United States Patent

Wunder et al.

[15] **3,639,157**

[45] **Feb. 1, 1972**

[54] PROCESS FOR FINISHING TEXTILE MATERIALS WITH A POLYMER OF A VINYL COMPOUND AND THE REACTION PRODUCT OF A POLYOL AND AN ORGANIC POLYISOCYANATE

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[22] Filed: **July 18, 1968**

[21] Appl. No.: **750,999**

Related U.S. Application Data

[63] Continuation of Ser. No. 438,102, Mar. 8, 1965, abandoned.

[30] **Foreign Application Priority Data**

Apr. 7, 1964 Germany ..... F 42239

[52] **U.S. Cl.** ..... **117/139.5 A**, 117/138.8 A, 117/141, 117/143 A, 117/145, 117/161 UC, 117/161 R, 260/29.6 R, 260/29.6 MN

[51] **Int. Cl.** **C08j 1/44**, C10m

[58] **Field of Search** ..... 117/139.4, 139.5 R, 141, 143 R, 117/145, 161 KP, 161 UC, 161 UT; 260/29.6 R, 29.6 H, 29.6 HN, 86.1 N, 859; 8/116.2, 127.6

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[57] **ABSTRACT**

Textile materials which have been treated with an aqueous liquor containing a polymer of a vinyl compound and the reaction product of excess organic polyisocyanate with a polyol. The textile materials have improved crease resistance.

10 Claims, No Drawings

PROCESS FOR FINISHING TEXTILE MATERIALS WITH A POLYMER OF A VINYL COMPOUND AND THE REACTION PRODUCT OF A POLYOL AND AN ORGANIC POLYISOCYANATE

This application is a continuation of Ser. No. 438,102, filed Mar. 8, 1965, and now abandoned.

This invention is concerned with a process for the production of finishes of textile materials and in particular with the production of urethane finishes of textile materials which have improved properties.

It has been proposed heretofore to coat textiles with both polyester and polyether urethanes for various purposes including the shrinkproofing of wool and the like. However, the heretofore known coatings and finishes have not been entirely satisfactory because the heretofore know textile finishing process often leads to unsatisfactory tear resistance in the finished textile material. Furthermore, the heretofore known textiles are often unsatisfactory with respect to crease resistance, abrasion resistance and retention of shape.

It is therefore an object of this invention to provide improved finished textile materials. Another object of this invention is to provide textile materials and finishes therefore which have improved tear strength. A further object of this invention is to provide improved textile materials which have improved crease resistance, abrasion resistance and improved ability to retain their shape. Still another object of this invention is to provide a method of finishing textiles and the finished textiles which may be based on cotton, cellulose, wool, silk, polyamides, polyurethane, polyesters, polycarbonate, polyacrylonitrile, polypropylene and the like.

The foregoing objects and others which will become apparent from the following description are accomplished generally speaking by providing textile materials which have been finished by treating them with polymers or copolymers prepared from vinyl monomers as well as reaction products which contain isocyanato groups. Therefore, the present invention contemplates textile materials which are treated with an aqueous liquor which contains polymers or copolymers prepared from vinyl or divinyl monomers as well as reaction products containing isocyanato groups prepared from compounds having at least two hydroxyl groups and a molecular weight of about 500 to about 6,000 and an organic polyisocyanate.

The present invention therefore contemplates improved textile materials of natural or synthetic origin which have improved crease resistance, abrasion resistance, and ability to retain their shape. The textile material which may be treated in accordance with the present invention may be based on cotton, regenerated cellulose, wool, silk, polyamides, polyurethane, polyesters, polycarbonates, polyacrylonitrile, polypropylene and the like. The process of the invention is particularly noteworthy in that the tear resistance of the textile material treated according to the invention is either unaffected or slightly affected by the process of the present invention.

Any suitable vinyl or divinyl monomer may be used for incorporation into the liquor to be applied to the textile material in accordance with the present invention including for example ethylene, propylene, vinyl chloride, vinyl acetate, vinyl ethers such as vinyl ethyl ether, also styrene or divinylbenzene, butadiene, isoprene or chloroprene as well as alpha, beta-unsaturated carboxylic acids such as acrylic acid and methacrylic acid and their nitriles, esters and amides, Polymers having groups capable of a reaction with isocyanates are generally preferred; these include for instance the polymers or copolymers prepared from acrylic acid, methacrylic acid, their hydroxyalkyl esters or amides, as well as the copolymers obtainable when N-methylol-acrylamide, N-methylol-methacrylamide or their derivatives prepared by a reaction with alcohols containing at least one further functional group are copolymerized with other olefinically unsaturated compounds, for instance, in accordance with the process of French Pat. No. 1,328,255.

