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STABLE CONDENSATES OF UREA AND FORMALDEHYDE IN THE PRESENCE OF METHANOL

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This invention concerns soluble, stable condensates of urea and formaldehyde prepared in the presence of methanol and methods for preparing said condensates. These condensates are particularly effective agents for finishing textiles. They are effective, for example, in the mechanical finishing of cottons, especially for glazing and embossing. They help stabilize rayon fabrics. They are highly effective agents for durably stiffening nylon and comparable yarns and fabrics.

Urea-formaldehyde condensates have been prepared in a variety of types and forms which can be utilized for textile finishing of specific sorts. The condensates are most conveniently utilized in liquid or solution forms. These, however, are ordinarily not very stable in warm weather unless they are stored under refrigeration. The condensates are applied from aqueous baths which also contain catalysts for curing the condensates in or on fabrics. Such baths have a relatively short useful life, because, again, the condensates previously known are not very stable, especially under these conditions. There is thus a definite need for a stable urea-formaldehyde condensate which possesses the convenience of liquid form, which is reactive and which is useful for imparting desirable finishes to textile fabrics.

The known urea-formaldehyde condensates have not been found useful for the finishing of nonhydrophylic filamentous yarns or fabrics, such as cellulose acetate, nylon, Orlon, or Dacron, where a durable, crisp yet resilient quality is desired. Rather, previously disclosed urea-formaldehyde condensates have not adhered well to such materials and tended to lessen or detract from their innately resilient and crush-resistant qualities. A finishing agent which would impart a durable, crisp finish to nylon, acetate or similar fabrics with improvement in resiliency and accentuation of the natural crush-proofnes of such fabrics has long been desired.

It is an object of this invention to supply a stable textile finishing condensate in liquid form. It is an object to provide a textile finishing agent which is stable in treating baths containing a curing catalyst. It is also an object to provide a urea-formaldehyde condensate which is particularly useful for imparting a crisp, resilient finish to nylon and other synthetic fibers.

These objects are accomplished by reacting urea and formaldehyde together under particular conditions with control of concentrations, pH's, and temperature. In the process of this invention urea and formaldehyde are reacted in concentrated solution in a proportion between 1:2.5 and 1:3 at a pH between 7.5 and 9 at a temperature of about 60° to 80° C. until not over 15% of the formaldehyde can be found as determined by titration for alkalinity of a cold sodium sulfite solution added to a sample of the reaction mixture, adjusting the pH of the reaction mixture to a value from 3.8 to 3.0, and with methanol present in a ratio from 2.5:1 to 4:1 for methanol to urea, heating the reaction mixture under reflux for 5 to 60 minutes. The time used here will be

determined by the degree of condensation and polymerization desired. The minimum time gives a suitable reaction product, but with longer times products giving stiffer finishes are formed.

This procedure yields a condensate in solution which could be used directly upon dilution with water. For normal handling and shipping, however, the pH of the reaction mixture is brought to about 7 and the mixture is then heated at not over 60° C. under reduced pressure until a nonvolatile content of 85% to 100% is reached, as determined by stripping at low pressure and at temperatures below 50° C.

In the initial condensation on the alkaline side formaldehyde is used at a concentration from 35% to 60% or more. Aqueous formaldehyde with 35% to 50% formaldehyde content may be taken at the start and, if necessary, the reaction is heated below 55° C. under reduced pressure to take off water and leave less than 30% of water in the alkaline reaction product. It is best to have the water content between about 5% and 16% in the alkaline reaction product. Instead of use of all aqueous formaldehyde there may be used paraformaldehyde together with some aqueous formaldehyde, since the presence of water here seems to promote the reaction. In this case the water content will be suitably low from the start. Again, there may be taken as a starting material a commercial urea-formaldehyde product having a 1:5 mole ratio of urea to formaldehyde and containing about 15% water. Urea is added to such product to bring the urea to formaldehyde ratio within the required range. In a comparable manner a simple molecular methylol urea may be treated in concentrated solution with formaldehyde to give the required ratio between 1:2.5 and 1:3.0 for urea to formaldehyde. When paraformaldehyde is used or the concentrated 1:5 urea-formaldehyde preparation, it is not necessary to take off water and methanol may be added to the mixture even at the start.

The pH of the urea-formaldehyde mixture is brought in the first stage to a value between 7.5 and 9, preferably 8 to 8.5. This pH level is most conveniently reached by addition of a small amount of sodium hydroxide or sodium carbonate.

With the pH at the proper value the reaction mixture is heated. A temperature of 60°–80° C. is suitable and reaction at this temperature level normally takes place in 15 to 40 minutes. But if water above the prescribed limits is present, excess is first taken off under reduced pressure. It is best at this stage to keep the temperature below 60° C.

The reaction is considered sufficiently complete when upon treatment of a sample of reaction mixture with sodium sulfite in the cold followed by titration for alkalinity, it appears that 85% or more of the formaldehyde has reacted. This test gives a value which depends upon actual free formaldehyde and upon formaldehyde which is available from some reversion of the reaction product. The test is, therefore, an empirical one, but one which serves with sufficient accuracy to determine when the first stage of reaction has been sufficiently completed. (Cf. S. S. Sadtler, Am. J. Pharm. 76, 847 (1904).)

