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2,715,078

PROCESS OF IMPREGNATING CELLULOSIC MATERIAL WITH THERMOSETTING RESIN

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No Drawing. Application October 27, 1948,
Serial No. 56,911

9 Claims. (Cl. 117—56)

The present invention relates to an improved process for producing shrink-resistant cellulosic textile materials, and particularly shrink-resistant regenerated cellulose textiles.

It is one object of the present invention to provide a process for improving the dimensional stability of cellulosic textile materials without appreciably lowering the tensile strength of such materials.

A further object of the present invention is the efficient utilization of thermo-setting resins in regenerated cellulose textile impregnation whereby substantially all of the thermosetting resin employed is deposited in and on the textile.

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

The invention is carried out in general by first saturating a cellulosic textile material, preferably regenerated cellulose textile materials, with a long aqueous bath consisting of a small amount, say about 0.2 to 2% by weight, based on the material, of a cationic surface active agent. The temperature of the bath during this treatment is between about 100° F. and 200° F. and the treatment is carried out until substantially all of the cationic surface active agent has exhausted from the bath onto the textile material. When larger amounts of cationic surface active agent are employed in the bath, the treatment need only be carried out until from about 0.2 to 2% by weight of agent, based on the treated material, has been exhausted onto the material.

After the above described treatment, the material may be rinsed and/or dried, if desired. However, it is preferable not to dry the material at this stage. Whether rinsed or not, the material is subsequently saturated with a long aqueous bath comprising initially a monomeric or substantially unpolymerized alkylated melamine-formaldehyde, urea-formaldehyde or alkylated urea-formaldehyde condensation product or mixtures thereof until substantially all of the condensation product has exhausted or migrated from the bath onto the material. It is essential that the temperature of this bath be at least 115° F. and generally not more than about 180° F. during this particular treatment. Generally speaking, the resin bath consists primarily of water and the aforementioned condensation products, but preferably contains in addition a small amount, say about 0.5 to 1.5% by weight of alkali metal salt or water soluble alkali earth metal salt to assist the exhaustion or migration of condensation product from the bath onto the material. However, it is essential in carrying out the present invention that the bath be substantially free of acid or latent curing catalysts for the condensation products.

In general, from about 3 to 25% by weight of condensation product, based on the treated material, is employed in the long aqueous bath. Substantially all of the condensation product is exhausted onto the material in accordance with the present invention, therefore, the material contains substantially all of the condensation

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product used and the long aqueous bath is substantially free of same after the treatment is completed.

The resin treated material may be rinsed, if desired, and is extracted to remove excess water therefrom prior to the drying of the material and the curing or insolubilization of the resin. The extracted material may first be dried at relatively low temperatures, that is temperatures, for example, between about 140° to 225° F. and then subjected for short periods of time to temperatures between 250° to 350° F. to cure or insolubilize the resin, or drying of the material and curing of the resin may be accomplished at the same time by heating the material at temperatures between about 250° to 350° F.

As examples of cationic surface active agents which are employed in accordance with the present invention may be mentioned surface active quaternary ammonium salts as, for example, cetyl methyl dibenzyl ammonium chloride, cetyl pyridinium chloride and the corresponding sulfates and bromides, stearyl dimethyl ethyl ammonium bromide, and the like; surface active sulphonium salts, as, for example, cetyl diethyl sulphonium chloride, lauryl dimethyl sulphonium chloride and the like; and surface active phosphonium salts as, for example, stearyl trimethyl phosphonium chloride, cetyl dimethyl benzyl phosphonium chloride and the like. Of the above mentioned compounds the surface active quaternary ammonium salts and particularly cetyl dimethyl benzyl ammonium chloride, cetyl pyridinium chloride and stearyl trimethyl ammonium chloride are preferred.

