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MODIFIED METHYLATED MELAMINE-
FORMALDEHYDE COMPOSITIONS

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The present invention relates to modified compositions comprising methylated melamine-formaldehyde condensation products and to methods of preparing such compositions, and more particularly to modified compositions comprising methylated melamine-formaldehyde condensation products for use in the finishing of textile materials such as cotton fabrics.

It has been proposed heretofore to prepare aqueous solutions of methylated melamine-formaldehyde condensation products by reacting methyl alcohol with mono- or polymethylol melamine to provide methyl ethers of the melamine-formaldehyde condensation product in an aqueous solution. The solutions thus obtained are known to contain small amounts of free formaldehyde and the condensation products therein often contain unetherified methylol groups. It has also been proposed heretofore to impregnate various textile materials including cotton fabrics with such solutions, after which the impregnated textile material is calendered and cured, or cured by heating at elevated temperatures to polymerize the condensation product and provide a wash resistant finish.

The above solutions of monomeric or slightly polymerized methylated melamine-formaldehyde condensation products normally provide finished fabrics having a soft and pleasing touch. While this is a desirable end result for some purposes as, for example, in certain types of wearing apparel, it is considered desirable, in the case of some types of fabrics such as curtain fabrics and in other uses, to obtain a fabric or textile material which has a crisp or stiffened finish. In the case of cotton fabrics which are used in making curtain fabrics, for example, it is desired to provide a crisp or stiffened finish. It is extremely difficult, however, to obtain a crisp finish with the aqueous solutions of methylated melamine-formaldehyde condensation products described above. Moreover, it has been found that cotton fabrics impregnated with such solutions and then cured have low tear strength and thus are generally unsatisfactory for many of the uses for which they would ordinarily be employed.

In accordance with the present invention, it is possible to provide modified aqueous solutions of methylated melamine-formaldehyde condensation products which when used to impregnate cotton fabrics, for example, and then cured, provide a cotton fabric having a crisp permanent finish and a considerably higher tear strength than is possible with the prior art solutions described above.

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It is one object of this invention to provide a process for preparing modified aqueous compositions comprising methylated melamine-formaldehyde condensation products which when applied to textile materials, particularly cotton fabrics, and cured provide a material having a crisp substantially permanent finish and good tear strength.

It is a further object of this invention to provide modified aqueous solutions of methylated melamine-formaldehyde condensation products, which solutions are substantially free of uncombined formaldehyde and are infinitely dilutable with water without precipitation of the condensation product.

Still further objects and advantages of this invention will appear in the following description and the appended claims.

The present invention, in brief, is based on the discovery that when certain nitrogen-containing compounds, as, for example, urea or ammonia are added to an infinitely dilutable alkaline aqueous solution of methylated melamine-formaldehyde condensation products containing free formaldehyde and the resulting mixture is heated until the solution is free of uncombined formaldehyde and the particle size of the condensation product is increased and the heating is discontinued while the solution is still infinitely dilutable, a composition is obtained which when applied to cotton fabrics, for example, and then cured provides a finished material which has a considerably higher tear strength and a crisper finish than the same fabric which is treated with the initial formaldehyde containing solution of the condensation product.

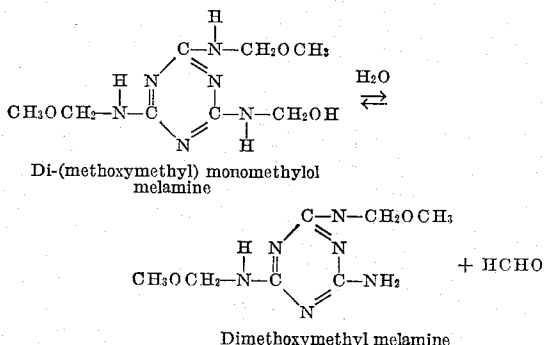
As examples of nitrogen-containing compounds which are suitable for use in the processes of this invention may be mentioned water-soluble formaldehyde-reactable nitrogen-containing compounds consisting of nitrogen and hydrogen atoms and which in some instances contain oxygen atoms but which do not contain any other atoms. Examples of such compounds are ammonia and ammonium hydroxide. It is also possible to use formaldehyde-reactable nitrogen-containing compounds which have amino or imido groups and consist of nitrogen, hydrogen and carbon and which in some instances also include oxygen and sulfur atoms but no other atoms. Urea, thiourea and melamine are examples of such compounds. Other suitable compounds which may be mentioned include monoethanolamine, diethanolamine, water-soluble alkylene polyamines such as ethylene diamine,

