United States Patent [19]

Vail et al.

[11] **3,877,872**

[45] **Apr. 15, 1975**

[54] **PROCESS FOR IMPROVING ABRASION RESISTANCE OF RESILIENT FABRICS AND THE PRODUCT PRODUCED**

[75] Inventors: **Sidney L. Vail**, New Orleans, La.; **Alvin H. Young**, New York, N.Y.; **Gerald B. Verburg**, Metairie, La.

[73] Assignee: **The United States of America as represented by the Secretary of Agriculture**, Washington, D.C.

[22] Filed: **Oct. 6, 1972**

[21] Appl. No.: **295,778**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 772,386, Oct. 31, 1968, abandoned.

[52] **U.S. Cl.** **8/183;** 8/115.6; 8/186; 8/187

[51] **Int. Cl.** **D06m 1/00**

[58] **Field of Search** 8/115.6, 116.4, 181, 183, 8/186, 187

[56] **References Cited**

UNITED STATES PATENTS

3,434,794	3/1969	Tovey	8/116.4 X
3,451,763	6/1969	Weiss	8/116.4 X
3,658,458	4/1972	Gale	8/116.4 X

Primary Examiner—Stephen J. Lechert, Jr.

Attorney, Agent, or Firm—M. Howard Silverstein; Max D. Hensley

[57] **ABSTRACT**

Wet fixation of N-methylol resins to produce cotton fabrics suitable for durable press may be achieved through the use of inert additives in the fixation step. The fixation step may be carried out in conventional equipment used for drying textiles. The inert additive apparently prevents collapse of the fiber during the fixation-drying step.

4 Claims, No Drawings

PROCESS FOR IMPROVING ABRASION RESISTANCE OF RESILIENT FABRICS AND THE PRODUCT PRODUCED

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This is a continuation-in-part of application Ser. No. 772,386, now abandoned, filed Oct. 31, 1968.

The search for improved methods of treatment of cotton to produce commercially acceptable durable-press fabrics has resulted in several new processes. One of the more promising, a wet-fixation process, was first introduced by the National Cotton Council of America in 1966 [Textile Research Journal 37, 70 (1967)]. It involves the fixation of a polymer-former and a cross-linker to cotton fabric under aqueous, acidic conditions. In this laboratory process the fabric, padded with the solution of reagents at a pH of 2, is heated in a sealed container (plastic bag) to achieve fixation of the resins. The first or fixation step appears to be the more important phase of the process. Part of the resin content is firmly fixed in the cotton fibers and the fabric, after rinsing and application of catalysts and softener, can be used in the production of durable-press garments.

A major advantage of the process is that an essentially odorless, sensitized fabric is produced for use in the manufacture of durable-press garments. In addition, the cured fabrics are smooth drying with less impairment of tearing strength and Stoll flex abrasion than conventionally treated fabrics with equivalent smooth-drying properties.

The purpose of the present study is to improve the process in a practical sense. Laboratory procedures have been studied which are potentially more adaptable to commercial finishing. More specifically, this application deals mainly with a major process variation of the treatment, i.e., fixation of the resins in a semi-dry state in the presence of an inert additive. The fixation step, as described in this invention, may be carried out using conventional equipment used for drying textiles. The fixation can be carried out rapidly in an open state and no bag or container is required. Further, the amount of resin required on the fabric is much lower than conventional treatments, i.e., resins add-ons in this invention are from about 3 to 6 percent.

These and some of the other advantages of this process are seen in the following general description.

1 Cellulosic fabric is padded through a resin bath at a pH of about 2 which contains 10–20 percent of a methylated methylolmelamine (hereafter abbreviated MMM), 5–20 percent of another cross-linking agent, and 10–20 percent of an inert additive.

2 In the fixation step, the wet fabric is partially dried in an oven to remove part of the water present. Time and temperature for this step will depend upon the weight of the fabric used. Satisfactory conditions for a 3.0–3.5 oz. printcloth are three minutes at 58°C.

These conditions must be such that the resin add-on (calculated after step 3) is less than 8 percent. Also these conditions must be such that a high degree of polymerization of the reactants is not achieved, i.e., the materials fixed in the fabric must be highly capable of further crosslinking of the cellulose. Conditions which favor the polymerization reaction at this point produce a boardy fabric which cannot be used to produce a durable press fabric with acceptable strength and resistance to abrasion.

3 The partially dried fabric is neutralized, washed, and dried.

4 Curing catalyst and softeners (or other auxiliaries) are added to the fabric in a conventional manner.

5 Fabric is dried and treated as a sensitized fabric for durable press.

Many MMM resins are satisfactory for this process. However, those resins which contain from at least one to six methoxymethyl groups and one or two methylol groups (where possible) appear to be preferred. The methylation of the methylolmelamines should be carried out under conditions which keep polymerization at a minimum.

The second crosslinking agent can be selected from a number of agents but N,N-dimethylol carbamates or N,N'-dimethylol dihydroxyethyleneurea (DMDHEU) generally are preferred.

