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METHYLOL ACETONE RESIN PRECONDENSATE AND METHOD OF IMPREGNATING FABRICS THEREWITH

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The present invention relates to an acetone formaldehyde monomeric precondensation product having primary utility for the permanent finishing of textiles, to the method of forming the monomer, and the application thereof in the permanent finishing of textiles.

The reaction of acetone with formaldehyde so far as it is understood, to date, involves formation of an intermediate ketonic product by substitution of one or more methyl hydrogens of the acetone with methylol groups, the dehydration thereof to a vinyl ketone and the final polymerization of the unsaturated ketone. The formation of intermediate precondensate and final dehydration and polymerization are each catalysed by alkali. The reaction is exothermic. The reagents react in such widely variable proportions that the reaction has generally been uncontrollable. Hence attempt by prior workers in the art at stopping the reaction at the precondensate stage has resulted in a product containing substantial quantities of polymer.

The acetone-formaldehyde reaction product has been proposed for fiber treatment both where substantial resinification has resulted to a degree wherein the product is substantially insoluble in water, and also where only slight polymerization has resulted. Thus, even in prior art application of an intermediate precondensate the product has contained such quantities of polymer that application thereof to textile, while effective to shrinkproof the same, has resulted in filling and stiffening the textile to a permanent stiff handle.

This known process of treating textile, therefore, is useful only where a substantial degree of stiffening of the fabric is permissible or desirable. For many fabrics, however, particularly fine fabrics of the character of rayon and other artificial or natural cellulosic textile, the stiffening thereof is undesirable and unacceptable to the industry so that general application of this type of permanent finishing material has been avoided.

It has been found, according to the present invention, that rigid control of the reaction to form a monomeric acetone-formaldehyde precondensate, free of any polymer, yields a superior product for the permanent finishing of textiles including fine fabrics of the character of rayon, to adequately impart thereto full shrink resistant characteristics after washing, without noticeably stiffening the fabric or otherwise impairing the characteristic soft handle thereof.

It is accordingly a primary object hereof to react acetone and formaldehyde under conditions of rigid control to produce a precondensate which substantially corresponds to tetra methylol acetone and is substantially free of polymers.

It is a further object to effect such condensation in the presence of a critically controlled quantity of alkaline catalyst to produce precondensate of a monomeric polymethylol acetone free of polymeric products.

It is a further object to shrinkproof soft fabrics with such precondensate without impairing the soft handle

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thereof. Other objects will be inherent in this specification of the invention.

According to prior art practices various alkaline materials have been used to catalyze the acetone formaldehyde reaction, such as alkalis, alkali carbonates, alkali earth hydroxides, phosphates, sulphites and the like. Part of such catalyst is lost by being continuously converted to a formate salt through the standard Cannizzaro reaction for conversion of formaldehyde to methyl alcohol and formic acid. This is probably the reason why rather large amounts of alkaline catalysts have been used in the prior processes. Any excess of alkali, however, tends to accelerate the condensation of acetone with formaldehyde as well as the polymerization so that in prior art practices the excessive use of alkali has invariably resulted in failure to control the reaction to produce a precondensate intermediate free of polymerized vinyl ketones and of undesirable by-products.

According to the present invention it is found that rigid limitation of the quantity of alkali metal hydroxide to the highly critical range of 0.025 to 0.1 mol of hydroxide per mol of acetone, results in exhaustion of the alkali and termination of the reaction at the precondensate stage to effect a methylol acetone product free of vinyl acetones and polymers thereof. The proportions of acetone and formaldehyde are limited to 4 mols of formaldehyde per mol of acetone whereby methylol substitution upon the acetone is limited to a maximum of 4 methylol groups per mol of acetone, although as known in the art higher methylol substitution is possible. The alkali is exhausted at this stage so that the pH of the reaction mixture will drop from the original 10 to 11 down to a substantially neutral pH of 7 to 8.

