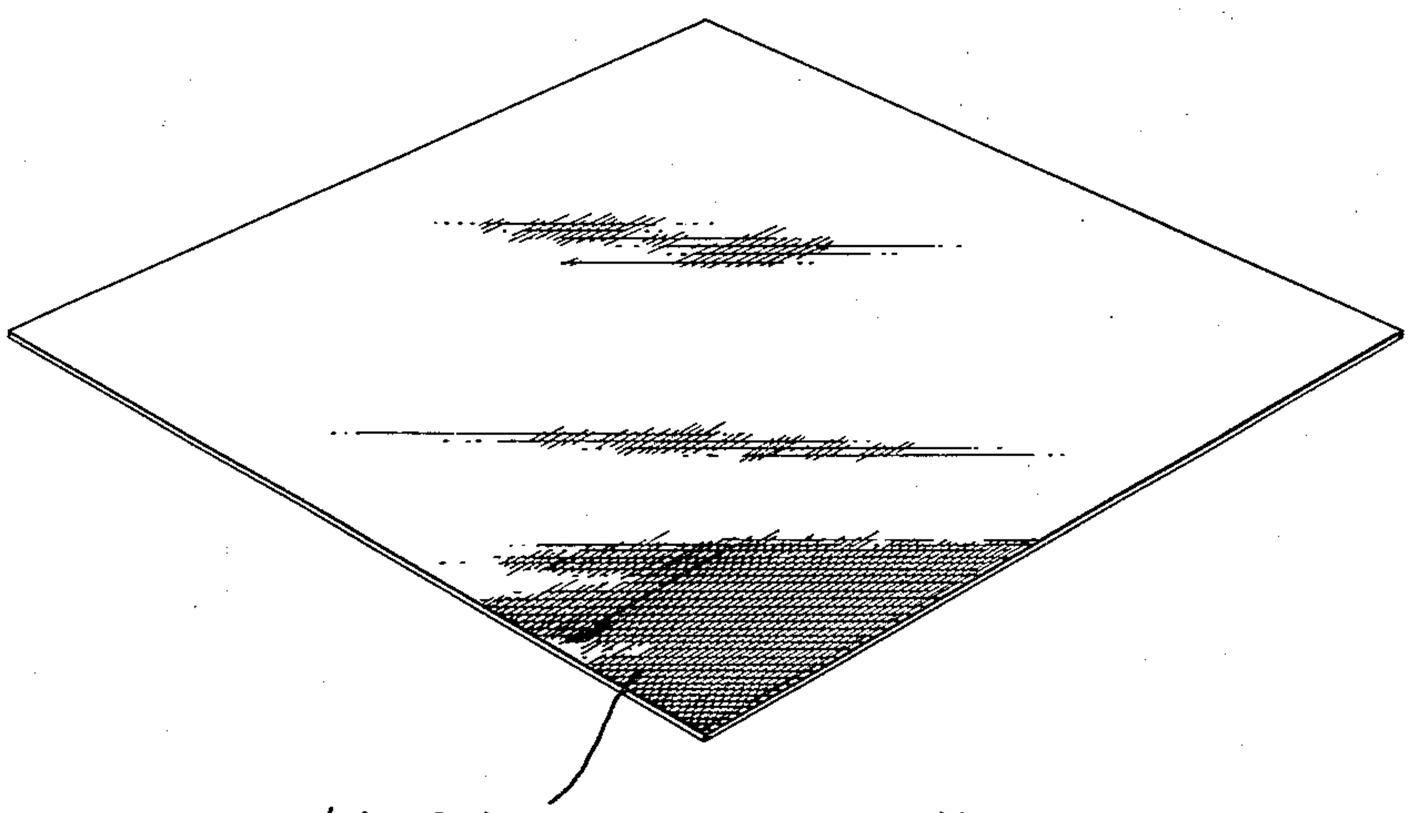
Sept. 2, 1958 T. E. ZURAWIC ET AL 2,850,407

TEXTILE FINISHING COMPOSITIONS CONTAINING ADDUCT OF β-AMINO LOWER ALKYL CARBAMATE AND FORMALDEHYDE, METHOD OF APPLYING SAME, AND THE TREATED TEXTILE

Filed May 28, 1956



Textile fabric provided with crease resistant finish comprised of thermoset resinous formaldehyde adduct of β-amino lower-alkyl carbamate reaction product.