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water-soluble alkyl primary and secondary amines containing 3 to 6 carbon atoms such as propyl amine or diethyl amine and the like. Dicyandiamide is specifically excluded, however, since it forms condensation products which polymerize under alkaline conditions, and is not suitable for the purposes of this invention.

Urea is one of the cheapest of the above described nitrogen-containing compounds and gives the best results and accordingly is preferred for the purposes of the invention. Ammonia and melamine are the nitrogen-containing compounds of second choice.

Heretofore, the aqueous solutions of methylated melamine-formaldehyde condensation products which have been prepared commercially for textile purposes contain small amounts, that is, from about 0.1 to 5%, on the weight of the solution, of free formaldehyde. This free formaldehyde is present either because an excess amount of formaldehyde is used in preparing such condensation products and is not combined with the melamine and/or because the polymethylol melamines which are reacted with methanol to form the methylated melamine-formaldehyde condensates are not completely etherified and contain some unetherified methylol groups which dissociate partially in aqueous solutions to form free formaldehyde according to the following equation:



The above equilibrium is not strictly equal and the tendency is stronger for the unetherified methylol group to dissociate into free formaldehyde and the amino group as illustrated in the right hand side of the equation.

It is believed that the free formaldehyde in the solution is what causes the excessive loss in tear strength when the condensation product is applied, for example to cotton fabrics. By reacting the free formaldehyde in such solutions with an amount of the nitrogen-containing compounds (such as urea) sufficient to react with all of the free formaldehyde in the aqueous solution of the methylated melamine-formaldehyde condensation product, it is possible in accordance with this invention to eliminate the free formaldehyde from the solution and thus provide compositions which when applied to cotton fabrics and cured have a high tear strength compared to cotton fabrics treated with the initial solutions. Moreover, by simultaneously increasing the particle size of the condensation product by heating, it is possible to prepare a composition which provides a crisp permanent finish when applied to textile fabrics.

As has been pointed out previously herein the aqueous solutions of methylated melamine-formaldehyde condensation product, which solutions are one of the essential starting materials in the process of this invention, should be alkaline

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and infinitely dilutable, that is, infinitely dilutable with water. Such solutions should have a pH of at least 8.0 and not greater than 11, and preferably within the range of 9.0 to 10.5. Such solutions generally also contain from about 0.05 to 5% by weight of free formaldehyde, and will, in most instances, contain from 0.1 to 3% by weight of free formaldehyde depending on the manner in which they are prepared. The concentration of the condensation product in such solutions may vary widely, for example, between about 10 and 85% by weight based on the solution. However, since the present invention is directed primarily to the treatment of commercial solutions, it is preferred to employ aqueous solutions which contain about 50 to 80% by weight of the methylated melamine-formaldehyde condensate. Colloidal solutions of methylated methylol melamines are not contemplated herein.

The methylated melamine-formaldehyde condensate in the aqueous solutions described immediately above should be water-soluble and the aqueous solutions thereof should be infinitely dilutable, but the condensates may vary considerably in chemical composition. For practical purposes, the condensation products employed herein should preferably contain at least 2 mols of combined formaldehyde and 1 mol of combined methanol for each mol of melamine or, stated in another way, they preferably should contain at least an amount of combined formaldehyde and combined methanol equivalent to monomethoxymethyl monomethylol melamine. Condensation products containing 6 mols of combined formaldehyde and 6 mols of combined methanol per mol of melamine and the intermediate condensation products are also useful. Best results are obtained by starting with aqueous solutions of condensation products which contain from 2 to 5 mols of combined formaldehyde and 1 to 3.5 mols of combined methanol for each mol of melamine and these products are accordingly preferred.

