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METHOD OF MAKING WRINKLE RESISTANT
FABRIC AND COMPOSITION THEREFORMyrtle Joanne Spangler and Rosser Lee Wayland,
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IncorporatedNo Drawing. Application March 9, 1954,
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6 Claims. (Cl. 117-56)

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This invention relates to the production of wrinkle-resistant cellulosic textile fabrics, particularly cotton fabrics, characterized by an absence of deleterious chlorine retention properties.

Polymethylol melamines and dimethylol ethylene urea are both known to produce satisfactory wrinkle resistance when applied to cotton fabric. Yet, heretofore, there have been distinct disadvantages when either the polymethylol melamines or the dimethylol ethylene ureas are used for producing wrinkle resistance and/or other permanent effects on cotton fabrics. One primary disadvantage of both products is chlorine retention; the molecules of resin pick up and retain chlorine. The harmful effect of this chlorine retention in the case of the polymethylol melamines is exhibited primarily in the form of extreme yellowing, whereas the harmful effect in the case of the dimethylol ethylene urea is exhibited primarily in loss in tensile and tear strength of the fabric.

It has now been found that 1 mol of a polymethylol melamine combined with about $2\frac{1}{4}$ mols of dimethylol ethylene urea and properly applied to cotton fabrics will produce a high degree of wrinkle resistance without the yellowing or strength losses heretofore experienced.

One important aspect of this invention is the discovery that the desired results are obtained by using a ratio of $2\frac{1}{4}$ mols of dimethylol ethylene urea for each mol of polymethylol melamine. The second important aspect of this invention is that the desired results are obtained by combining the proper resin forming materials with a "thorough" or "hard" cure as is more fully described hereinafter.

In some instances the ratio can be changed slightly, but to assure uniformly optimum results under commercial conditions adherence to the $2\frac{1}{4}$:1 ratio has been found preferable.

In general, the mode of treating fabric with the combined products of this invention is the same as that for either of the products alone, namely, by use of the conventional steps of impregnating fabric with resin and an acidic catalyst in water solution, drying the fabric and curing the resin on the fabric.

While the general mode of fabric treatment with the resinous products of this invention involves no departure from standard practice in making fabrics wrinkle resistant with prior art resins and while one highly advantageous feature of the resin combination of this invention is its insensitivity to varied treating conditions; nevertheless, it is critical that the curing step be car-

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ried out under conditions sufficient to fix substantially all the resin on fabric. Curing conditions accomplishing this result may be defined as those curing conditions which are necessary to obtain a "hard" or "harder than normal" cure. It is known in the art that a "harder than normal" cure can be obtained by the following means:

1. Raising the curing temperature.
2. Lengthening the curing time.
3. Increasing the amount of acidic catalyst.
4. Lowering the amount of alkali in the fabric.

There are limitations to which any one of these contributing factors may be increased to offset the lack or decrease of another, and in commercial practice it is desirable to achieve a hard cure by a balanced combination of all these factors. For example, fabric containing .5% alkali titrated as NaOH can be treated with 10% of the preferred resin of this invention and 2% of catalyst AC, and that amount of alkali cannot be overcome by time and temperature of curing as the fabric will be destroyed by excessive heat before a "hard cure" will be obtained within the meaning of this specification. In such an instance, a "hard cure" should be obtained by either neutralizing the fabric in advance or using a much larger amount of catalyst.

With the exception of Example X, all the fabrics used in the examples of this patent application were soured and contained only about .05% alkali, whereas in standard practice prior to this invention, fabrics contain a larger amount of alkali to the extent of from about .25% to 1%. With the proper alkalinity in the fabric and the proper amount of catalyst in relation thereto a satisfactory curing time and temperature can be very readily determined by treating some fabric, determining loss of strength of the treated fabric by the AATCC scorch test for chlorine retention and, if necessary, adjusting the curing time and temperature until the treated fabric loses no more strength than the same fabric without the treatment. In general, the higher the curing temperatures for any given curing time, the lower the strength loss from chlorine retention.

Thus it will be seen that a hard cure within the meaning of this invention can only be obtained under conditions of catalysis in which there is an amount of acidic catalyst sufficient to neutralize all the alkali in the fabric plus an amount of catalyst sufficient to catalyze the curing of the resin, the latter being equivalent to about 1 to 2% measured as catalyst AC, and the former may be easily calculated from basic in-

organic chemistry. At 70% pick-up, it has been determined that .13% catalyst AC will neutralize about .31% NaOH on fabric. Catalyst AC is approximately 37% 2 methyl, 2 amino propanol hydrochloride.

