3,309,165
PROCESS OF IMPROVING THE TENSILE STRENGTH AND INCREASING RESISTANCE TO MICROBIOLOGICAL DETERIORATION OF CELLULOSE TEXTILE CONTAINING CURED AMIONPLAST RESIN BY STEAMING

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The invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to us of any royalty thereon.

This invention relates to a procedure which will reverse the tensile strength loss of cotton textiles normally associated with the use of condensation resins employed to render cellulosic fibers resistant to microbiological deterioration.

It should be noted that condensation resins are also used to impart wash and wear properties in fabrics and the treatment procedure of this invention will also reverse the tensile strength loss that occurs in these treated fabrics.

One of the practical means of providing a durable, colorless, rot-resistant treatment to cotton is through the application of the acid colloid of trimethylolmelamine. Formic acid colloid of trimethylolmelamine is applied to fabric by essentially the same conventional method used for resin finishing, namely padding, drying and curing. This technique was developed at the Southern Regional Research Laboratory, U.S.D.A. and will hereafter be referred to as the Southern Regional process or SRRL.

It is well known that for many years that aminoplast resins applied by the conventional process to cotton will render it resistant to microbial attack. Acid coloid have been used by others but the techniques utilized produced stiff cotton goods with a variable degree of rot resistance.

Resin treatment of cotton cloth to make it resistant to attack by microorganisms, as practiced by the dry cure method exemplified by the Southern Regional process, has a serious drawback, namely, a substantial loss in tensile strength of the treated material. This process essentially involves padding the scoured cotton fabric in a treatment solution containing 17% trimethylolmelamine, 20% formic acid and 63% water. The fabric which now has about an 80% wet pickup passes through a drying oven at 80° C. (176° F.) for 4 minutes, followed by curing at 140° C. (284° F.) for 4 minutes. Final resin deposition in the fabric for optimum resistance to microbial deterioration is about 12%. Fabric treated by this procedure undergoes 25–50% loss in tensile strength. For example, blue line 8 oz. cotton duck has a tensile strength of about 100 lbs. per square inch. The tensile strength of this fabric after treatment by Southern Regional process containing 11.8% resin addition becomes lowered to about 75 lbs. per square inch.

This loss in tensile strength is probably a result of cross-linking of the resin in association with the cellulose. Any loss in tensile strength of a fabric is considered undesirable and in practice may render the material too weak for certain end item use.

The Arigal process of Ciba Ltd. in conjunction with U.S. Patent No. 3,020,419 to A. Rupert, claims to overcome the customary loss in tensile strength by depositing a synthetic resin in the fiber, this resin is not cured in an ordinary way, but fixed in the presence of water. The insolubilization of the resin within the fibers provides a permanent barrier against microbial attack. No reaction takes place with cellulose and the properties of the fiber are hardly affected. The water absorption capacity of the fiber remains unchanged and its tensile strength remains unchanged.

The water present in the wet fixation hinders the cross-linking of the cellulose to such an extent that it hardly occurs in condensation-resin finishing. Some crosslinking can be obtained in wet fixation by working at higher temperatures or lengthening the reaction time. This would lead to the usual modification in the properties of the treated fabric and cause loss of strength. Crosslinking is not necessary for conversion, since insolubilized resin provides an adequate mechanical barrier against microorganism.

The Arigal process can be carried on either semicontinuously by a wet-aging process at room temperature or at a slightly higher temperature or on a continuous basis using a conventional steamer. The main obstacle to processing on standard equipment by this process is the risk that the condensation-resin solution would migrate during wet fixation. Measures taken to overcome this included the use of high rates of impregnation and higher concentrations of condensation-resin or the concentration of condensation-resin solution taken up by the fiber has to be increased by partial drying of the impregnated fabric.

The following procedures for treatment of cotton fabric by the wet fixation process are recommended by A. Rupert (American Dyestuff Reporter, vol. 50, pages 21–24) in using the Arigal process:

(1) Continuous steam process.—The fabric is padded with a solution of Arigal (melamine-formaldehyde precondensate) to which hydrogen peroxide is added, and then squeezed and dried to a residual moisture of 20–40%. The impregnated fabric is then steamed for at least eight minutes with saturated steam in a continuous ager. This procedure leads to the formation of formic acid by the oxidation of formaldehyde with hydrogen peroxide. The insolubilization of the resin within the fiber takes place rapidly.