In the presence of the alkali hydroxide the reaction is spontaneous and will run even when the mixture of reagents is substantially cold, but the rate of reaction will vary with the temperature. For this reason, temperatures as high as 40° C. to 50° C. may be used where efficient cooling and slow addition of the catalyst is practiced to offset release of heat, under which conditions the reaction may be completed in a very short time. However, it is preferred to effect the reaction in the temperature range of 10° C. to 25° C. allowing the reaction to run to completion over a period of 5 to 8 hours. It will be appreciated that even lower temperatures may be used with a consequent longer reaction time to effect completion thereof.

The alkali metal hydroxide with 4 mols of formaldehyde per mol of acetone used at a maximum of 0.1 mol would be exhausted to produce tetra methylol acetone. Use of a lesser quantity of alkali down to a .025 mol minimum results in lower substitution products such as from 1 to 4 methylol groups per mol of acetone. However, it is possible, operating anywhere in the specific range of alkali given (.025 to 0.1 mol) to terminate the reaction after substitution with less than 4 methylol groups by acidifying the reaction at an intermediate stage, the neutralization of the alkali operating to terminate the reaction. The intermediate precondensate thus produced containing 1 to 4 methylol groups is stable in acid or neutral condition.

The reaction mixture starting with 4 mols of formaldehyde to 1 of acetone and containing the critical quantity of alkali in the range of .025 to 0.1 mol if allowed to proceed to completion at a temperature of about 20° C. will form a colorless syrupy liquid precondensate having a specific gravity of 1.12 with which the end point is identified. As indicated it is possible to stop the reaction at an intermediate point before the specific gravity of 1.12 is reached by quenching the reaction by addition of sufficient acid to neutralize the alkali whereby a syrup comprising an intermediate poly methylol acetone is pro-

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duced having anywhere from 1 to 4 methylol groups per mol of acetone. It is found again that the specific gravity of the syrup can be used to critically control the degree of substitution. The practical lower limit of the specific gravity at which the reaction may be quenched to obtain a syrupy precondensate having definite shrinkproofing utility is 1.07. A reaction mixture quenched at a gravity below this lower limit will have inadequate shrinkproofing characteristics. Syrup produced with a gravity above 1.12 has exceeded the end point and contains polymers which tend to stiffen the fabrics. Thus applicants' permanent finishing reagent is a colorless syrupy precondensate having a critical specific gravity in the range of 1.07 to 1.12 and comprising a monomeric poly methylol acetone having 1 to 4 methylol groups and being free of polymers. It is infinitely stable in storage in the neutral or slightly acid condition.

The syrupy product is infinitely soluble in water and the reaction may be carried out in the presence of water, but the addition of water is unnecessary. However, where water is present the identification of the product in terms of the specific gravity is necessarily adjusted to the modification thereof by a water content.

PREPARATION OF PRECONDENSATE

Example I

150 parts of acetone, 840 parts of 37% by weight of formalin and 14 parts of 41.7% by weight of sodium hydroxide solution, all parts by weight, are cooled to 20° C. and mixed. The mixture has a pH between 10 and 11 and a specific gravity of 1.04 before the reaction starts. The reaction is spontaneous and as it proceeds the mixture increases in specific gravity so that when the reaction is completed a specific gravity of 1.12 is reached. At this point the reaction stops and the reaction mixture is a syrupy solution, only faintly alkaline having a pH between 7 and 8. It is not essential that the reaction temperature be rigidly controlled except that preferably it is not allowed to exceed approximately 40° C. The reaction run, at an average temperature of 25° C., will terminate in about 6 to 8 hours. The product, having a specific gravity of 1.12, corresponds to tetra methylol acetone. To impart additional stability it is desirable to make the syrupy reaction product slightly acid.

Example II

The reaction mixture of Example I is again allowed to react, and as the reaction proceeds, the specific gravity of the reaction mixture is determined at intervals. The reaction is then terminated by acidifying with dilute hydrochloric acid to a pH of 6 when the reaction mixture has reached a specific gravity of 1.095.

It will be understood in both Examples I and II that no water is contained in the reaction mixture other than the exact quantities mentioned for formalin and alkali and the specific gravities accordingly are given on this basis. However, the reaction may be carried out in the presence of various quantities of water, in which event the specific gravities of the solution will be different and may be recalculated on the basis of the amount of water present. Both products of Examples I and II are water soluble and may be used for permanent finishing as further described hereinbelow, in aqueous solution. The products formed are colorless and stable, and provided they have been rendered faintly acid they may be concentrated by evaporation at elevated temperatures without detriment.

