ACETYLENE DIUREA-FORMALDEHYDE REACTION PRODUCT AND TREATMENT OF TEXTILES THEREWITH

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The present invention relates to the treatment of cel- lulose-based textile fabrics with aminoplast resin-forming materials to produce wrinkle resistant and dimensional stability without subjecting the fabric to the usual hazards of chlorine retention.

Commercial production of wrinkle resistant cotton and rayon heretofore has involved use of aminoplast resin-forming materials. These materials have an affinity for chlorine after they are cured on the fabric. In hypo-chlorite bleaching of prior aminoplast resin-treated fab- rics, the resin picks up some of the chlorine. Subsequent ironing causes release of the chlorine as hydrochloric acid, always damaging the cellulose. In some instances, the fabric is completely destroyed. This phenomenon is known in the trade as chlorine retention. Heretofore, it has been commercially impossible to produce satisfactory wrinkle resistant cotton textile fabrics with aminoplast resins without concomitant chlorine retention.

It has now been found that a properly modified aminoplastic can be used to produce the desired degree of wrinkle resistance without subjecting the fabric to the usual hazards of chlorine retention. In making a preferred modified aminoplast resin, it has been found desirable to react the aminoplast with an excess of formaldehyde in a pH range between 2 and 5 at low temperatures and in the presence of a minimum amount of water. A preferred aminoplast for this purpose is the acetylene diurea described in our pending application S. N. 222,298, filed April 21, 1951, abandoned which is reacted with more formaldehyde to form tetramethyl acetylene diurea.

Thus, the preferred materials of this invention are reaction products of tetramethyl acetylene diurea and a large excess of formaldehyde. The reaction of acetylene diurea with up to 4 mols of formaldehyde to form the tetramethyl derivative is a standard technique.

By large excess is meant from about 6 to 17 mols of paraformaldehyde for each mol of tetramethyl acetylene diurea. It is preferred to use about 9 mols, as little improvement is noted when a larger excess is used.

We are unable to explain the chemical basis of the products which permit the non-chlorine-retentive characteritics of the chemical products used for fabric treatment in this invention, but the results obtained thereby are none the less desirable.

It does appear fairly certain that the heating of the formalin and acetylene diurea or methylol thereof in the presence of triethyl amine serves to form tetra- methyl acetylene diurea. The modifications making possible the beneficial results of this invention appear to take place on the acid side. It is preferred to keep the pH at about 4.3 during this reaction, but desirable products have been produced at a pH range from 2 to 5. It also appears that a certain amount of water favors the proper reaction. Some water is necessary, but the preferred product cannot be formed unless a substantially water-free form of formaldehyde, such as flake para-

formaldehyde, is used. It is, of course, conceivable to use gaseous formaldehyde. For the same reason it is preferred to adjust the pH with concentrated HCl. Cooling during reaction appears to favor production of the preferred reaction product and the reaction temperature should be kept below 50° C. There are indications that the reactions of this invention are reversible and that low temperature storage aids in preservation of the desired product. In any event, low temperature storage is desirable. By low temperature storage is meant storage at below room temperature and preferably as low as 0° C.

In applying the product of this invention to textile fabrics, we have found that the process disclosed and claimed in pending application, S. N. 274,310, filed February 29, 1952, Patent No. 2,724,664, appears to give the most satisfactory results.

The invention will be better understood by reference to the detailed examples below.

EXAMPLE A
Preparation of acetylene diurea

Glyoxal (30.3% Solution) ------- 1680 lbs. 1 mol
Urea --------------------------- 1800 lbs. 3.4 mols

Hydrochloric Acid Solution
(28% HCl by weight) ---------- 150 lbs.

Place the glyoxal in a stainless steel reaction kettle equipped with stirrer, steam coils, cooling jacket and a thermometer. Add the urea while stirring constantly. Much of the urea remains undissolved, but sufficient does dissolve to cause the temperature to fall as low as 40° F.