Thus, cellulosic fabric is neutralized by souring or otherwise, impregnated with from about 50 to 100% of its weight of a 5% to 20% aqueous solution of catalyst and the combination of $2\frac{1}{4}$ mols of dimethylol ethylene urea and 1 mol of a polymethylol melamine, dried to a moisture content of below about 10%, and cured for about 1 to 5 minutes at a temperature of about 360° F. for the shorter time and 280° F. for the longer time.

Polymethylol melamines may be mixed with dimethylol ethylene urea in the water solution which is to be applied to the fabric at the time of its application to the fabric.

However, it has been found that a more uniformly satisfactory fabric product is produced on a commercial scale when the polymethylol melamine is condensed with the dimethylol ethylene urea prior to preparation of a mix for treating fabrics.

If the mol ratio of dimethylol ethylene urea to polymethylol melamine is changed from $2\frac{1}{4}$:1 to $1\frac{1}{4}$:1, the fabric treated therewith will be subject to the yellowing described above and the degree of yellowing will be considerably greater than that experienced with the optimum mol ratios and for some purposes it is commercially unsatisfactory. On the other hand, shifting the mol ratio to $3\frac{1}{4}$:1 tends to lower the strength of the treated fabric below that of fabrics treated in accordance with this invention tends to lower the wrinkle resistance of the fabric and imparts to the treated fabric a lack of uniformly low loss of strength when tested for chlorine retention by the AATCC scorch test.

Although the invention is not limited to any particular catalyst, it has been found that amine hydrochloride type catalysts produce fabrics having better properties of wrinkle resistance in relation to strength loss than other catalysts such as diammonium phosphate, other inorganic acid formers and acids, and the like.

The term "polymethylol melamine" has been used to define any melamine nucleus having from 2 to 6 methylol groups and the lower alkanol ethers of these polymethylol melamines. The commercial melamines useful for treating textiles are understood to be the dimethyl ether of trimethylol melamine and mixtures of dimethylol melamines with trimethylol melamine. The former is sold as melamine resin M-3 and as Resloom M-75 Special. The latter is sold as "Resloom HP." These commercial products can be used interchangeably in producing textile fabrics in accordance with the present invention.

Dimethylol ethylene urea is commercially available in 50% solution as "Zeset S" or as "Rhonite R-1." The products may be used interchangeably in the practice of the present invention. Likewise, certain other methylol cyclic ureas may be used with methylol melamines to enhance the properties thereof. In general, these compounds can be described as low chlorine retentive dimethylol ring compounds having a single urea group in the ring. Such a product is the dimethylol tetrahydro 1 (2) pyrimidone disclosed in copending application Serial Number 385,719, filed October 12, 1953.

Example I

270 parts (.88 mol) of Resloom M-75 Special

(an 80% solids solution of methylated trimethylol melamine), 584 parts (2 mols) of Zeset S (50% dimethylol ethylene urea) were mixed with 8.5 parts of 37% hydrochloric acid and stirred for $2\frac{1}{2}$ hours at 30° C., after which 4 parts of caustic and water were added to bring the pH to 10. The product was a water soluble liquid, substantially colorless, and having a viscosity about the nature of very thin motor oil. The product is stable at room temperature for six months or more.

Example II

7% of the product of Example I and 1% of catalyst AC (2 methyl, 2 aminopropanol-1 hydrochloride) in water solution were placed in a conventional pad box. A bleached and mercerized and soured cotton gingham fabric containing about .05% alkali titrated as NaOH and running about $4\frac{1}{2}$ yds. per pound was passed through the pad and impregnated with about 80% of its weight of the pad liquor. After impregnation the fabric was dried to a moisture content of about 3%. The dried fabric was then heated for $2\frac{1}{2}$ minutes at 300° F. to cure the resin after which it was washed to remove any residual resin or catalyst. The finished fabric showed high wrinkle resistance, high tensile strength, high tear strength, and on the AATCC scorch test for chlorine retention, it showed an average loss of strength about equal to that of the same mercerized and bleached but otherwise untreated fabric.

Another portion of the same cotton gingham fabric was treated as above except that it was cured at 270° F. for about 80 seconds. The tear strength of the treated fabric showed almost no reduction over the untreated. The wrinkle resistance was below a satisfactory level and the chlorine retention reflected as strength loss on the AATCC scorch test showed the product to be unsatisfactory. However, both samples showed negligible yellowing when boiled for ten minutes in a 5% Clorox solution wherein the liquor ratio was 30 to 1. (Clorox is a 5% solution of sodium hypochlorite.)