(2) Semi-continuous wet aging.—The fabric is impregnated with Arigal C and hydrogen peroxide, squeezed, and if necessary, dried to a residual moisture content of at least 20%. The fabric is then wrapped in plastic sheets to prevent drying. The rolls are kept either at room temperature, or slightly above, until the wet fixation process has been completed which usually required 1–4 days, depending on the temperature, 75°–80° F.
Formic acid process.—Hydrogen peroxide is replaced by small amounts of formic acid which are not added to the impregnation bath but applied to the fabric after impregnation by spraying or nip-paddling, etc. The resin is fixed wet by one of the methods previously described. The Cyansta Sta-Tuff Finish is also a resin treatment process using Aerotech Sta-Tuff Resin A and Aerotech Sta-Tuff Accelerator B and curing by the wet fixation process at a convenient temperature. Although little information is made available on the nature of the specific resin, it is presumed to be a fully methylated methylolmelamine. The catalyst and accelerator employed in this process are also different from the Ciba process, but the treated fabric presumably protects in a manner similar to the Ciba process; the resin is insolubilized within the fiber by the wet fixation process and the properties of the fabric are hardly changed. The tensile strength of the fabric in unaffected which is indicative of no crosslinking with the cellulose.

The object of this invention is to provide a procedure which will reverse the loss of tensile strength associated with the conventional heat curing in the dry state of resin treatment procedures used to impart rot and weather resistance to cotton fabric.

No established satisfactory procedure is known for reversing tensile strength loss associated with the dry heat cure resin treatment of cotton fabric. Rupert’s procedure hereabove described states the use of his wet fixation process does not permit any reaction to take place with the cellulose and the properties of the fabric are hardly affected. Thus, no crosslinking is effected and no loss in tensile strength takes place, which is in contrast to the curing of resins by dry heat. At elevated temperatures Rupert, however, notes that crosslinking will occur.

However, with the Southern Regional process, a reaction apparently does take place between the resin and the cellulose as evidenced by a loss in tensile strength after treatment, thus resulting in chemically modified cellulose. This reaction probably results in crosslinking between the cellulose chains; however as pointed out in “Developments in Industrial Microbiology,” 2, pages 79-91 by W. N. Berard et al.; and in “Textile Finishing Bulletin No. 136,” American Cyanamid Co., Textile Resin Department by T. F. Cook; resin finishes such as the acid colloid finish of the Southern Regional process do not act as a physical barrier to prevent microbiological attack as previously postulated but rather as a chemical barrier which renders cotton resistant to microbiological deterioration. The Arigal process, however, claims protection by providing an insoluble resin finish which acts as a mechanical barrier against microorganisms.

This invention is, therefore, a process for reversing the undesirable mechanical damage done to the physical properties of cotton fiber as a result of depositing condensation resins in the cotton fiber, and at the same time permitting retention of the desirable characteristic of resistance to microbiological deterioration.

The procedure for reversing the tensile strength loss in cotton fabric treated by the Southern Regional process as previously described in detail, consists in immediately thereafter or after an indefinite storage period, subjecting this treated fabric to steam under pressure (16-18 lbs./sq. in.) and at a temperature of 252°-255° F. for a period of 2-20 minutes. This treatment leaves the mechanical properties of the fabric unchanged along with its resistance to microbiological deterioration. An 11.8% resin add-on to blue line 8 oz. duck gives the before and after soil burial tensile strength values as recorded in the following table.

### Table

<table>
<thead>
<tr>
<th>Treatment on 8 oz. Blue Line Duck</th>
<th>Original</th>
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<tr>
<td></td>
<td>12</td>
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<td></td>
<td>26</td>
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<td>48</td>
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</table>

1. Controls—untreated
2. Untreated Controls Autoclaved 3 min. 16-18 lbs. pressure (252-255° F.) Post Exhaust
3. 11.8% Resin add-on (no autoclaving) Fast Exhaust
4. 11.8% Resin add-on Autoclaved 3 min. 16-18 lbs. pressure (252-255° F.) Post Exhaust
5. 11.8% Resin add-on Autoclaved 3 min. 16-18 lbs. pressure (252-255° F.) Fast Exhaust
6. SRRL-Treatment—Wet cured at room temp. for 4 days by Rupert Process
7. SRRL-Treatment—Wet cured at room temp. for 6 days by Rupert Process and dried at 80°C
8. SRRL-Treatment—Wet cured at room temp. for 7 days by Rupert Process
9. SRRL-Treatment—Wet cured at room temp. for 2 days by Rupert Process and dried at 80°C

Prior art as taught by Rupert’s wet fixation process might lead to the conclusion that emulsions of hardenable aminoplasts such as methylolmelamine when applied to cellulosic fibrous material can be fixed to the fabric thereby rendering it resistant to microbiological deterioration with no loss of tensile strength, but the Table above shows that this conclusion is not factual when applied to the Southern Regional process.