Any suitable polyol preferably having a molecular weight of from about 500 to about 6,000 may be used including polyhydric polyalkylene ethers, polyhydric polyesters and the like. Specific examples of polyhydric polyalkylene ethers are for example, polyethylene glycol-1000, polypropylene glycol-2000, polybutylene glycol-1500, polyhexylene glycol-2000 and the like. Specific examples of polyesters are those obtainable from dicarboxylic acids such as succinic acid, adipic acid, sebacic acid, maleic acid and the like and polyhydric alcohols such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butane diol, neopentyl glycol, 1,10-decane diol and the like. The most preferred compounds are those which have a molecular weight within the range of from about 800 to about 3,500 and whose hydroxyl number is 30 to 250. The most preferred acids and alcohols are those which have from two to 10 carbon atoms.

Any suitable polyisocyanate may be used, but it is preferred to use an aliphatic or cycloaliphatic diisocyanate such as, for example, tetramethylene diisocyanate, hexamethylene diisocyanate, 1,4-cyclohexane diisocyanate, 4,4'-dicyclohexyl methane diisocyanate, and also 2,4- and 2,6-hexahydrotoluylene diisocyanate. Aromatic diisocyanates are also suitable, such as p-phenylene diisocyanate and 2,4- or 2,6-toluylene diisocyanate, as well as triisocyanates such as the reaction product of the formula $OCN-(CH_2)_6-N[-CONH-(CH_2)_6-NCO]_2$ obtainable from 3 mols of hexamethylene diisocyanate and 1 mol of water.

The preparation of the reaction products with free isocyanate groups is straightforward. One merely combines an excess of the organic isocyanate based on the hydroxyl groups of the polyol and allows the mixture to react. It is preferred to use a slightly elevated temperature to promote the reaction and the polyols preferably having from two to six hydroxyl groups while organic diisocyanates are preferred. The product containing the free isocyanate groups are then mixed with the polymers or copolymers preferably in the ratio of 0.25 to 4 parts of the vinyl or divinyl monomers per part of the compound containing free isocyanate groups. This product may then be combined with sufficient water to make an aqueous liquor having 5 to 70 percent by weight of the total polymer including the polymers based on the vinyl or divinyl compounds and those based on the reaction product which contain isocyanate groups. It is also possible to use the isocyanate groups by applying them in the form of the bisulphite addition products.

The treatment of the textile materials with the aqueous liquor can be carried out by impregnating the textile material with the aqueous liquor, for example, by submerging the textile in the aqueous solution of polymers and then squeezing off until their increase in weight amounts to 60 to 100 percent. The textile materials are thereafter allowed to dry. It is also possible to spray a textile material with aqueous liquor and then dry the textile material. It is preferred to store the treated material at room temperature of about 20° to 30° C. for several days after the treatment.

Any suitable textile material including those of cotton, regenerated cellulose, wool, silk, nylon, spandex, polyester fibers, polycarbonates, polyacrylonitrile, polypropylene and the like may be used.

As pointed out above, the textile materials are improved particularly with regard to crease resistance, abrasion resistance and retention of shape. They may be used for the production of clothing, various coverings and the like.

The invention is further illustrated by the following examples in which parts are by weight unless otherwise specified.

EXAMPLE 1

A cotton fabric is impregnated with an aqueous liquor which contains, per liter, about 200 grams of a 40 percent aqueous dispersion of a copolymer made from about 85 parts of ethyl acrylate and about 15 parts of beta-hydroxypropyl methacrylate as well as about 330 parts of the emulsion of an

reaction product having isocyanate groups described below. The fabric is then squeezed off until its increase in weight amounts to about 100 percent, and dried at about 80° to 110° C. for about 2 to 5 minutes.

The resultant finishing effect is evident from the following table which also reproduces the corresponding technological data obtained for the same fabric by means of the known crease-resistance agent dimethylol-ethylene urea.