Example III

The cotton gingham fabric of Example II was impregnated with a solution of 12% of the product of Example I and 1% by weight based on total weight solution of catalyst AC. The fabric was then dried in accordance with Example II and three portions were separately cured at 300° F. for 2 minutes, 320° F. for 80 seconds and at 380° F. for 80 seconds. All three portions were then washed and dried and tested. All three had no more strength loss than untreated fabric when tested for chlorine retention and all three showed no substantial yellowing when tested with hot Clorox as described above. The two samples cured at a higher temperature had a considerably higher degree of wrinkle resistance than the sample cured at the lower temperature but the sample cured at the lower temperature had a higher tear strength and a higher tensile strength. All three samples were commercially satisfactory.

Example IV

The cotton fabric of Example II was impregnated with a water solution of 8% of the product of Example I and 1% by weight catalyst AC based on the bath. The fabric was dried and cured in a single heating unit for 3 minutes at 350° F. The product was free from chlorine retention and free from yellowing in hot Clorox.

The wrinkle resistance was satisfactory and the tear strength of the fabric also was generally satisfactory.

Example V

270 parts (.88 mols) of Resloom M-75 Special and 584 parts (2 mols) of a 50% solution of dimethylol ethylene urea (Rhonite R-1) were dissolved in water and diluted to a 10% solution. 1½% of catalyst AC was then added to the solution and the bleached, mercerized and soured cotton gingham fabric of Example II was impregnated with about 60% of its weight of this solution, dried at about 250° F. to a moisture content of about 5%. It was then cured at 160° C. for 80 seconds. The finished fabric was washed and dried and tested according to the test methods set forth in Example II. The product was substantially the same as the product of Example II and commercially satisfactory in all respects. This Example was repeated using 540 parts of the 80% methylated trimethylol melamine instead of 270. The fabric product did not pass the hot Clorox test but turned a light yellow which rendered the fabric commercially unsatisfactory in whites. This example was again repeated, changing the amount of Rhonite R-1 from 584 parts to 876 parts and using 270 parts of the methylated trimethylol melamine solution. The fabric product showed considerably greater strength loss than untreated fabric on the scorch test.

Example VI

50 parts of Resloom HP (said to be a mixture of dimethylol melamine and trimethylol melamine by its manufacturer) were dissolved in 146 parts of Zeset S and 41 parts formalin (37%) at pH 9-10, by heating. This product was diluted to 8% and applied to the same fabric in accordance with the first procedure of Example V and with the same results.

Example VII

42 parts of formaldehyde (37%) were added to 90 parts of Resloom M-75 Special with stirring and the mixture was brought to pH 9-10 with caustic and condensed for 15 minutes at 170° F. While still hot, 195 parts of Zeset S were added and the mixture was stirred until cool.

In a second separate reaction, this exact procedure was followed with 83 parts of formaldehyde (37%).

The first product was a mixture of Zeset S and a partially methylated methylol melamine averaging about 4.5 methylol groups per melamine nucleus and the second product was a mixture of Zeset S and partially methylated hexamethylol melamine.

Both products were applied to the same cotton fabric according to the first procedure set forth in Example V and the results of that example were generally duplicated.

Example VIII

A 12% aqueous solution of the product of Example I containing 2% catalyst AC and 2% of Profine (a long chain fatty acid ester sold as a softener) was applied to a previously soured all viscose shirting weight gabardine containing about .05% alkali titrated as NaOH in a conventional pad. The fabric was dried at about 250° F. for about 2 minutes and cured for eight minutes at about 320° F. This treated fabric

exhibited no yellowing and no loss of strength from chlorine retention.

Example IX

305 parts of Resloom M-75 Special were placed in a reaction chamber and 515 parts of Rhonite R-1 (mol ratio of 1:1.75) and thoroughly mixed by stirring. 7% of this mixture in water with about 2% on the bath weight of catalyst AC were padded onto a bleached, mercerized and soured cotton gingham fabric containing about .05% alkali titrated as NaOH running about 4.5 yards per pound. The fabric picked up about 80% based on its weight of the solution. The fabric was then dried by conventional means and cured 70 seconds at 360° F. The thus treated fabric had good physical properties and possesses uniformly low deleterious chlorine retention properties when tested by the AATCC scorch testing method. However, when treated with 5% Clorox at the boil for ten minutes, it yellowed more than an untreated fabric subjected to the same treatment and more than the same fabric treated in an identical manner with the product of Example I, but much less than the same fabric treated in an identical manner with Resloom M-75 Special alone. This fabric appears to be a fairly satisfactory commercial, non-yellowing product.