INVENTORS.
Theodore E. Zurawic
William F. Tousignant

BY Griswold & Burdick
ATTORNEYS

United States Patent Office

2,850,407

Patented Sept. 2, 1958



2,850,407

# TEXTILE FINISHING COMPOSITIONS CONTAINING ADDUCT OF B-AMINO LOWER ALKYL CARBAMATE AND FORMALDEHYDE, METHOD OF APPLYING SAME, AND THE TREATED TEXTILE

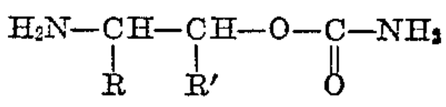
Theodore E. Zurawic and William F. Tousignant, Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

Application May 28, 1956, Serial No. 587,596

15 Claims. (Cl. 117—139.4)

This invention relates to, and has as among its principal objectives, the provision of certain thermosetting resinous compositions and formulations adapted to provide such compositions that have particular utility and are especially suited for being employed and applied as finishes for improving the crease and wrinkle resistance and the dimensional stability of textile materials. It also has reference to, and it is among the objects of the invention to provide, a method for utilizing such resinous compositions and the formulations that yield them for improving the crease resistance and dimensional stability of cloth and fabric constructed from various textile fiber materials and to furnish crease resistant and dimensionally stable textile materials by practice of the method and utilization of the resinous compositions of the invention.

Resinous compositions, in accordance with the present invention, are comprised of a thermoset adduct of from 2.0 to 4.0 moles of formaldehyde with each mole of modified urea in a reaction product of 1.0 mole of urea and between about 0.7 and 1.5 moles of an alkylene oxide, said reaction product consisting preponderantly of β-amino lower-alkyl carbamates having the general formula:



wherein R and R′ are members of the class consisting of hydrogen and lower-alkyl groups of from 1 to 4 carbon atoms, the sum of the carbon atoms present in R and R′ combined being not greater than four. It is usually more beneficial for the resinous composition to be comprised of an adduct containing in the neighborhood of 3 moles of formaldehyde with each mole of modified urea in a β-amino lower-alkyl carbamate reaction product of about 1.0 mole of urea and about 0.85 mole of the lower alkylene oxide.

Advantageously, the thermoset resinous formaldehyde adduct compositions of the invention are provided from an aqueous formulation that is adapted to be applied to a textile material and cured in situ to form the resinous composition on the textile material as a crease resistant finish. Such a formulation may be comprised of an aqueous solution containing the β-amino lower-alkyl carbamate and the formaldehyde, which may be partially adducted in the formulation, along with a suitable curing catalyst, which may be an acid catalyst or other type of curing accelerator for assisting in the formation of the thermoset formaldehyde adduct, and a minor proportion of polyvalent metal ions, such as metal ions selected from the group consisting of zinc ions, magnesium ions and aluminum ions which augment the efficacy of the formulations and improve their heat stability so as to minimize the possibility of discoloring the textile material during the thermal curing of the formulation to provide the resinous composition finish. Usually, the aqueous, catalyst-containing formulations for providing the resinous compositions may be prepared as water white solutions having a pH between about 2.0 and 7.0 that may contain as much as 70 percent by weight of active solids, based on the weight of the formulation.



When heated and evaporated to dryness, the formulations produce a hard, brittle, clear, water-insoluble, thermoset, resinous composition. The formulations, as indicated, are adapted to be prepared as concentrated, dilutable stocks that do not require additional activating additaments or ingredients for subsequent use in the finishing of textile materials. The formulations of the invention may be stored for considerable periods without occasioning deleterious consequences and without diminishing their efficacy for the desired purpose. In addition, the formulations are ordinarily compatible with a variety of other materials such as various latexes, silicone emulsions and the like that are often used for textile finishing purposes.

The crease resistance and dimensional stability of cloth, fabric and other textile fiber materials may be significantly improved by a method which comprises subjecting the textile material to an applicating, thermoset resin-providing formulation in accordance with the invention, impregnating the material with between about 5 and 30 percent by weight and, for many purposes, with between about 5 and 15 percent by weight of active solids from said formulation, based on the dry weight of said textile material, and subsequently exposing the impregnated textile material to a resin curing temperature between about 300 and 400° F. for a period of time between about one and five minutes. Lower curing temperatures generally require longer curing times. Advantageously, the aqueous applicating formulation may contain between about 5 and 40 percent by weight of solids although in many instances it may be convenient for the formulation to be employed with an active solids content of between 15 and 25 percent by weight. It is usually beneficial for the formulation to have a minor proportion, generally between about 0.02 and 1.0 percent by weight, of a wetting agent incorporated therein to assist in the wet pick up of the active solids from the applicating formulation by the textile material. Improved curing results may often be obtained by drying the impregnated textile material at any water evaporating temperature beneath the curing temperature as, for example, in the neighborhood of 212° F. so that it may be substantially free from water before it is subjected to a curing temperature. It frequently may be desirable to employ a temperature of about 350° F. for about one to two minutes in order to cure the applied resinous material.