The condensation products employed in the present invention are well known products which may be prepared in various ways. The alkylated melamine-formaldehyde condensation products are suitably prepared, for example, by first reacting from about 2 to 6 molecular proportions of formaldehyde, as formalin, with 1 molecular proportion of melamine in an alkaline solution at temperatures between about 50 to 80° C. for a period of time sufficient to cause solution of the melamine. The resulting product is then further reacted under acid conditions with monohydric alcohols such as methanol, ethanol, isopropanol and the like, or dihydric alcohols having from 2 to 6 carbon atoms such as ethylene glycol, propylene glycol, diethylene glycol and the like at temperatures of from about 40 to 70° C. until a homogeneous solution is obtained, after which, the solution is neutralized with caustic soda using phenolphthalein as an indicator, and then cooled. Care should be taken during the preparation of the condensation product to avoid highly alkaline conditions during the preparation of the methylol melamine, highly acid conditions during the alkylation reaction and high temperatures during both reactions otherwise excessive polymerization of the condensation product may result, as evidenced by insolubility in water or water-alcohol mixtures.

Essentially the same procedure may be employed in the preparation of alkylated urea-formaldehyde resins except that smaller mol ratios of formaldehyde to urea are preferably used. Thus 1 and preferably 2 mols of formaldehyde, as formalin, are initially reacted with urea.

It is preferred to use in the practice of the present invention either methylated melamine-formaldehyde or methylated urea-formaldehyde condensation products, or melamine-formaldehyde and urea-formaldehyde addition products which have been alkylated with dihydric alcohols as described above, for the reason that such products are easily soluble in water and are readily prepared in a substantially monomeric or unpolymerized state.

In a preferred embodiment of the present invention a regenerated cellulosic fabric such as a fabric having a viscose rayon warp and filling is first saturated with from about 25 to 50 times its weight of an aqueous solution consisting of from about 0.6 to 1% by weight, based on

the initial fabric weight, of a surface active quaternary ammonium salt, the remainder of the solution being water. The temperature of the solution is between about 110° to 160° F. during the treatment. The duration of the treatment is about 45 minutes at 140° F. and at other temperatures depends upon the temperature employed, longer periods being required at lower temperatures. Completeness of the exhaustion of cationic agent is indicated by absence of a precipitate when a small portion of solution is shaken with an equal portion of 1/4% soap solution and the solution is allowed to stand.

The fabric is then saturated with from about 25 to 50 times its initial weight of an aqueous solution consisting of from about 7 to 13% by weight, based on the initial weight of the material, of a methylated melamine-formaldehyde and/or methylated urea-formaldehyde condensation product. The resin solution is initially prepared by dissolving the required amount of substantially monomeric condensation product either as a syrup or solid product in water and is then heated to a temperature between about 140° to 160° F. and maintained between these temperatures during the treatment of the fabric. The resin or condensation product migrates or exhausts from the bath onto the fabric in about 60 minutes when the bath temperature is 160° F. At lower temperatures a longer treating period is required to obtain substantially complete exhaustion. Completeness of the treatment may be determined by mixing a small portion of the bath with acid and heating on a hot plate. If little or no resin is formed, the treatment is considered substantially complete.

A rapid exhaustion of the condensation product onto the fabric is facilitated by adding a small amount of inorganic salt, as hereinbefore described, to the resin bath.

The resin treated fabric is extracted either by centrifuging, padding, vacuum extraction and the like until it contains from about 80 to 150% water based on the initial fabric weight, and is then dried at a temperature between about 160° to 220° F. The fabric is then heated at a temperature between about 270° to 320° F. until the resin thereon is cured or insolubilized. Curing may be accomplished at 290° F. in about 5 minutes and this time varies corresponding to the curing temperature used.

The fabrics, yarns and the like which have been treated in accordance with the present invention have excellent dimensional stability and a soft hand, and a tensile strength which is substantially the same as the untreated material. The tensile strength of the treated material is quite surprising in view of the fact that the application of the same condensation product by conventional padding lowers the tensile strength of the material considerably.

A further understanding of the present invention will be obtained from the following examples which are intended only to be illustrative thereof, parts and percentages being by weight.