Inert additives were selected from a group of materials which were expected to keep the cellulosic fiber (cotton, for example) in a swollen state. Such materials include tetraethylene glycol dimethyl ether (abbreviated TDM). Zinc nitrate or magnesium chloride has been found to be satisfactory as curing catalyst. Emulsified polyethylene was used as softener when a softener was desired.

Valko, et al. [Textile Research Journal 37, 253 (1967)] have recently discussed the use of nonreactive and co-reactive additives for the purpose of obtaining an improved abrasion resistance-wrinkle-recovery angle relationship. Our work with the same two-component system (melamine plus cross-linker) was performed under different conditions than those used by Valko and has produced different effects. A highly wrinkle-resistant, abrasion-resistant cotton fabric can be obtained from the fixation of a two-component system which has a swelling agent present. The aqueous resin mixture-TDM solution at pH of about 2, is padded onto cotton fabric, and the wet fabric is heated in an oven until it is barely moist to the hand. From this point on, it is treated in the same manner as any other wet-fixed fabric. Our process is different from Valko's double cure of two-component systems in at least two important respects: (1) A higher percentage of reactants are required, and (2) the fixation conditions or "first cures" are much milder, e.g., 58°C. for 3–4 minutes rather than 80°C. for 15 minutes. For simplicity the process of this invention will be called "moist fixation."

Table I compares various fixation conditions and their effect upon the physical properties of the fixed and the cured fabric.

TABLE I

Procedures and Pad Bath Concentrations as in:	Fixation Conditions	Add-on (%)	Abrasion Resistance (% of orig.)	Wrinkle Recovery Angle (W+F) (deg.)	Tearing Strength (% of orig.)
Example 2	15 min/82°C	17.8	19	285	26
Example 1	15 min/82°C	16.1	16	290	27
Example 1	10 min/75°C	15.4	30	290	36
Example 1	3 min/58°C	4.0	121	253	60

Fixation for 15 minutes at 82° provides the equivalent of a harsh, conventional pad-dry-cure finish. Abrasion resistance of the cured fabric is very poor. The milder fixation conditions of 3 minutes at 58° provides a sensitized fabric which can be used to produce an abrasion and wrinkle-resistant fabric with only a moderate add-on of resin. The moderate wrinkle resistance can be improved through the use of more reagents and/or use of softeners as shown in Table II.

TABLE II

Procedures and Pad Bath Concentrations as in:	Fixation Conditions	Abrasion Resistance (% of orig.)	Wrinkle Recovery Angle (W+F) (deg.)	Tearing Strength (% of orig.)
Example 3	3 min/58°	114	285	98
Example 4	6 min/50°	72	295	82

The effects of the use of polyurethanes (an elastomer) in the various treatments are noted in Table III. The polyurethane was obtained from Wyandotte Chemicals Corporation and was identified as E-406A. The material may be further described as anionic, emulsifiable, high molecular weight polymers that form strong elastic films upon drying and heat-fusing the polymer particles at elevated temperatures.

TABLE III

Procedures and Pad Bath Concentrations as in:	Fixation Conditions	Abrasion Resistance (% of orig.)	Wrinkle Recovery Angle (W+F) (deg.)	Tearing Strength (% of orig.)
Example 5*	3.5 min/58°	154	271	92
Example 6	3.5 min/58°	311	293	98
Example 7	3.5 min/58°	262	299	96

*No polyurethane pretreatment

In Examples 6 and 7 the polyurethane was applied to the cotton fabric before moist fixation. However, if the polyurethane emulsion is compatible with the softener-curing catalyst system, it can be added at this point. The polyurethane is particularly useful in situations where the wrinkle recovery angles of the treated fabrics from a process are in need of being increased. If the polyurethane (or other elastomer) is used prior to moist fixation, then the elastomer must be able to resist hydrolysis under the acidic (pH=2) conditions of the pad bath containing the polymer-formers and cross-linkers.

The processes of this invention can be used to treat substantially any hydrophilic fibrous cellulosic material (including blends) such as cotton, rayon, ramie, jute, and the like.

The following examples are given by way of illustration and not by way of limitation of the invention. The detailed procedures given below in the examples are illustrative, and are not the only or specific conditions for the production of an acceptable finished textile. Many variations or additions within these procedures can be made, as will be readily apparent to those skilled in the art. In the examples, all parts and percentages are by weight unless noted otherwise. The fabrics were tested by the following methods: Wrinkle recovery angle, Monsanto method, American Society for Testing Materials (ASTM) test D 1295-60T; tearing strength, Elmendorf method, ASTM test D 1424-63, Stoll flex abrasion resistance, ASTM test D 1175-64T. Both abrasion and tearing strength are reported as percent of the original, untreated fabric which had been laundered once. This is noted in the tables as "percent of orig.".