Now add the hydrochloric acid, which brings the pH to between 1 and 2. Start heating the mixture by means of the steam coil. As the mixture heats, an exothermic reaction starts. At about 150° F. a granular white precipitate forms. When the temperature reaches 190° F., the reaction is well under way, and the heating is discontinued. If left alone at this stage, the reaction mixture continues to heat up and finally boils and foams violently. Accordingly, the temperature is allowed to rise to 200° F. and then the mixture is cooled by means of the cooling jacket to 195° F. It is kept at this temperature of 195–200° F. for ten minutes, at which time the intensity of the reaction has abated. The temperature is then allowed to rise to 200–205° F. and kept at this range for another thirty minutes. At the end of that time, the exothermic reaction is over, as shown by the fact that the mixture starts to cool normally.

The mixture is then cooled to about 180° F. merely to facilitate handling, and brought to a pH of 7–8 with about 20 lbs. of sodium hydroxide dissolved in water. The pH before the addition of the NaOH has risen from the initial 1 to 2 to between 4 and 5.

At this stage the reaction mixture is a yellow brown slurry, which, if not stirred constantly and vigorously, separates rapidly into a cream-colored solid, the acetylene diurea, and a coffee-colored liquid. If properly stirred, it is sufficiently homogeneous so that samples may be withdrawn for analysis.

This neutral slurry is then pumped into a large, 2500-gallon tank, equipped with a perforated false bottom fitted with a filter cloth. The tank resembles a very large Buckner type funnel, and like the funnel the space under the perforated false bottom is connected to a vacuum pump so that the liquid above the false bottom can be filtered through the filter cloth.

Such a reaction as above described gives approximately 900 lbs. dry weight of acetylene diurea, corresponding to a yield of approximately 72%. Five such reactions are usually run to give a total of 4500 lbs. dry weight of acetylene diurea. The acetylene diurea is stirred with

United States Patent Office

2,803,564  Patented Aug. 20, 1957
about five times its weight of water, and the water filtered off. This stirring and filtering is continued until a sample of the acetylene diurea gives a resinous product of the desired lightness of color. After the final washing and the removal of as much water as possible by filtration, the cake contains approximately 4500 lbs. dry weight of acetylene diurea, corresponding to an over-all yield of approximately 72%, and approximately 6000 lbs. of retained water.

EXAMPLE B

Preparation of the trimethylol acetylene diurea resinous product

To the wet cake above described is added 7700 lbs. of formalin, which contains 37.5% formaldehyde by weight. This is in the ratio of three mols of formaldehyde to one mol of acetylene diurea. The mixture is then stirred until it is a thick slurry and NaOH solution added slowly and carefully until the pH is between 9 and 10. The amount of NaOH required depends upon the amount of formic acid which is always present in commercial formalin in small but variable amounts.

A mild exothermic reaction takes place, and the acetylene diurea dissolves to give a light yellow-brown solution of fairly low viscosity. The mixture is stirred until it is certain that all of the acetylene diurea has dissolved. It is then brought to a pH of 4 or slightly lower, by careful addition of HCl, and allowed to stand at least twelve hours. Some polymerization takes place, and the viscosity increases until the solution is about as viscous as thin motor oil.

At the end of this time the mixture is brought to a pH of 6 to 7 with NaOH, which stops the polymerization. The solution is filtered, and is ready for use.

EXAMPLE 1

Preparation of the modified acetylene diurea

One mol of acetylene diurea prepared according to Example A was mixed with 4 mols of formalin (37% aqueous formaldehyde). Eight mols of flake paraformaldehyde (91%) were added with stirring. Enough triethylene was then added to bring the mixture to between pH 8 and pH 11, preferably about pH 10. This required about 5% to 1% triethylene based on the total weight of the ingredients. The mixture was then heated with stirring to about 95° C. until it cleared, which required about 20 minutes. The clear solution was cooled and brought down to about pH 4.5 with hydrochloric acid. It was then stored at 0° C. for 24 hours, after which it was ready for use. The product is a substantially clear, syrupy liquid, water-soluble in all proportions.

EXAMPLE 2

One mol of the acetylene diurea prepared according to Example A was placed in a reaction kettle with 3 mols of formalin and enough caustic soda was added to bring it to about pH 10.5. This was then neutralized with hydrochloric acid and brought to about pH 4.5 and was then allowed to stand overnight. Nine mols of paraformaldehyde were added with stirring and about 1% triethylene was added to bring the mixture to about pH 10. Stirring was continued and the entire mixture was heated for 30 minutes at 90° C., at which time the mixture became a thin, clear, syrupy liquid. The liquid was then cooled and brought to pH 4 with hydrochloric acid and stored for 24 hours at 0° C.