Methanol, if not already present, may now be added to the reaction mixture in an amount to give at least a mole ratio of 2.5:1 to 4:1 of methanol to urea. Acid is added to bring the pH of the mixture quickly to a value of 3.8 to 3.0. A convenient acid for this purpose is phosphoric, particularly a solution of this acid in methanol. Other acids, such as hydrochloric, sulfuric, p-toluene, sulfonic, oxalic, and the like, which give the required low pH, may also be used.

The acidic reaction mixture is then heated under reflux for 5 to 60 minutes until the reaction mixture has become clear and reaction with methanol has occurred.

While the product can be used in this form, it is best to adjust the pH thereof to about neutrality. A pH of about 7 to 7.5 is best. Sodium or potassium hydroxide solution is conveniently used for this purpose. Excess methanol is distilled off and the mixture is heated under reduced pressure to remove most or substantially all of the volatile materials, including water and methanol. This yields a product having 85% to 100% of resinous materials, as determined by stripping under reduced pressure with heating to about 50° C. The product at this point has a Gardner-Holdt viscosity of B to I and usually yields 70–75% of cured resin solids when heated at 150° C. for 90 minutes. If desired, the product may be treated with charcoal or diatomaceous earth and filtered.

The product is a syrupy, water-soluble product, which is particularly useful for finishing several types of textiles. It has a methoxyl content of 20% to 25%. It is stable, as shown by storage tests at 46° C. for over twelve months and for well over a year at room temperatures. Yet applied to textiles along with a curing catalyst and then cured, it produces new and desirable effects which are relatively permanent.

Typical preparations of this product are described in the following illustrative examples. Parts are by weight.

Example 1

There are charged to a reaction vessel 60 parts by weight of urea and 211 parts of aqueous 50% formaldehyde. A small amount of aqueous 10% sodium hydroxide solution is added to bring the pH of the mixture above pH 8. The mixture is heated at about 75° C. for 20 minutes, at which time a determination of formaldehyde with cold sodium sulfite solution followed by titration of alkalinity shows that about 90% of the formaldehyde was reacted. The reaction is placed under reduced pressure and volatile material taken off to leave a solution of 85% nonvolatile material in the reaction vessel. Thereto is added 96 parts of methanol. The mixture is adjusted with a solution of equal parts of phosphoric acid and methanol to a pH of 3.3. The mixture was then heated to refluxing temperature and held there for 20 minutes. The reaction mixture is cooled to 55° C. and treated with three parts of aqueous 10% sodium hydroxide solution to bring the pH thereof to a value of 7. The neutral mixture is heated under reduced pressure, methanol and water being taken off. A yield of 174.4 parts of product is obtained.

The product is a clear, almost colorless liquid with a viscosity of D on the Gardner-Holdt scale. It has a specific gravity of 1.2.

This product imparts useful finishes to nylon fabrics. For example, nylon net veiling is passed through a bath composed of 40 pounds of the above condensate, 0.75 pound of ammonium chloride, and 0.25 pound of octylphenoxypolyethoxyethanol in 100 gallons of water. The fabric is passed between rollers, dried, and heated at 310° F. for two minutes. The fabric is washed in open width and dried. The finished fabric has an excellent, durable, springy finish and is stabilized against stretching.

Nylon marquisette is passed through a bath formulated as above, squeezed, dried, and cured for 30 to 60 seconds at 320° F. It is washed in open width and dried. The fabric has a durable, stiff finish. Durable, crisp finishes can similarly be imparted to acetate rayon fabrics, to silk fabrics, or to mixed rayon-nylon fabrics.

Example 2

A reaction vessel is charged with 96 parts of methanol, 18 parts of an aqueous 36.3% formaldehyde solution, and 78.5 parts of 91% paraformaldehyde flake. The mixture is adjusted to a pH of 8.5 with 10% sodium hydroxide solution and gently heated at reflux until it becomes clear. Urea is added in an amount of 60 parts, the pH of the mixture is readjusted, and the mixture is then heated at 70°–75° C. for 20 minutes. The mixture is treated with a solution of phosphoric acid in methanol to a pH of about 3.5 and heated under reflux for 15 minutes. The mixture is cooled to 55° C. Alkali solution is added to bring the pH to 7.2 and the mixture heated under reduced pressure to remove the bulk of volatile materials. The product is a clear, practically colorless syrup having a viscosity of G on the Gardner-Holdt scale. It has a specific gravity of 1.22 and is miscible with water in all proportions.

It, too, is an effective finishing agent, particularly for nylon, cellulose acetate, and silk fabrics. It is also useful for stabilizing rayon, giving a degree of stabilization, as measured after several washes equal to that obtained with twice the weight of a methylol urea. The fabric thus stabilized with the condensate of this invention retains a much greater proportion of its original abrasion resistance and tear strength than similar fabrics treated with previously known urea-formaldehyde condensates.