The textile material may be impregnated with the formulation in any desired manner. While it is usually convenient to immerse the textile material in an applicating bath of the formulation and subsequently squeeze it free of excess liquid, suitable impregnating results may also be achieved by spraying, brushing or otherwise coating or applying the formulation on the textile material.

Textile materials, particularly cloth and fabric, that are provided in accordance with the invention with a finish application of the thermoset resinous material have significantly enhanced crease and wrinkle resistance and improved dimensional stability. In addition, they have acceptably low chlorine retention characteristics and maintain their tensile strength in a suitable manner, even after exposure to chlorine. They are possessed of a good hand and retain their other desirable physical characteristics so that they may advantageously be employed for various clothing and other cloth and fabric uses. Finished materials in accordance with the invention are generally at least equivalent and may frequently be superior to materials that are provided with conventional melamine, ethylene urea and the like resin finishes employed for obtaining crease resistant properties. The textile materials that may be benefited by the practice of

the invention may be of any desired origin, natural, artificial and synthetic, including cotton, wool, silk, viscose and acetate rayon, and acrylic, polyamide, polyester and the like synthetic materials. Frequently, however, the greatest benefit may be secured when the invention is practiced with textile materials that consist of, comprise or contain natural or artificial cellulosic fibers, or both. A piece of crease resistant fabric finished with a thermoset resinous composition in accordance with the present invention is schematically depicted in the accompanying drawing.

The β-amino lower-alkyl carbamate reaction products of urea and a lower alkylene oxide that are utilized in the present invention and their manner of preparation may advantageously be in general accordance with those which have been disclosed by William F. Tousignant and Thomas Houtman, Jr., in their copending application having Serial No. 449,477 which was field on August 12, 1954. Such products may be prepared by gradually adding to and thoroughly mixing with liquified urea that is maintained in a reaction vessel at a reaction temperature beneath about 140° C. and under a pressure of from about 40 to 100 pounds per square inch (gauge), a substantially anhydrous alkylene oxide of the class consisting of ethylene oxide; 1,2-propylene oxide; 1,2-butylene oxide; and 2,3-butylene oxide at a rate in the range of from about 0.1 to 0.5 pound per hour per pound of urea charged until from about 0.85 to 1.2 molecular proportions of alkylene oxide have been reacted per molecular proportion of urea. While the essentially 1-methyl-2-amino ethyl carbamate product of the reaction between propylene oxide and urea may be converted to resinous formaldehyde adduct compositions from the formulations of the invention with particular advantage, other β-amino lower-alkyl carbamates may also be beneficially employed. Thus, for example, the essentially 2-amino ethyl carbamate product of reaction between ethylene oxide and urea may also be utilized. Likewise, the reaction product of butylene oxide with urea, consisting essentially of 1-ethyl-2-amino ethyl carbamate may be used. In addition, reaction products of mixed lower alkylene oxides and urea may be suitable for forming the formaldehyde adducts as may, in an analogous manner, the product of reaction between epichlorohydrin (which is also known as chloropropylene oxide) and urea and mixtures of various β-amino lower alkyl carbamates.

The formaldehyde that is incorporated in the resinous composition providing aqueous formulation may usually be added conveniently in the form of an aqueous solution, such as one that contains in the neighborhood of 37 perecent by weight of dissolver formaldehyde. If desired, compounds that yield formaldehyde such as paraformaldehyde, trioxane and the like may be employed in place of formaldehyde in the preparation of the formulations. As mentioned, some of the formaldehyde in the formulation may adduct with the dissolved β-amino lower-alkyl carbamate dissolved therein before the formulation is cured to a resinous composition. Despite this the active solids of the formulation remain soluble until they are purposely cured by exposure to a suitable curing temperature.