The starting solutions of methylated methylol melamine condensation products used in the processes of this invention may be prepared in various ways. Thus, in general, they may be prepared by first reacting from about 3 to 8 mols of formaldehyde in an alkaline aqueous solution with melamine, adding methanol and then reacting the resulting ingredients under acid conditions, after which the solution is made alkaline. One suitable method of preparing such solutions comprises first reacting melamine and an aqueous alkaline solution of formaldehyde, using about 3 to 8 mols of formaldehyde for each mol of melamine, at a temperature of about 60 to 90° C. until the melamine is substantially dissolved.

In the preparation of highly methylolated products, the melamine first dissolves, and then the addition product of the formaldehyde and melamine precipitates from the solution as the number of mols of combined formaldehyde per mol of melamine approaches 5 to 6. The methylating agent, which is preferably methanol, is then added to this solution. In general, about 10 to 30 mols of methanol are employed for each mol of melamine used, depending upon the degree of methylation or etherification desired. The solution is then acidified to a pH between about 2 and 5 with a strong mineral acid such as hydrochloric acid, phosphoric acid and the like. The resulting solution is then heated to a tem-

perature between 30 and 60° C. until a homogeneous solution is obtained and the condensation product contains the desired amount of combined methanol, after which the solution is neutralized to a pH between 8 and 11 with an alkaline compound, preferably an alkali metal hydroxide such as caustic soda or caustic potash. The solution is then cooled to about 10 to 25° C. Precipitated salts formed by the neutralization of the mineral acid with the alkaline compound are preferably removed at this stage by filtration, centrifuging or the like. The solution is then concentrated to the desired solids content by heating below 60° C. under vacuum.

In carrying out the processes of this invention the formaldehyde reactable nitrogen-containing compound such as urea or ammonia is added to the alkaline aqueous solution of methylated methylol melamine and the resulting mixture is heated until the mixture is free or substantially free of uncombined formaldehyde. By "substantially free" is means less than 0.01% by weight based on the solution. The heating is also continued until the particle size of the original condensation product has been increased. However, the heating is discontinued before the particle size of the condensation product has increased to such an extent that the product is no longer infinitely dilutable with water. Stated in another way, the heating is discontinued while the solution is still infinitely dilutable with water without precipitating part of the condensation product. The solution is then cooled. At this stage the solution is still clear and the particles of condensation product are below the colloidal range.

One practical procedure for determining when the particle size of the condensation product has been increased to the proper extent is by the salt titer test. The salt titer test consists in taking a sample of the solution and adjusting its condensation product concentration to 6% by weight by dilution with water, placing 25 cc. of the 6% solution in a 125 cubic centimeter Erlenmeyer flask and then adding an aqueous solution containing 20% by weight of sodium chloride until a 7 point newsprint placed underneath the flask is no longer legible. This is the end point of the test. The number of cubic centimeters of the sodium chloride solution required to bring the solution of the condensation product to this end point is the salt titer.

In general, the salt titer of the starting solution of the methylated methylol melamine condensation product at 6% by weight solids is dependent primarily on the degree of methylolation and etherification of the condensation product. Thus solution of condensation products which contain from about 2 to 5 mols of combined formaldehyde and 1 to 3.5 mols of combined methanol per mol of melamine at 6% by weight solids normally have a salt titer between about 50 to 90 with the higher value corresponding to the products having the smaller number of mols of combined formaldehyde and combined methanol. As the number of mols of combined formaldehyde and combined methanol per mol of melamine in the product of the starting solution is increased the salt titer of the solution at 6% solids decreases. Thus, a 6% by weight solution of a condensation product containing 6 mols of combined formaldehyde and 5 to 6 mols of combined methanol (the latter being the theoretical limit) has a salt titer between about 4 and 10.