In the treatment of fine fabrics such as those made from natural or artificial cellulose fibers, to retain the original soft handle thereof while shrinkproofing the same, the composition prepared as described above is used in a slightly alkaline aqueous treating bath. The concentrations of precondensate vary according to the type of fiber, the type of fabric and the type of precondensate. Where the composition has a specific gravity at

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the lower end of the range, such as about 1.095, or slightly above, 12-30 ccs. of the syrup (preferably 15 to 25 cc. for cotton fabric) formed such as in Example II, is diluted with water to form 100 ccs. of solution. Where the precondensate is in the higher specific gravity range, such as up to 1.12, the quantity of precondensate is reduced to the range of 5 to 20 ccs. of precondensate per 100 ccs. of aqueous solution, preferably 7 to 15 ccs.

For fabrics such as viscose rayon, and especially for fabrics which have a potentially high shrinkage, such as crepes, the proportion of precondensate in the aqueous bath may be considerably higher. Thus where the specific gravity is in the lower range, about 1.07, or slightly higher, as much as 40 to 60 ccs. of precondensate per 100 ccs. of aqueous solution could be used, and for such fabrics where the precondensate has the specific gravity in the upper range, about 1.12, 20 to 30 cc. of precondensate per 100 cc. of aqueous solution could be used. In spite of these high concentrations, the fabric retains a soft handle which is a result which has never been achieved by use of shrinkproofing resins heretofore made by condensing acetone and formaldehyde, or even when other resinous products are used that are known in the art, such as urea or melamine resins.

To accelerate the final condensation of the precondensate upon the fabric so that it may be set rapidly, the final textile treating bath is made slightly alkaline by addition thereto of 2-6 parts by weight of alkali carbonate such as sodium carbonate per one hundred parts by volume of impregnating solution. In this alkaline condition the condensation is completed by heating substantially dry impregnated fabric in the range of 100° C. to 150° C. preferably about 130° C. to 150° C.

FABRIC TREATMENT

Example III

The syrup of Example I having a specific gravity of 1.12 and corresponding to tetra methylol acetone is diluted with water to form a solution containing 12 ccs. of 1.12 specific gravity precondensate per 100 cc. of aqueous solution and, additional 3 parts by weight of sodium carbonate is dissolved in the treating bath. Cotton fabric is dipped therein and the excess fluid squeezed therefrom. The fabric is dried at a moderate temperature not exceeding 100° C. while holding the same at the desired dimension or slightly thereabove. After drying, the fabric is subjected to a short heat treatment of 130° C. to 140° C. for one or two minutes. It is then washed to remove soluble residues and finally dried again. It is found that the fabric still retains its original soft handle while being substantially fixed with respect to dimensions after repeated washings.

Example IV

The treatment herein described may be applied for fixation not only of the dimensions of the fabric, but also of mechanically produced effects, such as calendering, glazing, schreiner and embossing. In such treatment the fabric to be mechanically treated is impregnated with a solution as in Example III. The fabric is dried at a temperature below 80° C. so that some moisture is retained therein after empirical drying. The fabric is next mechanically deformed to give it the mechanical effect. The fabric is then heat treated by applying a one or two minute heat at a temperature of 135° C. to 145° C. to fix and resinify the composition therein. The fabric is then finally washed to remove soluble residues.

Example V

A viscose rayon fabric is dipped in a bath comprising 50 cc. of 1.095 specific gravity syrup, prepared as described in Example II, dissolved in 100 cc. of aqueous solution to which has been further added four parts

by weight of sodium carbonate. The dipped fabric is then dried as described in Example III; this fabric having its known high potential shrinkage and with the high content of precondensate in the treating bath is found to retain its soft handle while being fully shrink-proofed to repeated washings.

As thus described acetone formaldehyde precondensate is formed having a specific gravity in the range of 1.07 to 1.12 free of polymerization products, stable in neutral and acid condition and containing 1-4 methylol groups per mol of acetone.