Various acid curing catalysts and accelerator materials may be employed in the resinous composition-providing formulations of the invention. Advantageously an acid catalyst may be used which is selected from the group consisting of tartaric acid, adipic acid, citric acid and phosphoric acid. Phosphoric acid may be particularly desirable for employment in the practice of the invention. If desired, however, accelerator materials such as the alkanolamine hydrochloride type of catalyst and the like including 2-amino isopropanol hydrochloride, similar to that which is available from The Monsanto Chemical Company under the designation "Catalyst AC" may be employed. Usually, an amount of the catalyst between about 4 and 10 percent by weight, and preferably about 5 percent by weight, based on the weight of active solids in the formulation, may be found to be satisfactory.



It is generally beneficial to employ between about 0.02 and 0.30 moles of the polyvalent metal ion in the formulation per mole of modified urea contained therein. Generally, about 0.166 mole of the metal ion per mole of modified urea may be satisfactory. The polyvalent metal ion may be provided from such soluble salts as the sulfates which may be incorporated in the formulation for this purpose.

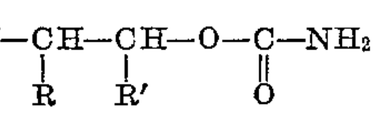
By way of further illustration, an applicating formulation for providing a crease resistant finish was prepared by mixing about 124 grams of the reaction product of propylene oxide and urea in a 0.85 to 1 respective mole ratio, about 220 grams of a 37 percent by weight aqueous solution of formaldehyde, about 40.6 grams of zinc sulfate heptahydrate, about 50 grams of water and a sufficient quantity of phosphoric acid to impart a pH of about 2.0 to the mixture. The resulting formulation was a water white liquid solution. It had a good shelf life, retaining its resin-providing capability and utility as an application formulation for crease resistant finishes after storage periods of as long as six months.

The prepared formulation, which was diluted with water to have about a 15 percent by weight active solids content, was employed to treat an 80 x 80 square-woven, pure finish cotton fabric that weighed about 4 ounces to the square yard. About 0.25 percent by weight of a nonionic detergent was incorporated in the diluted formulation to assist in the wet pick up of the formulation by the fabric. The fabric was immersed in the formulation and subsequently physically squeezed of enough excess liquid so that the pick up, based on the weight of the fabric, was about 13.56 percent by weight of active solids from the formulation, based on the weight of the fabric. The wet fabric was then dried at 212° F. for about five minutes and cured at 350° F. for about one and one-half minutes. It was then washed in a 0.25 percent by weight aqueous solution of mild soap and rinsed thoroughly with water at about 50° C. before being dried at 212° F. for five minutes. After being conditioned overnight at a constant room temperature and relative humidity, a portion of the finished fabric was subjected to a test using an apparatus known as the Monsanto Wrinkle Recovery Tester according to A. A. T. C. C. Tentative Test No. 66–53 which is presented at page 165 of the 1953 A. A. T. C. C. Yearbook. In the test, which consists essentially of pressing the creased fabric for a given period and measuring the retained angle of the crease, an angle of 0° indicates no wrinkle resistance while an angle of 180° indicates optimum wrinkle resistance. The wrinkle recovery of the fabric finished in accordance with the invention was determined to be about 152°. In comparison, the untreated fabric had a wrinkle recovery angle of only 70.5° and that of a similar fabric treated with a widely used and accepted commercially available crease resistant finish material, obtainable under the trademark "Rhonite R–1" from Rohm & Haas Co., was 151°. Furthermore, there was no discoloration imparted to the fabric treated in accordance with the invention due to the curing of the applied finish at the elevated thermosetting temperature and the chlorine retention of the treated fabric, as determined in accordance with A. A. T. C. C. Tentative Test No. 69–52, was found to be very low and well within the limits of commercial acceptability. The loss in tensile strength of the finished fabric, even after chlorination, was not excessive.

Similar excellent results may be obtained with other thermosetting formaldehyde adduct resinous finish compositions and formulations for providing them that are in accordance with the invention when they are employed in the foregoing manner on cotton, rayon and other textile cloth and fabrics in order to improve their crease and wrinkle resisting characteristics.