The salt titer is a measure of the particle size of the methylated methylol melamine condensation product in solution providing the chemical composition of the condensation product is the same. As the starting solution of the methylated methylol melamine condensation product is heated in the presence of the formaldehyde reactable nitrogen-containing compound such as urea or ammonia, the salt titer of the solution of the condensation product at 6% by weight solids decreases. The extent of this decrease in salt titer is dependent on the duration of heating and the temperature of heating. The final salt titer at which the solution is still infinitely dilutable with water and the condensation product has reached the desired particle size will vary with the particular chemical composition of the condensation product. Thus, in general, this point will be reached in the case of a 6% by weight solution of a condensation product containing from about 2 to 4 mols of combined formaldehyde and 1 to 3 mols of combined methanol per mol of melamine when the salt titer is between about 10 and 35, and preferably between 10 and 20. In the case of a 6% by weight solution of a condensation product containing from about 4 to 5 mols of combined formaldehyde this point is generally reached when the salt titer is between about 5 and 15. In the case of a 6% by weight solution of condensation products containing between 5 and 6 mols of combined formaldehyde and 4 to 6 mols of combined methanol per mol of melamine, this point is reached when the salt titer is between about 1 and 5. It is thus seen that the salt titer of the solution at 6% by weight solids, after heating, will be between about 35 and 1, depending on the chemical composition of the methylated methylol melamine in the solution.

As has been pointed out previously herein, the amount of formaldehyde-reactable nitrogen-containing compound such as urea or ammonia which is added should be sufficient to react with the free formaldehyde present in the starting solution of the methylated methylol melamine condensate and also the free formaldehyde which is formed by the dissociation of the unetherified methylol groups on the melamine molecule. In general, the amounts of such compound required will be between about 0.5 and 5% by weight based on the weight of the condensate in the solution. However, in some instances when the amount of free formaldehyde in the starting solution is low, it is possible to use amounts of the nitrogen-containing compound as low as 0.1% by weight based on the weight of the condensate in the solution. On the other hand, it is possible to use larger amounts of the nitrogen-containing compound, that is, up to 10% by weight based on the weight of the condensate in the solution when the starting solution contains large amounts of free formaldehyde or the condensate contains about 2 unetherified methylol groups per mol of melamine.

The temperature at which the alkaline aqueous solution of the methylated methylol melamine condensation product and the nitrogen-containing compound such as urea is heated may be varied appreciably. Generally, suitable results are obtained by heating the solution at a temperature between about 70 and 130° C. At temperatures between 100 and 130° C. the heating should be carried out in a closed vessel and under pressure. If temperatures below 70° C. are used, the heating period required is usually of such duration that the process is not economical.

from a commercial viewpoint. On the other hand, if temperatures above 130° C. are employed, it is difficult to control the salt titer and the particle size of the condensation product. The quality and uniformity of the product are best controlled at temperatures between about 90 and 105° C. and these temperatures are accordingly preferred for carrying out the process.

The time required to bring the solution of the nitrogen-containing compound such as urea and the methylated methylol melamine condensation product to the desired particle size or salt titer and to bring the solution to the stage where it is free or substantially free of uncombined formaldehyde is primarily dependent on the temperature used during the heating period. At solution temperatures of 90 to 105° C., the heating period required is generally between 1 and 5 hours. At temperatures of 70 to 90° C. heating periods of about 12 to 5 hours are normally required. At temperatures of 105 to 130° C. heating periods of 1 hour to 20 minutes are generally required.

During the heating period the pH of the solution may drop particularly when urea is used as the formaldehyde-reactable nitrogen-containing compound. This is not objectionable provided the pH of the solution does not drop below 8. However, if the pH of the solution does tend to drop below 8 the pH may be maintained above 8 by adding an alkaline compound such as an alkali metal hydroxide as, for example, caustic soda or an alkali metal carbonate as, for example, sodium carbonate.