Example I

A methylated melamine-formaldehyde condensation product was prepared as follows:

One mol of melamine was reacted with 5 mols of formaldehyde, as a 37% neutral formalin solution, at a temperature of about 90° C. until solution occurred. The solution was then cooled until the condensation product precipitated. This product was then separated from the solution and dried at low temperature, about 30° C., under vacuum. The dry product was reacted with about 14 mols of methyl alcohol, under reflux, in the presence of about 0.1 mol of hydrochloric acid. The reaction was allowed to proceed until the product dissolved, after which the solution was neutralized with caustic soda to the phenol-phthalein endpoint. This solution was then diluted with water until it contained about 0.16% condensation product. The condensation product is substantially unpolymerized.

One part of fabric consisting of a viscose rayon warp

and filling was first saturated in a dye beck with 50 parts of an aqueous solution consisting of water and 1%, based on the fabric, of cetyl dimethyl benzyl ammonium chloride. The temperature of the aqueous solution was approximately 140° F. and the treatment was carried out in the dye beck for a period of 45 minutes. The solution was then drained from the dye beck, the fabric was rinsed with warm water and 50 parts of the above described resin solution, which had been heated to 160° F., was run into the dye beck. The solution was maintained at 160° F., and the treatment in the dye beck was carried out for a period of about 75 minutes. The solution, which was substantially free of condensation product, was then drained and the fabric was successively rinsed with warm water, centrifuged until it contained about 120% water based on the initial fabric, framed to size and dried for 5 minutes at 180° F. The dry fabric was then heated for 5 minutes at 300° F. to insolubilize the resin.

The resulting fabric possesses good dimensional stability, that is, good resistance to shrinkage on laundering, has a soft hand and very low chlorine retention on bleaching with chlorine containing solutions. It also has a tensile strength which is substantially the same as untreated fabric from the same roll.

Example II

An all viscose rayon fabric was treated and finished in substantially the same manner as described in Example I, except the resin bath also contained 0.5 parts of sodium sulfate. The exhaustion of the resin from the bath to the fabric was substantially complete in about 55 minutes.

The resulting fabric had substantially the same characteristics in respect to dimensional stability, hand, chlorine retention and tensile strength as that produced in accordance with Example I.

As examples of alkali metal salts and water soluble alkaline earth metal salts which are employed instead of Na_2SO_4 in the foregoing example may be mentioned sodium chloride, potassium sulfate, potassium chloride, barium chloride, calcium chloride and the like.

Example III

Fifty parts of dimethylol urea containing about 16% water were heated with about 320 parts of methyl alcohol at a temperature of approximately 50° C. until a clear solution was obtained. About 0.30 part of 5N HCl was then added to the solution with vigorous agitation. The temperature of the solution was maintained at 40° C. for an additional 7 minutes and the solution was then neutralized with dilute caustic soda solution to the phenolphthalein endpoint. The resulting solution was diluted until it contained about 0.25% condensation product.

One part of fabric consisting of a viscose rayon warp and filling was first saturated in a dye beck with 40 parts of an aqueous solution consisting of water and about 0.9%, based on the fabric, of cetyl pyridinium chloride. The temperature of the aqueous solution was about 130° F. and the treatment was carried out in the dye beck for approximately 60 minutes. The solution was then drained from the dye beck and 40 parts of the above described resin solution which had been heated to about 140° F., was run into the dye beck. The resin solution was maintained between about 140° to 150° F. and the treatment of the fabric was carried out for a period of about 90 minutes. The solution which was substantially free of condensation product, was then drained and the fabric was successively centrifuged to remove excess water, framed to size and dried for about 7 minutes at 170° F. The dry fabric was then heated for about 10 minutes at 270° F. to insolubilize the resin.

The resulting fabric possess good dimensional stability and has substantially the same tensile strength as an untreated fabric from the same roll. It has slightly higher chlorine retention and a firmer hand than the fabric prepared in accordance with Example I.