The product is readily prepared by reaction of 4 mols of formaldehyde per mol of acetone in the presence of a maximum of .1 mol of caustic alkali to produce a precondensate corresponding to tetra methylol acetone which comes to a natural end point at temperatures below 50° C. without polymerization. The process is such that variation of the catalyst content is possible for forming intermediate precondensates having less than 4 methylol groups such as 1 to 4 methylol groups per acetone molecule. Less alkali, as low as .025 mol of alkali per mol of acetone may be used or the reaction may be controlled with any quantity of alkali in the range of .025 to a .1 mol of alkali by quenching the reaction prior to completion by neutralizing the alkali content. The precondensates formed having a specific gravity in the critical range of 1.07 to 1.12 having 1 to 4 methylol groups per mol of acetone being useful for treatment of fabrics without impairing the soft handle thereof.

We claim:

1. The method of forming a polymer-free monomeric methylol acetone having 1 to 4 methylol groups useful for shrink-proofing of soft textiles without substantial discoloring and impairing the soft handle thereof comprising reacting about 4 mols of formaldehyde and 1 mol of acetone at a temperature below about 50° C., the reaction being initiated in the presence of 0.025 to 0.1 mol of alkali metal hydroxide to obtain a non-alkaline syrupy liquid containing residual quantities of unreacted formaldehyde and identifiable by having a specific gravity in the range of 1.07 to 1.12 when the reaction product contains a residual water content which would be present when the formaldehyde used in the reaction is a 37% by weight formaldehyde solution in water.

2. The method of forming a polymer-free monomeric methylol acetone having 1 to 4 methylol groups useful for shrink-proofing of soft textiles without substantial discoloring and impairing the soft handle thereof comprising reacting about 4 mols of formaldehyde and 1 mol of acetone at a temperature below about 50° C., the reaction being initiated in the presence of 0.025 to 0.1 mol of alkali metal hydroxide, and continuing until the reaction terminates by exhaustion of the free alkali in the reaction whereby a colorless syrupy liquid is obtained free of polymers and further identifiable by having a specific gravity in the range of 1.07 to 1.12 when the reaction product contains a residual water content which would be present when the formaldehyde used in the reaction is a 37% by weight formaldehyde solution in water.

3. The method of forming a polymer-free monomeric methylol acetone having 1 to 4 methylol groups useful for shrink-proofing of soft textiles without substantial discoloring and impairing the soft handle thereof comprising reacting about 4 mols of formaldehyde and 1 mol of acetone at a temperature below about 50° C., the reaction being initiated in the presence of 0.025 to 0.1 mol of alkali metal hydroxide, and terminating the reaction by acidifying the reaction mixture to remove unreacted alkali metal hydroxide therefrom when a syrupy liquid reaction product free of polymers is obtained identifiable by having a specific gravity in the range of 1.07 to 1.12 when the reaction product contains a residual water content which would be present

when the formaldehyde used in the reaction is a 37% by weight formaldehyde solution in water.

4. The method of permanent finishing of fabrics without substantially affecting the soft handle and color thereof, comprising: subjecting the fabric to an aqueous alkaline solution containing a polymer-free monomeric methylol acetone comprising a syrupy liquid precondensate formed by reacting 4 mols of formaldehyde and 1 mol of acetone in the initial presence of 0.025 to 0.1 mol of an aqueous solution of alkali metal hydroxide, having 1 to 4 methylol groups per molecule of acetone and further identifiable by having a specific gravity in the range of 1.07 to 1.12 when the reaction product contains a residual water content which would be present when the formaldehyde used in the reaction is a 37% by weight formaldehyde solution in water while maintaining the reaction temperature below about 50° C.; drying the fabric and heating the dry fabric to a temperature exceeding 100° C. and for a short period sufficient to condense and polymerize the monomeric methylol acetone in situ in the fabric.