After the heating has been carried out to the desired extent as hereinbefore indicated, the solution is cooled to a temperature of about 15 to 30° C. In order to prevent any substantial increase in polymerization or particle size of the condensation product at the end of the heating period, it is preferred to carry out the cooling as rapidly as possible. The cooled solution is preferably adjusted to a pH between 9 and 11 with an alkaline compound such as caustic soda or sodium carbonate if the pH is below 9.

A further understanding of the processes of this invention will be obtained from the following specific examples which are intended to illustrate the invention, but not to limit the scope thereof, parts and percentages being by weight.

EXAMPLE I

A. Preparation of aqueous solution of methylated methylol melamine

One mol of melamine was reacted with about 4.5 mols of formaldehyde in the form of 37% neutral formalin under reflux at a pH of about 8.6 (glass electrode) at a temperature of 70° C. until the melamine was substantially dissolved. After a further reaction of about 5 minutes, 20 mols of methanol were added and the pH was adjusted to 4.0 (glass electrode) with phosphoric acid. The reaction was then continued for an additional 15 minutes at a temperature of approximately 40° C. The pH of the solution was then adjusted to 10.1 (glass electrode) with caustic soda. The resulting solution was then cooled and filtered and was found to contain 40% methanol, 24% condensation product, 2% free formaldehyde and 34% water. The condensation product in the solution contained about 3.5 mols of combined formaldehyde and 2.2 mols of combined methanol for each mol of melamine.

The above solution was concentrated to 60% solids by heating the solution at 50° C. under a vacuum. The resulting solution was infinitely dilutable with water and contained about 0.5% free formaldehyde. This solution had a salt titer of 81 at 6% solids, as determined by the salt titer test hereinbefore described.

Seven hundred parts of this solution and 14 parts of urea were stirred under reflux for 3½ hours at a temperature of 96° C. At the end of this time the solution had a salt titer at 6% solids of 12.5 and a pH of 8.1. The solution was cooled rapidly to a temperature of 25° C. and the pH was adjusted to 10.1 with caustic soda. The specific gravity of the solution was 1.181, and the solution was infinitely dilutable with water without precipitation of the condensate therein.

The above solution was diluted with water until it contained 10% solids, and then 1.2% of ammonium thiocyanate, based on the 10% solution, was added as a curing catalyst for the condensate in the solution. A strip of 80 x 80 cotton fabric was immersed in the solution and thoroughly wetted out therein and then passed between squeeze rolls at a pressure of 160 pounds per linear inch. This gave a pick-up of 90%. The squeezed fabric was then framed and dried for 5 minutes at 180° F. and heated for 5 more minutes at 300° F. to cure the condensate to a water-insoluble state.

A strip of the same fabric from the same roll was treated in the same manner with a 10% solution of the methylated methylol melamine condensation product which was not heated with urea and which had a salt titer of 81 at 6% solids.

Both fabrics were tested for tear strength and stiffness, the tear strength being measured by an Elmendorf tearing tester and the stiffness being tested by a Gurley stiffness tester with the following results:

Solution Used	Salt Titer	Average Tear Strength	Stiffness
Unmodified methylated methylol melamine (not heated with urea)...	81	395	4.6
Modified methylated methylol melamine (heated with urea).....	14	454	5.0

The modified solution of methylated methylol melamine (heated with urea) provided a fabric which showed improved tear strength and a crisper finish as compared to the fabric treated with the unmodified methylated methylol melamine solution.

In the above example other curing catalysts are also useful instead of ammonium thiocyanate as will be apparent to those skilled in the textile art. Thus it is possible to use ammonium chloride, diammonium phosphate, salts of amino alcohols as, for example, the hydrochloride or phosphate of 2-amino-2-methyl propanol-1, the hydrochloride or phosphate of 2-amino butanol-1 and the like.

EXAMPLE II

A modified solution of methylated methylol melamine was prepared according to the procedure described in Example I except that ammonia was used instead of urea. A solution was obtained which had substantially the same properties as the solution prepared with the urea of Example I. This solution also provided a cotton fabric which was similar in tear strength and

stiffness to the fabric treated with the urea modified solution of Example I.