Example IV

Two mols of formaldehyde, as 37% formalin, were reacted with 1 mol of urea at a pH of 7.0 (glass electrode), the pH having been adjusted by the addition of 20% aqueous caustic soda solution. The mixture was heated with reflux at a temperature of 70° C. until the reaction mass begins to form a syrupy mass on cooling to 20° C. The product consisted essentially of a 55% solution of water-soluble urea-formaldehyde condensation product in water. The resin solution was diluted with water until it contained about 0.18% of condensation product.

One part of a fabric consisting of viscose rayon warp and filling was first saturated in a dye beck with 50 parts of an aqueous solution consisting of water and 0.9%, based on the fabric, of stearyl trimethyl ammonium chloride. The temperature of the aqueous solution was about 150° F. and the treatment was carried out in the dye beck for a period of 40 minutes. The solution was then drained from the dye beck, the fabric was well rinsed with warm water and 50 parts of the above described resin solution which had been heated to 120° F., was run into the dye beck. The solution was maintained at about 120° F. and the treatment of fabric therewith was carried out for 120 minutes. The dye beck was then drained, and the fabric therein was successively rinsed with water, centrifuged until it contained about 100% water, based on the initial fabric, framed to size and dried for 4 minutes at 200° F. The dry fabric was then heated for 4 minutes at 310° F. to insolubilize the resin thereon.

The resulting fabric possessed a soft hand and good dimensional stability and its tensile strength was essentially as good as untreated fabric from the same roll.

Although the invention has been described primarily with reference to the treatment of regenerated cellulose fabrics it is also practiced with good results on other cellulosic textile fabrics fabricated from cotton, linen, ramie and other natural cellulose yarns and/or mixtures thereof with regenerated cellulose filaments and yarns. The materials treated are preferably fabrics such as knitted or woven fabrics, but they may also be yarns, fibers, staple fibers and filaments which are to be woven, knitted or otherwise utilized in the preparation of fabrics, cloth and the like.

The term "long aqueous bath" as employed herein is intended to cover aqueous solutions having a weight ratio of at least 10 parts of solution to every 1 part of fabric or material being treated. Such solutions may weigh up to 70 times the weight of material being treated, but preferably weigh from 25 to 50 times the weight of the material which is to be treated therein.

Various modifications in the practice of the present invention will be apparent to those skilled in the art and it is intended that the present invention be limited only by the scope of the appended claims.

What is claimed is:

1. The method of producing a shrink-resistant cellulosic textile material which comprises immersing a cellulosic textile material in from 10 to 70 times its weight of an aqueous solution of from about 0.2 to 2% by weight, based on said material, of a cationic surface active agent; allowing substantially all of said agent to migrate from said solution onto said material, the temperature of said solution being between about 100 and 200° F. during this step; immersing said material in from 10 to 70 times its initial weight of an aqueous solution comprising initially from about 3 to 25% by weight, based on the initial weight of the material, of a substantially unpolymersed condensation product selected from the group consisting of urea-formaldehyde, alkylated melamine-formaldehyde and alkylated urea-formaldehyde condensation products and mixtures thereof, said last named solution being substantially free of curing catalysts for said condensation product; allowing said textile material to remain in contact with the solution of said condensation product for a period

of at least 60 minutes and until substantially all of the condensation product migrates from said solution onto the material, the temperature of the last named solution being between about 115 and 180° F. during this step; extracting said material to remove excess solution therefrom; and then drying and heating said material to insolubilize said condensation product.