For example, blue-line fabric treated in a freshly prepared solution by the Southern Regional process except substituting Rupert’s wet-cure process (curing the treated fabric in a plastic bag for 4 and 7 days at room temperature) for the drying (80°C) and curing at 140°C resulted in the following: the blue-line fabric treated by this process did, in fact, retain its tensile strength while having a resin add-on of 12.5% and 12.9% respectively as monitored by nitrogen analysis determined after boiling the treated fabric for 3 minutes; this fabric, however, after 16 weeks burial retained only 37% and 11% of its tensile strength; however, drying the fabric at 80°C (176°F) (not to be confused with dry curing which is done at 140°C (284°F)) the fabric retained 86% and 56% of its tensile strength respectively after 16 weeks soil burial. Although wet curing applied to the SRRL process did prevent loss in tensile, it certainly did not offer the protection in soil burial provided by the autoclaving treatment of this process.

The greater resistance of the wet cured blue-line fabric, as noted in the Table, followed by drying at 80°C over the wet cured fabric is probably a result of a reaction between the resin and fabric noted in drying, although 80°C is not usually considered a dry curing temperature.

The application of the wet fixation process of Rupert to the SRRL technique does not provide the degree of rot resistance to the Southern Regional process that might be expected. If the wet fixation process is followed, the degree of rot resistance is greatly reduced over that which is obtained by the Southern Regional process followed by autoclaving as disclosed in the above Table. Thus, this clearly indicates that the reaction between the resin and cellulose as controlled by the wet fixation process is a...
different chemical or physical phenomenon than exists between the cellulose and the resin undergoing a dry cure at elevated temperatures (140° C.) followed by autoclaving as described in the present process. This view is advanced as a rebuttal to a possible opinion that the application of this process to reverse the strength loss of the Southern Regional process is merely the application of the Ruptel or wet cure process at a different stage in the treatment procedure.

It should be noted that in order to form an insoluble condensation product within a fabric treated with an aminoplast resin by the conventional process such as the Southern Regional treatment, it is necessary to first dry the treated fabric and then subject the fabric to an elevated temperature such as 140° C. for approximately 4 minutes. By hardening in the dry state, water insoluble products are formed that cause a reduction in the tensile strength of the fabric.

By contrast, Ruptel's process called wet-fixing, is a process whereby instead of hardening the aminoplast in the dry state, it can be converted into the insoluble state without previous drying and without completely removing the water derived from the impregnating solution so that a condensation product is formed in the wet state. Ruptel states that in the wet-fixing process the reaction takes a different course and the properties of the fiber are unchanged in the way they are by dry heat hardening. Fundamental differences in the course of the reaction and the effects produced occur depending on whether dry hardening or wet fixing is used.

Reference is made to a publication in 1955 on “Some Controversial Aspects of Crease Resistance of Cellulose Fabrics,” Textile Research Journal 25 pages 24–40 by A.C. Nuesela et al. therein is listed nine possible reactions when a difunctional resin-former is polymerized or cured within cellulose fibers. Three possible reactions involving only the resin polymerization and no bonding to cellulose can occur; (1) cyclic dimer, (2) linear polymer, and (3) thermoset polymer. The remaining six indicate possible modes of reaction with cellulose and include; (4) simple crosslink, (5) linear polymer, crosslinked to cellulose, (6) cyclic polymer, crosslinked to cellulose, (7) monomer, linked to only one cellulose chain, (8) linear polymer, linked to only one cellulose chain, and (9) cyclic polymer, linked to only one cellulose chain.

It is assumed that Ruptel’s and Cyansta-Tuff finish process belongs in one of the first three classes, and the Southern Regional process belongs to one of the latter six, probably by methylene groups crosslinking glucose units through ether formation.

In Linken et al. article in 1956 entitled, “Cellulose Interactions and Certain Textile Resin,” it is pointed out that lowering of the tensile or breaking strength in cotton fabrics is an index of crosslinking. Since Ruptel’s process shows little or no loss in tensile strength, there is no reaction with cellulose, whereas the treatment of this process brings about a loss in tensile strength which is indicative of crosslinking.

This leads to the conclusion that the Ruptel process and the SRRL process herein described are chemically different and therefore not synonymous in any way, other than that of providing two distinct methods for imparting rot and weather resistance to cotton fabric. Also the present process makes possible a dry cure process that has the advantage of a wet cure process in eliminating tensile loss of treated fabric without the loss of the protective treatment against microbial attack.