Although the effects of the modified solutions of this invention have been described in the examples with reference to cotton fabrics, it is also possible to obtain improved tear strength and a crisper finish with such solutions in the case of other cellulosic fabrics and textile materials. Thus good results are obtained on regenerated cellulosic textile materials such as viscose and cuprammonium rayon fabrics. Moreover, although the solutions are especially suitable for the treatment of cellulosic textile materials they are also suitable for use on other textile materials made of wool, mixed wool and cellulose and on synthetic textile materials generally where improved tear strength and a crisp finish is desired.

Various modifications and changes in the processes and compositions of this invention will be apparent to those skilled in the art to which they appertain without departing from the spirit and intent of the present invention. It is to be understood, therefore, that it is intended that the scope of the present invention be limited only by the scope of the present claims.

What is claimed is:

1. A process according to claim 12, but further characterized in that the nitrogen containing compound is urea.

2. A process of modifying aqueous compositions comprising methylated melamine-formaldehyde condensation products which comprises heating at a temperature of 70 to 105° C. a mixture of (1) an alkaline aqueous solution of a methylated methylol melamine condensation product containing 2 to 5 mols of combined formaldehyde and 1 to 3.5 mols of combined methanol per mol of melamine, said solution having a salt titer at 6% by weight solids between 50 and 90, a pH between 8 and 11, a solids content of 10 to 85% by weight, being infinitely dilutable with water without precipitation of the condensation product and containing from 0.05 to 5% by weight of free formaldehyde, and (2) from 0.1 to 10% by weight, based on the condensation product, of a nitrogen-containing compound selected from the group consisting of ammonium hydroxide, urea, thiourea, monoethanolamine, diethanolamine, water-soluble alkylene poly-primary amines and water-soluble alkyl primary and secondary monoamines containing 3 to 6 carbon atoms, said mixture being heated until the solution has a salt titer at 6% by weight solids between 5 and 20, while maintaining the pH of the solution between 8 and 11, said heating being carried out when at 70 to 90° C. for about 12 to 5 hours and when at 90 to 105° C. for between 5 and 1 hour, and then cooling the solution, said salt titer being determined as defined in the eighteenth paragraph of the foregoing specification.

3. A process of modifying aqueous compositions comprising methylated melamine-formaldehyde condensation products which comprises heating at a temperature of 90 to 105° C. a mixture of (1) an alkaline aqueous solution of a methylated methylol melamine containing from about 2 to 5 mols of combined formaldehyde and 1 to 3.5 mols of combined methanol per mol of melamine said solution having a salt titer at 6% by weight solids between 50 and 90, a pH between 8 and 11, a solids content of 10 to 85% by weight, a free formaldehyde content of 0.05 to 5% and being infinitely dilutable with water without precipitation of the condensation product, and (2) from

0.1 to 10% by weight, based on said condensation product, of a nitrogen-containing compound selected from the group consisting of ammonium hydroxide, urea, thiourea, monoethanolamine, diethanolamine, water-soluble alkylene poly-primary amines and water-soluble alkyl primary and secondary monoamines, said mixture being heated until the solution is substantially free of uncombined formaldehyde and has a salt titer at 6% by weight solids between 5 and 20, while maintaining the pH of the solution between 8 and 11, said heating being carried out for a period between 5 and 1 hours, and then rapidly cooling the solution to between 15 and 30° C., said salt titer being determined as defined in the eighteenth paragraph of the foregoing specification.

4. A process according to claim 3, but further characterized in that the nitrogen-containing compound is urea.

5. A process according to claim 3, but further characterized in that the nitrogen-containing compound is ammonium hydroxide.

6. A process according to claim 3, but further characterized in that the nitrogen-containing compound is thiourea.

7. A process according to claim 3, but further characterized in that the nitrogen-containing compound is monoethanolamine.