5. The method of permanent finishing of fabrics formed of cellulosic fibers without substantially affecting the soft handle and color thereof, comprising: subjecting the fabric to an aqueous alkaline solution containing a polymer-free monomeric methylol acetone comprising a syrupy liquid precondensate formed by reacting about 4 mols of formaldehyde and 1 mol of acetone in the initial presence of 0.025 to 0.1 mol of an aqueous solution of alkali metal hydroxide, having 1 to 4 methylol groups per molecule of acetone and further identifiable by having a specific gravity in the range of 1.07 to 1.12 when the reaction product contains a residual water content which would be present when the formaldehyde used in the reaction is a 37% by weight formaldehyde solution in water while maintaining the reaction temperature below about 50° C.; drying the fabric and heating the dry fabric to a temperature exceeding 100° C. and for a short period sufficient to condense and polymerize the monomeric methylol acetone in situ in the fabric.

6. The method of permanent finishing of fabrics and simultaneously ornamenting the same by mechanical treatment thereof of the character of calendering, glazing, schreiner and embossing without substantially affecting the soft handle and color thereof, comprising: subjecting the fabric to an aqueous alkaline solution containing a polymer-free monomeric methylol acetone comprising a syrupy liquid precondensate formed by reacting about 4 mols of formaldehyde and 1 mol of acetone in the initial presence of 0.025 to 0.1 mol of an aqueous solution of alkali metal hydroxide, having 1 to 4 methylol groups per molecule of acetone and further identifiable by having a specific gravity in the range of 1.07 to 1.12 when the reaction product contains a residual water content which would be present when the formaldehyde used in the reaction is a 37% by weight formaldehyde solution in water while maintaining the reaction temperature below about 50° C.; drying the fabric empirically at a temperature not exceeding about 80° C. to allow the fabric to retain some moisture; mechanically treating the fabric to produce therein mechanical effects; and heating the dry fabric to a temperature between about 100° C. and 150° C. for a short period sufficient to condense and polymerize the monomeric methylol acetone in situ in the fabric.

7. A monomeric precondensation product useful for shrink-proofing of soft fabrics without substantial discoloring and impairing the soft handle thereof, said product comprising a substantially neutral water soluble colorless syrupy liquid free of polymers, said syrupy liquid comprising a mixture of methylolacetones predominating in methylolacetones having 3 to 4 methylol groups per acetone molecule together with free formaldehyde, free acetone, alkali metal formate,

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methanol, and water, and characterized by having a specific gravity in the range of 1.07 to 1.12 when the reaction product contains a residual water content which would be present when the formaldehyde used in the reaction is a 37% by weight formaldehyde solution in water, said precondensation product being formed by the reaction of about 4 mols of formaldehyde and 1 mol of acetone in the presence of about 0.025 to 0.1 mol of alkali metal hydroxide at a temperature below about 50° C.

8. A monomeric precondensation product useful for shrink-proofing of soft fabrics without substantial discoloring and impairing the soft handle thereof, said product comprising a substantially neutral water soluble colorless syrupy liquid free of polymers, said syrupy liquid comprising a mixture of methylolacetones predominating in methylolacetones having 4 methylol groups per acetone molecule together with free formaldehyde, free acetone, alkali metal formate, methanol, and water, and characterized by having a specific gravity of approximately 1.12 when the reaction product contains a residual water content which would be present when the formaldehyde used in the reaction is a 37% by weight formaldehyde solution in water, said precondensation product being formed by the reaction of about 4 mols of formaldehyde and 1 mol of acetone in the presence of about .05 to 0.1 mol of alkali metal hydroxide at a temperature below about 50° C.

9. A monomeric precondensation product useful for shrink-proofing of soft fabrics without substantial discoloring and impairing the soft handle thereof, said product comprising a substantially neutral water sol-

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uble colorless syrupy liquid free of polymers, said syrupy liquid comprising a mixture of methylolacetones wherein approximately 3 mols of formaldehyde have reacted with 1 mol of acetone containing trimethylol acetone together with free formaldehyde, free acetone, alkali metal formate, methanol and water, and characterized by having a specific gravity of about 1.095 when the reaction product contains a residual water content which would be present when the formaldehyde used in the reaction is a 37% by weight formaldehyde solution in water, said precondensation product being formed by the reaction of about 4 mols of formaldehyde and 1 mol of acetone in the presence of about 0.025 to 0.1 mol of alkali metal hydroxide at a temperature below about 50° C., and terminating the reaction by neutralizing the excess alkali when the said specific gravity of about 1.095 has been obtained.

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