It should be emphasized that the process of Ruptel is aimed to prevent crosslinking at suggested temperatures of anywhere from room temperature to 80° C., noting that crosslinking at high temperature appears to suggest that such action should be avoided. The present process permits the crosslinking to take place with resultant loss in tensile strength, but reverses this by autoclaving, either at the time of manufacture or at a later date. This process is distinctly different than the Ruptel process where no crosslinking occurs and can be used with fast dry cure techniques where wet cure methods destroy the effectiveness of the dry cure treatment as shown in the Table.

Fabric treated by water soluble aminoplast textile resins show excellent resistance to cellulosic microorganisms, however none of them have resistance to non-cellulosic fungi. As a result, resin finished cotton will support the surface growth of other fungi where the source of food is not the cotton fibers but rather from an external source such as oil, dirt or soil of some undetermined nature and thus lose the aesthetic appearance of the fabric.

Experiments show that resin treated cotton duck that has undergone autoclaving surprisingly shows greater resistance to surface growth than does the fabric treated by the regular Southern Regional process. This is also an advantage over Ruptel’s process since it has been found necessary to add a fungicide to the fabric to prevent surface growth, although the Cyansta Tuff finish claims to offer resistance to surface growing fungi.

In Ruptel’s process, as well as in the St-Tuff finish care must be exercised to protect the fabric or yarn against water drops or splashes. During the wet fixation process when steam is used, condensed water is constantly being formed and must be removed by periodic opening of traps, but at the same time care must be exercised to prevent the excess loss of steam. The condensation of water on fabric or yarn in wet fixation will retard the fixation with the resulting migration of the resin. Also, if the material dries out locally or the material comes in contact with metal parts it will result in local drying which results in dry curing and a loss in tensile strength. This is also applicable to the Cyansta St-Tuff finish.

This process circumvents these disadvantages. The fabric or yarn is padded as previously described and the material is dried uniformly with a minimum of resin migration. Once the resin is dried, it is fixed and is not removed to any appreciable mount by subsequent autoclaving. Thus, resin migration is prevented and there is no need to control the condensation of steam in this process.

The salient features of this process that are considered important are as follows:

(a) The treatment definitely reverses the tensile loss associated with the heat curing process as shown in the table above;
(b) Experiment shows that the fixation of the resin by the wet fixation is not more complete than the dry heat fixation followed by two minutes autoclaving;
(c) The durability of the conversion of the fabric is definitely proven in that this process conserves the fabric after approximately one year's soil burial as shown in the foregoing table;
(d) Tests also shown that the wet fixation process does not impart the degree of resistance as found by this process when applied to SRRL procedures.
(e) The time advantage is important in that the wet fixation process using steam under pressure requires thirty minutes exposure whereas the present procedure requires only a total of six to eight minutes, i.e., four to six minutes dry curing plus two minutes autoclaving. This represents a 70-80% savings in processing time, required to provide the desired end product and the time advantage is even greater if the wet cure process is used at room temperature where the curing is a matter of one to four days.

The treatment of this process and its accompanying advantages have been described in detail.

What is claimed is:

1. The process which comprises treating cellulose textile material with an aminoplast textile resin and an acidic catalyst, dry curing said textile resin on the textile material at high temperatures whereby the cellulose textile is...
cross-linked with said resin, the original tensile strength of the cellulose textile material is reduced and said resin cured textile is resistant to microbiological deterioration and weather; heating said resin cured textile material with steam at a temperature of about 252°F to about 255°F, at a pressure of about 16 to 18 lbs. per sq. in. for a period of about 2 to 20 minutes whereby said resin cured textile has its original loss in tensile strength decreased and its resistance to loss of tensile strength through microbiological deterioration is further increased.

2. The process of claim 1 wherein said aminoplast textile resin is trimethylol melamine.

3. The process of claim 2 wherein said acidic catalyst is formic acid.

4. The process which comprises treating scoured cellulose textile material by padding it with a solution consisting of about 17% trimethylol melamine, about 20% acid catalyst and about 63% water, passing said padded cellulose textile material through a dry oven at about 80°C, curing said dried textile material at about 140°C, whereby the cellulose textile is cross-linked by the trimethylol melamine, the original tensile strength of the cellulose textile material is reduced and said resin cured textile is resistant to microbiological deterioration and weather;

heating said resin cured textile material with steam at a temperature of about 252°F to about 255°F, at a pressure of about 16 to 18 lbs. per sq. in. for a period of about 2 to 20 minutes whereby said resin cured textile has its original loss in tensile strength decreased and its resistance to loss of tensile strength through microbiological deterioration is further increased.

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H. WOLMAN, Assistant Examiner.