8. A process of modifying aqueous compositions comprising methylated melamine-formaldehyde condensation products which comprises heating at a temperature of 90 to 105° C. a mixture of (1) an alkaline aqueous solution of a methylated methylol melamine condensation product containing from about 2 to 5 mols of combined formaldehyde and 1 to 3.5 mols of combined methanol per mol of melamine, said solution having a salt titer at 6% by weight solids between 50 and 90, a pH between 9 and 10.5, a solids content of 50 to 80% by weight, a free formaldehyde content between 0.1 and 3% by weight and being infinitely dilutable with water without precipitation of said condensation product, and (2) from 0.5 to 5% by weight, based on said condensation product, of urea, until the solution is substantially free of uncombined formaldehyde and has a salt titer at 6% by weight solids between 10 and 20 while maintaining the pH of the solution between 8 and 10.5, said heating being carried out for a period between 5 and 1 hours, cooling the solution rapidly to between 15 and 30° C. and adjusting the pH of the solution between 9 and 11, said salt titer being determined as defined in the eighteenth paragraph of the foregoing specification.

9. A composition prepared according to the process of claim 11.

10. A composition prepared according to the process of claim 8.

11. A process of modifying aqueous compositions comprising a methylated melamine-formaldehyde condensation product which comprises forming a mixture of (1) an alkaline aqueous solution of a methylated methylol melamine condensation product containing 2 to 5 mols of combined formaldehyde and 1 to 3.5 mols of combined methanol per mol of melamine, said solution having a salt titer, as defined in the eighteenth paragraph of the foregoing specification, at 6% by weight solids between 50 and 90, a pH between 8 and 11, a solids content of 10 to 85% by weight, being infinitely dilutable with water without precipitation of said condensation product and containing free formaldehyde, and (2) a nitrogen-containing compound selected from

the group consisting of ammonium hydroxide, urea, thiourea, monoethanolamine, diethanolamine, water-soluble alkylene poly-primary amines and water-soluble alkyl primary and secondary monoamines containing 3 to 6 carbon atoms, said nitrogen compound being employed in an amount sufficient to react with all of the free formaldehyde in said solution, heating said mixture to a temperature between 70 and 130° C. until the solution has a salt titer, as defined in the eighteenth paragraph of the foregoing specification, at 6% by weight solids between 5 and 20 while maintaining the pH of the solution above 8, said heating being carried out when at 70 to 90° C. for about 12 to 5 hours, when at 90 to 105° C. for between 5 and 1 hours and when at 105 to 130° C. for 1 hour to 20 minutes, and then cooling said solution.

12. A process of modifying aqueous compositions comprising a methylated melamine-formaldehyde condensation product which comprises heating at a temperature of 70 to 130° C. a mixture of (1) an alkaline aqueous solution of a methylated methylol melamine condensation product containing 2 to 5 mols of combined formaldehyde and 1 to 3.5 mols of combined methanol per mol of melamine, said solution having a salt titer, as defined in the eighteenth paragraph of the foregoing specification, at 6% by weight solids between 50 and 90, a pH between 8 and 11, a solids content of 10 to 85% by weight, being

infinitely dilutable with water without precipitation of said condensation product and containing 0.05 to 5% by weight of free formaldehyde, and (2) a nitrogen-containing compound selected from the group consisting of ammonium hydroxide, urea, thiourea, monoethanolamine, diethanolamine, water-soluble alkylene poly-primary amines and water-soluble alkyl primary and secondary monoamines containing 3 to 6 carbon atoms, said nitrogen compound being employed in an amount sufficient to react with all of the free formaldehyde in said solution, said mixture being heated until the solution has a salt titer, as defined in the eighteenth paragraph of the foregoing specification, at 6% by weight solids between 5 and 20 while maintaining the pH of the solution between 8 and 11, said heating being carried out when at 70 to 90° C. for about 12 to 5 hours, when at 90 to 105° C. for between 5 and 1 hours and when at 105 to 130° C. for 1 hour to 20 minutes, and then cooling the solution.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,318,560	Ripper	May 4, 1943
2,456,568	Scott	Dec. 14, 1948
2,466,457	Lynn	Apr. 5, 1949
2,529,856	West	Nov. 14, 1950