What is claimed is:

1. Applicating formulation that is adapted to provide crease-resisting thermoset resinous textile finishes upon being subjected to resin curing temperatures between about 300° and 400° F. for a period of time between about one and five minutes, said formulation comprising, in aqueous solution, a reaction product of 1.0 mole of urea and between about 0.7 and 1.5 moles of an alkylene oxide, said reaction product consisting preponderantly of β-amino lower-alkyl carbamates having the general formula:



wherein R and R′ are members of the class consisting of hydrogen and lower alkyl groups of from 1 to 4 carbon atoms, the sum of the carbon atoms present in R and R′ combined being not greater than 4; between about 2.0 and 4.0 moles of formaldehyde for each mole of modified urea in said β-amino lower alkyl carbamate reaction product; a catalyst for curing the β-amino lower-alkyl carbamate reaction product and the formaldehyde to a resinous formaldehyde adduct composition; and a minor proportion of polyvalent metal ions selected from the group consisting of zinc ions, magnesium ions and aluminum ions.

2. The formulation of claim 1, wherein the catalyst is an acid catalyst selected from the group consisting of tartaric acid, adipic acid, citric acid and phosphoric acid.

3. The formulation of claim 1, wherein the catalyst is phosphoric acid.

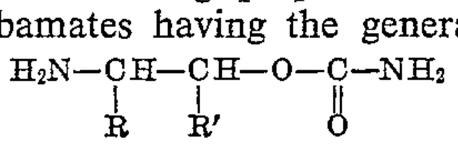
4. The formulation of claim 1, wherein the catalyst is present in an amount between about 4 and 10 percent by weight, based on the weight of the active solids in the formulation.

5. The formulation of claim 1, wherein the polyvalent metal ion is present in an amount between about 0.02 and 0.30 mole for each mole of modified urea in the β-amino lower-alkyl carbamate reaction product.

6. The formulation of claim 1, wherein the pH is between about 2.0 and 7.0.

7. The formulation of claim 1, containing as much as 70 percent by weight of dissolved active solids, based on the weight of the formulation.

8. Method for improving the crease resistance of textile materials which comprises impregnating the textile material with between about 5 and 30 percent by weight of active solids from a resinous formaldehyde adduct composition-providing formulation containing, in aqueous solution, a reaction product of 1.0 mole of urea and between about 0.7 and 1.5 moles of an alklyene oxide, said reaction product consisting preponderantly of β-amino lower-alkyl carbamates having the general formula:





wherein R and R′ are members of the class consisting of hydrogen and lower alkyl groups of from 1 to 4 carbon atoms, the sum of the carbon atoms present in R and R′ combined being not greater than 4; between about 2.0 and 4.0 moles of formaldehyde for each mole of modified urea in said β-amino lower-alkyl carbamate reaction product; a catalyst for curing the β-amino lower-alkyl carbamate reaction product and the formaldehyde to a resinous formaldehyde adduct composition; and a minor proportion of polyvalent metal ions selected from the group consisting of zinc ions, magnesium ions and aluminum ions; and subsequently exposing said impregnated textile material to a resin curing temperature between about 300 and 400° F. for a period of time between about one and five minutes.

9. In the method of claim 8, the urea-alkylene oxide reaction product that is dissolved in said aqueous formulation being the product of the reaction between about 0.85 mole of the alkylene oxide for each mole of urea.

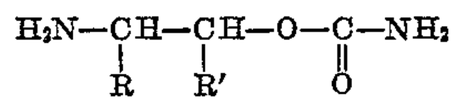
10. A method in accordance with the method set forth in claim 8, wherein the alkylene oxide is propylene oxide.

11. The method of claim 8, wherein the formulation for impregnating the textile material contains between about 5 and 40 percent by weight of dissolved active solids.

12. The method of claim 8 and including the step of drying the impregnated textile material substantially free from water before exposing it to a curing temperature.

13. In the method of claim 8, exposing the impregnated textile material to a resin curing temperature of about 350° F. for a period of time of about one to two minutes.

14. A textile material provided with a crease resistant finish that is comprised of a thermoset resinous composition comprising an adduct of from 2.0 to 4.0 moles of formaldehyde with each mole of modified urea in a reaction product of 1.0 mole of urea and between about 0.7 and 1.5 moles of an alkylene oxide, said reaction product consisting preponderantly of β-amino lower-alkyl carbamates having the general formula:



wherein R and R′ are members of the class consisting of hydrogen and lower alkyl groups of from 1 to 4 carbon atoms, the sum of the carbon atoms present in R and R′ combined being not greater than 4.

15. The textile material of claim 14 containing between about 5 and 30 percent by weight of the finish, based on the weight of the textile material.

No references cited.