Example X

A 10% aqueous solution of the product of Example I containing 6% catalyst AC was padded onto a cotton fabric which had not been soured and which contained about .35% alkali measured as NaOH. The fabric was dried and cured at 360° for 70 seconds. When tested the fabric showed high wrinkle resistance, good physical properties and was about like untreated fabric with respect to yellowing on hot Clorox treatment or repeated Clorox laundering. The fabric was also not subject to chlorine retention degradation on the AATCC scorch test in excess of the degradation of untreated fabric.

Another sample of the same fabric was treated under identical conditions except that the amount of catalyst was reduced to 2%. A wrinkle resistant fabric free from yellowing was obtained but it was badly degraded by chlorine retention when tested on the AATCC scorch test.

Thus, it will be seen that hot Clorox yellowing and strength loss from chlorine retention can be avoided in the production of wrinkle resistant cotton fabrics by using a resin-forming material which combines 1 mol of a polymethylol melamine with about 2¼ mols of dimethylol ethylene urea either precondensed or mixed and curing the fabric under conditions hard enough to assure that substantially all the resin is fixed thereon.

The ratio of 2¼ mols of dimethylol ethylene urea to one mol of polymethylol melamine has been established by calculations based on the specifications of the product manufacturers as set forth herein.

While the beneficial results of the invention diminish gradually as the mol ratios are varied from the 2¼:1 optimum so that there are no sharply defined limits of the invention in this respect, as a practical matter, successful commercial use of the invention lies within the mol ratio limits of about 3¼:1 and 1¾:1 (dimethylol ethylene urea to polymethylol melamine).

When the resinous product of this invention is used on rayon fabric, it is sometimes desirable to combine it with a non-resinous stabilizing material such as the products described in copending applications Serial No. 222,297, filed April 21, 1951, and Serial No. 286,038, filed May 3, 1952.

This application is a continuation in part of application Serial Number 393,242, filed November 19, 1953, and now abandoned.

We claim:

1. In the process of treating bleached and mercerized cotton textile fabrics wherein fabric is impregnated with an aqueous solution containing a heat activated acidic catalyst and from about 5% to 20% of a resin-forming material and the impregnated fabric is heated to dry the fabric and cure the resin, that improvement which comprises substantially neutralizing the alkali in the fabric prior to completion of the cure, using as the resin-forming material a polymethylol melamine and dimethylol ethylene urea in the ratio of one mol of the former to from about $1\frac{3}{4}$ to $3\frac{1}{4}$ mols of the latter, and said curing being within the range of about 1 to 5 minutes at about 360° F. for the shorter time and 280° F. for the longer time, and the curing time being long enough and the curing temperature being high enough within said range to reduce the strength loss of the treated fabric to about that of untreated fabric when tested by the AATCC scorch test method, whereby highly wrinkle resistant cotton fabric is obtained with low strength loss and the treated fabric is substantially free from yellowing and acid degradation caused by chlorine retention.

2. The process as set forth in claim 1 wherein said neutralization is accomplished by acidifica-

tion of the fabric prior to impregnation with the resin solution.

3. The process as set forth in claim 1 wherein said neutralization is accomplished by using, in addition to the usual catalyst concentration, an excess of acid forming catalyst, the excess being that amount required to neutralize substantially all the alkali in the fabric.

4. The process as set forth in claim 1 wherein the mol ratio is about $2\frac{1}{4}$ mols of dimethylol ethylene urea to 1 mol of polymethylol melamine.

5. The process as set forth in claim 1 wherein the alkali content of the fabric being treated has been substantially reduced by souring prior to resination, the mol ratio is about $2\frac{1}{4}$ mols of dimethylol ethylene urea to 1 mol of polymethylol melamine, and the catalyst is an amine hydrochloride.

6. A water soluble resin-forming product suitable for treatment of cotton textile fabrics to produce permanent wrinkle-resistance and other permanent effects without deleterious chlorine retention properties consisting essentially of one mol of a polymethylol melamine and $2\frac{1}{4}$ mols of dimethylol ethylene urea.

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