EXAMPLE 1

An 80 × 80 cotton printcloth (3.4 oz/sq. yard), which had been desized, scoured, and bleached, was padded in the usual manner with two dips and two nips in the following aqueous pad bath which had been adjusted to pH 2 with hydrochloric acid:

First Pad Bath

Reagent	Percent
MMM	10
DMDHEU	9
TDM	10

The wet fabric was then pinned on a pin frame and heated under the fixation conditions shown in the tables. Following fixation the fabric was washed immediately to remove the acid and any unreacted materials and then dried. The "fixed" fabric was then padded as before in an aqueous pad bath with the following composition:

Second Pad Bath

Reagent	Percent
Magnesium chloride hexahydrate	4

The wet fabric was again pinned on a pin frame and dried in an oven at 60°C. for seven minutes. Final curing of the resins was obtained in a second oven by heating the fabric on a pin frame for three minutes at

160°C. The fabric was washed and dried prior to testing. See the appropiate table for testing results.

EXAMPLE 2

Same as Example 1 except the concentration of TDM in the first pad bath was 20 percent.

EXAMPLE 3

The procedures were the same as in Example 1; however, the pad baths had the following compositions:

First Pad Bath

Reagent	Percent
MMM	20
DMDHEU	20
TDM	20

Second Pad Bath

Zinc nitrate hexahydrate	0.5
Polyethylene solids	1.0

EXAMPLE 4

Same as Example 3 except the second pad bath had the following composition:

Second Pad Bath

Reagent	Percent
Magnesium chloride hexahydrate	4.0
Polyethylene solids	2.0

EXAMPLE 5

Same as Example 4 except a seven ounce twill fabric was used instead of the printcloth and the percentage of magnesium chloride hexahydrate in the second pad bath was 2.0 percent

EXAMPLE 6

Same as Example 5 with the following changes:

The fabric was given a pretreatment prior to padding in a second pad bath. In this pretreatment the fabric was padded with an aqueous emulsion containing 12 percent polyurethane (E-406A, supplied by Wyandotte Chemicals Corporation) and the wetted fabric was dried for ten minutes at 60°C.

EXAMPLE 7

Same Example example 6 except that the second pad bath contained:

Second Pad Bath

Reagent	Percent
MMM	20
Dimethylol isopropyl carbamate	20
TDM	20

We claim:

1. A process for treating a cellulosic fabric to produce a commercially acceptable durable-press fabric which process consists of:

a. padding the cellulosic fabric through a resin bath at a pH of about 2 which bath contains from about 10 to 20 weight percent of a methylated methylolmelamine, from about 5 to 20 weight percent of a crosslinking agent selected from a group consisting of N,N-dimethylol carbamates and N,N′-dimethylol dihydroxyethyleneurea and from about 10 to 20 weight percent of tetraethylene glycol dimethyl ether,

b. heating the padded cellulosic fabric in an open state at a temperature of about 58° C. for a period of about 3 minutes to permit unrestrained evaporation of moisture from said fabric and, without any further heating, then neutralizing, washing and drying the cellulosic fabric,

c. padding the washed and dried cellulosic fabric from step (b) with an aqueous solution free of crosslinking agent and containing from about 0.5 to 4.0 weight percent of an acid catalyst selected from a group consisting of magnesium chloride hexahydrate and zinc nitrate hexahydrate and from about 0 to 2 weight percent of emulsified polyethylene,

d. drying the cellulosic fabric from step (c) for a period of about 7 minutes at a temperature of about 60° C., and

(e) curing the fabric from step (d) for a period from about 3 to 5 minutes at a temperature of about 160° C.

2. A process for treating a cellulosic fabric to produce a commercially acceptable durable-press fabric which process consists of:

a. padding a cellulosic fabric in an aqueous solution containing about 12 weight percent of an anionic, emulsifiable, high molecular weight polyurethane,

b. drying the padded cellulosic fabric for a period of about 10 minutes at a temperature of about 60° C.,

c. padding the cellulosic fabric from (b) through a resin bath which bath contains from about 10 to 20 weight percent of a methylated methylolmelamine, from about 5 to 10 weight percent of a crosslinking agent selected from a group consisting of N,N-dimethylol carbamates and N,N′-dimethylol dihydroxyethyleneurea and from about 10 to 20 weight percent of tetraethylene glycol dimethyl ether,

d. heating the cellulosic fabric from (c) in an open state at a temperature of about 58° C. for a period of about 3 minutes to permit unrestrained evaporation of moisture from said fabric and, without any further heating, then neutralizing, washing and drying the cellulosic fabric,

e. padding the washed and dried cellulosic fabric from step (d) with an aqueous solution free of crosslinking agent and containing from about 0.5 to 4.0 weight percent of an acid catalyst selected from a group consisting of magnesium chloride hexahydrate and zinc nitrate hexahydrate and from about 0 to 2 weight percent of emulsified polyethylene,

f. drying the cellulosic fabric from step (e) for a period of about seven minutes at a temperature of about 60° C., and

g. curing the fabric from step (f) for a period from about 3 to 5 minutes at a temperature of about 160°.

3. The product produced by the process of claim **1.**

4. The product produced by the process of claim **2.**

* * * * *