2. The method of improving the shrink-resistance of a cellulosic textile material which comprises immersing said material in from 10 to 70 times its weight of an aqueous solution of from about 0.2 to 2% by weight, based on said material, of a surface active quaternary ammonium salt, the temperature of said solution being between about 100 and 200° F. and the material and solution being in contact with each other until substantially all of said agent has migrated from said solution to said material; immersing said material in from 10 to 70 times its initial weight of an aqueous solution comprising initially from about 3 to 25% by weight, based on the initial weight of the material, of a substantially unpolymersed condensation product selected from the group consisting of urea-formaldehyde, alkylated melamine-formaldehyde and alkylated urea-formaldehyde condensation products and mixtures thereof, said last named solution being at a temperature between about 115 and 180° F. and being substantially free of curing catalysts for said condensation product; allowing said textile material to remain in contact with the solution of said condensation product for a period of at least 60 minutes and until substantially all of said condensation product migrates from the solution onto the material; extracting said material to remove excess solution therefrom; and then drying and heating said material to insolubilize said condensation product.

3. The method of improving the shrink-resistance of a regenerated cellulose textile material which comprises immersing said material in from about 25 to 50 times its weight of a water solution of from about 0.6 to 1% by weight, based on the initial material weight, of a surface active quaternary ammonium salt, the temperature of said solution being between about 110° to 160° F. and the solution and material being in contact with each other until substantially all of said surface active salt has migrated from said solution onto said material; immersing said material in from about 25 to 50 times its initial weight of an aqueous solution comprising initially from about 7 to 13% by weight, based on the initial material weight, of a substantially unpolymersed condensation product selected from the group consisting of urea-formaldehyde, alkylated melamine-formaldehyde and alkylated urea-formaldehyde condensation products and mixtures thereof, said solution being at a temperature between about 140° to 160° F. and being substantially free of curing catalysts for said condensation product; allowing said textile material to remain in contact with the solution of said condensation product for a period of at least 60 minutes and until substantially all of said condensation product migrates from said solution onto said material; extracting said material to remove excess solution therefrom; and then drying and heating said material to insolubilize said condensation product.

4. The method of improving the shrink-resistance of a regenerated cellulose textile material which comprises immersing said material in from about 25 to 50 times its weight of a water solution of from about 0.6 to 1% by weight, based on the initial material weight, of a surface active quaternary ammonium salt, the temperature of said solution being between about 110° to 160° F. and the solution and material being in contact with each other until substantially all of said surface active salt has migrated from said solution onto said material; immersing said material in from about 25 to 50 times its initial weight of an aqueous solution consisting essentially of water, from about 0.5 to 1.5% by weight of a water soluble salt selected from the group consisting of

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alkali metal and water soluble alkaline earth metal salts and initially from about 7 to 13% by weight, based on the initial material weight, of a substantially unpolymerized condensation product selected from the group consisting of urea-formaldehyde, alkylated melamine-formaldehyde and alkylated urea-formaldehyde condensation products and mixtures thereof, said solution being at a temperature between about 140° to 160° F. and being substantially free of curing catalysts for said condensation product; allowing said textile material to remain in contact with the solution of said condensation product for a period of at least 60 minutes and until substantially all of said condensation product migrates from said solution onto said material; extracting said material to remove excess solution therefrom; and then heating said material to dry same and insolubilize said condensation product.

5. The method according to claim 1, but further characterized in that a methylated melamine-formaldehyde condensation product is employed.

6. The method according to claim 1, but further characterized in that a methylated urea-formaldehyde condensation product is employed.

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7. The method according to claim 2, but further characterized in that cetyl dimethyl benzyl ammonium chloride is employed as the surface active quaternary ammonium salt.

8. The method according to claim 2, but further characterized in that cetyl pyridinium chloride is employed as the surface active quaternary ammonium salt.

9. The method according to claim 2, but further characterized in that stearyl trimethyl ammonium chloride is employed as the surface active quaternary ammonium salt.

References Cited in the file of this patent

UNITED STATES PATENTS

15	2,137,465	Thackston	Nov. 22, 1938
	2,339,203	Stiegler	Jan. 11, 1944
	2,420,157	West	May 6, 1947
	2,421,363	Young	May 27, 1947
20	2,426,770	Grim	Sept. 2, 1947

FOREIGN PATENTS

483,496	Great Britain	Apr. 21, 1938
496,830	Great Britain	Nov. 18, 1938