The condensates of this invention may be mixed with a polyhydric alcohol such as glycerine or pentaerythritol in a treating bath and the bath applied to wool, which is then dried and cured. The wool is rendered felt-proof.

The condensates may be used in conjunction with other textile finishing agents, such as polymeric urea-formaldehydes of known types, dispersions of alkyd resins or polymeric vinyl esters, quaternary ammonium salts, sulfonated oils, etc.

I claim:

1. A process for preparing water-soluble, stable urea-formaldehyde condensates which comprises reacting urea and formaldehyde together in a mole ratio between 1:2.5 and 1:3 at a temperature between 60° and 80° C. and at a pH between 7.5 and about 9 in an aqueous solution containing less than about 30% of water, continuing the reaction in the presence of about 5% to 30% of water until at least 85% of the formaldehyde appears chemically bound, as determined by titration of alkalinity of a cold sodium sulfite solution of a sample of the reaction mixture, adjusting the pH of the reaction mixture to a value from 3.8 to 3, and with methanol present in a mole ratio to the urea taken of 2.5:1 to 4:1 heating the acidic reaction mixture under reflux for 5 to 60 minutes.

2. The product of the process of claim 1.

3. A process for preparing water-soluble, stable urea-formaldehyde condensates which comprises reacting urea and formaldehyde together in a mole ratio between 1:2.5 and 1:3 at a temperature between 60° and 80° C. and at a pH between 7.5 and about 9 in an aqueous solution containing less than about 30% of water, continuing the reaction in the presence of about 30% to 5% of water until at least 85% of the formaldehyde appears chemically bound, as determined by titration of alkalinity of a cold sodium sulfite solution of a sample of the reaction mixture, adjusting the pH of the reaction mixture to a value from 3.8 to 3, with methanol present in a mole ratio to urea taken of 2.5:1 to 4:1 heating the acidic reaction mixture under reflux for 5 to 60 minutes, adjusting the pH of the reaction mixture to about 7, and heating the mixture below 60° C. under reduced pressure, thereby removing volatile material.

4. A process for preparing water-soluble, stable urea-formaldehyde condensates which comprises reacting urea and formaldehyde in a mole ratio between 1:2.5 and 1:3 at a temperature between 60° and 80° C. and at a pH between 7.5 and about 9 in a solution containing about 5% to 16% of water, continuing the reaction until at least 85% of the formaldehyde appears chemically bound, as determined by titration of alkalinity of a cold sodium sulfite solution of a sample of the reaction mixture, adding methanol in an amount providing a mole ratio of methanol to urea of 2.5:1 to 4:1, adjusting the pH of the reaction mixture to 3.8 to 3, heating the thus acidified mixture containing methanol under reflux for 5 to 60 min-

utes, adjusting the pH of the mixture to 7 to 7.5, and heating the mixture below 60° C. under reduced pressure.

5. A process for preparing water-soluble, stable urea-formaldehyde condensates which comprises preparing a reaction system comprising methanol, paraformaldehyde, aqueous formaldehyde, and urea, reacting urea and formaldehyde together in the reaction system in a mole ratio between 1:2.5 and 1:3 at a temperature between 60° and 80° C. and at a pH between 7.5 and about 9, the reaction system containing about 5% to 16% of water, continuing the reaction until at least 85% of the formaldehyde appears chemically bound, as determined by titration of alkalinity of a cold sodium sulfite solution of a sample of the reaction mixture, adjusting the pH of the reaction mixture to a pH of 3.8 to 3, with methanol present in a mole ratio to urea taken of 2.5:1 to 4:1 heating the acidic reaction mixture under reflux for 5 to 60 minutes, adjusting the pH of the reaction mixture to a pH of 7 to 7.5, and heating it below 60° C. under reduced pressure.

6. The product of the process of claim 5.

7. A process for preparing water-soluble, stable urea-formaldehyde condensates which comprises mixing urea and aqueous formaldehyde solution having a formaldehyde content from about 35% to 50% in a proportion to give a mole ratio of urea to formaldehyde between 1:2.5 and 1:3, adjusting the pH of the resulting mixture to 8 to 8.5, reacting the urea and formaldehyde at a temperature of 70° to 75° C., removing water from the reaction mixture under reduced pressure at a temperature below about 55° C. to a water content between 5% and 16% of tthe mixture, adding methanol thereto in amount giving a mole ratio to urea taken of 2.5:1 to 4:1, adjusting the pH of the mixture to a pH of 3.8 to 3, heating the acidic mixture under reflux for 5 to 60 minutes, adjusting the pH of the reaction mixture to 7 to 7.5, and heating it below 60° C. under reduced pressure with removal of volatile matter.

References Cited in the file of this patent

UNITED STATES PATENTS

2,171,882	Ludwig	Sept. 5, 1939
2,191,957	Edgar	Feb. 23, 1940
2,260,890	Edgar	Oct. 28, 1941
2,645,625	Bonzagni	July 14, 1953
2,670,341	Joffe	Feb. 23, 1954

FOREIGN PATENTS

406,540	Italy	Dec. 2, 1943