EXAMPLE 3

One mol of the product prepared according to Example B was placed in a reaction kettle and 8 mols of flake paraformaldehyde were added with stirring. Enough triethylene was added to bring it to pH 10 and the entire mass was then heated at about 95° C. for 20 minutes. At the end of the heating, the pH was about 7.5 and a small amount of hydrochloric acid was added to bring the pH below 7. The mixture was cooled to about 38° C. and enough acetic acid added to bring it to about pH 4.8. The resulting solution was then cooled to about 30° C. and placed in containers for use.

EXAMPLE C

Preparation of stearamido methyl pyridinium nitrate composition

413 lbs. of stearamide (Armid HT sold by Armour & Co.) and 103 lbs. paraformaldehyde are added with stirring to 196 lbs. of perchloethylene (a substantially inert solvent for purposes of this invention) held at 160° F. The paraformaldehyde and stearamide are reacted at 210° F. for one hour after which 133 lbs. of pyridine nitrate are added. The reaction continues at 210° F. for 30 minutes. The mixture is stirred throughout the reaction.

The pyridine nitrate used in this reaction is an approximately 88% pure product containing excess pyridine to the extent that a 10% solution of it has a pH of about 4.35. It has been found that if 55 lbs. of the pyridine reaction mixture are added slowly to 77 lbs. of pyridine with cooling and stirring, a satisfactory pyridine nitrate can be produced.

The reaction product of paraformaldehyde, stearamide and pyridine nitrate is artificially slowly cooled and solvents are added to form the finished products as follows:

When the reaction mass reaches 198° F. -- add 77 lbs. butanol.
When the reaction mass reaches 176° F. -- add 33 lbs. isopropanol.
When the reaction mass reaches 150° F. -- add 56 lbs. methanol.

The product is light tan paste at room temperature and tends to stiffen to a solid at lower temperature. It is water dispersable in warm water for immediate use as a catalyst.

EXAMPLE 4

5% of the product of Example 1 was dissolved in water to which was added 1% of the catalytic product made according to Example C and 2% of catalyst A. C. (a product sold by Monsanto Chemical Co. and believed to be 2,2-methylamino propanol hydrochloride as 50% solids). The product of Example C was put in solution by heating with a small portion of the 5% solution of the product of Example 1. A carded gingham cotton fabric weighing about 3 oz. per yard was padded with the freshly prepared solution and picked up about 80% of its weight. The fabric was then air dried and cured for one minute and 20 seconds at 180° C. This produced a fabric product with a commercially satisfactory wrinkle resistance, a reasonably high tear and tensile strength, and the fabric appeared to be as good as untreated fabric with respect to chloride damage. In some instances of testing, the resination appeared to have imparted protective action against chlorine damage to the fabric.

EXAMPLE 5

The process of Example 4 was repeated, except that the product of Example 2 was used in place of the product of Example 1. The treated fabric showed the same characteristics as the fabric treated in accordance with Example 4, except that the product of this example had a slightly higher tear and tensile strength.

We claim:
1. The process of preparing textile treating materials which comprises reacting one mol of acetylene with diurea from about 3 to 4 mols of formaldehyde to produce the methylated compound, and then reacting the thus formed polyacetylene acetylene diurea with from about 6 to 17 mols of formaldehyde in the presence of a small amount of water less than the amount required to
5 supply the total quantity of formaldehyde as a 37% solution, said last reaction being carried out at a pH between 2 and 5 and at a relatively low temperature in the nature of about 90 to 95° C.

2. The reaction product of one mol of acetylene dithrea, about 3 to 4 mols of aqueous formaldehyde and from 6 to 17 mols of paraformaldehyde prepared according to the process of claim 1.

3. The process of producing a wrinkle resistant cellulosic fabric without subjecting the fabric to the usual hazards of chlorine retention, which comprises treating said fabric in the presence of an acidic catalyst with the reaction product of claim 2, drying the fabric, and curing the reaction product thereon.

4. A wrinkle resistant cellulosic fabric without the usual hazards of chlorine retention, produced according to the process of claim 3.

5. A process as set forth in claim 1 wherein the amount of formaldehyde is about 9 mols of paraformaldehyde and the pH is about 4.3.

References Cited in the file of this patent

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