Table

	Untreated fabric	Fabric treated according to the invention	Fabric treated with dimethylol ethylene urea
Dry creasing angle: degrees			
Warp	48	135	138
Weft	59	138	140
Wet creasing angle: degrees			
Warp	62	146	126
Weft	80	138	128
Loss of tear resistance	—	1.5%	35.2%
Abrasion resistance according to Schopper	190 revs.	620 revs.	130 revs.

Finishing with the crease resistance agent dimethylol-ethylene urea was carried out in the usual manner by impregnating the fabric with an aqueous liquor containing, per liter, about 100 grams of dimethylol-ethylene urea as well as about 10 grams of magnesium chloride; the fabric was then squeezed off until its increase in weight amounted to about 100 percent, and heated at about 150° C. for about 5 minutes.

The above-mentioned emulsion of the reaction product containing isocyanate groups was prepared as follows:

About 3,000 grams of a polypropylene glycol having a molecular weight of about 2,000, an —OH number of about 55.5 and an acid number <0.5 were heated with about 535 grams of hexamethylene diisocyanate at about 110° C. for about 2 hours and thereafter at about 130° to 140° C. for another about 1½ hours. An emulsion was then prepared from about 300 grams of the resultant reaction product, whose content of free isocyanate groups amounts to about 3.9 percent, about 300 grams of ethyl acetate and about 400 grams of water with the addition of about 5 grams of lauryl sulphate.

EXAMPLE 2

A cotton fabric is impregnated with an aqueous liquor which contains, per liter, about 200 grams of a 40 percent aqueous dispersion of a copolymer made from about 85 parts of butyl acrylate, about 10 parts of butadiene and about 5 parts of methacrylic acid amide as well as about 330 grams of the emulsion of the reaction product having isocyanate groups described in example 1. The fabric is thereafter squeezed off until its increase in weight amounts to about 100 percent and dried at about 80° to 100° C. for about 4 minutes.

The advantageous effect obtained on the fabric treated in the manner described and stored at room temperature for about 5 days are evident from the following table:

	Dry creasing angle		Wet creasing angle		Loss of tear re-sistance
	a	b	a	b	
Untreated fabric	48°	59°	62°	80°	—
Fabric treated according to the invention	130°	150°	135°	132°	7%

EXAMPLE 3

A rayon staple fabric is impregnated with an aqueous liquor which contains, per liter, about 200 grams of a 38 percent aqueous dispersion of a copolymer made from about 65 parts of vinyl chloride and about 35 parts of ethylene as well as about 330 grams of the emulsion of an reaction product having isocyanate groups described in example 1. The fabric is then squeezed off until its increase in weight amounts to about 100 percent and dried at about 80° to 100° C. for about 4 minutes.

The fabric finish is largely crease resistant. At the same time, its abrasion resistance has been considerably increased. This is evident from the following table which also specifies the abrasion resistance result obtained on a rayon staple fabric treated with dimethylol-ethylene urea by the method described in example 1:

	Abrasion resistance according to Schopper
Untreated fabric	470 revs
Fabric treated according to the invention	640 revs
Fabric treated with dimethlol-ethylene urea	230 revs

EXAMPLE 4

A cotton fabric is impregnated with an aqueous liquor which contains, per liter, about 200 grams of the 40 percent aqueous dispersion of a copolymer described in example 2 as well as about 330 grams of the emulsion of an reaction product having isocyanate groups described below. The fabric is then squeezed off until its increase in weight amounts to 100 percent, and dried at about 80° to 100° C. for about 4 minutes.

The advantageous effects obtained on the fabric treated in the manner described and stored at room temperature for about 5 days are evident from the following table:

	Dry creasing angle		Wet creasing angle		Loss of tear re-sistance
	a	b	a	b	
Untreated fabric	48°	59°	62°	80°	—
Fabric treated according to the invention	130°	123°	143°	138°	2.4%

The above-mentioned emulsion of the reaction product containing isocyanate groups was prepared as follows:

About 600 grams of a branched polypropylene glycol, which was prepared by the propoxylation of trimethylol-propane and has a molecular weight of about 3,000, an —OH number of about 56 and an acid number <0.5, were heated to about 90° C. with about 115 grams of 2,4-toluylene diisocyanate for about 90 minutes. An emulsion was then prepared from about 300 grams of the resultant reaction product, whose content of free isocyanate groups amounts to 4.1 percent, about 300 grams of ethyl acetate and about 400 grams of water with the addition of about 5 grams of lauryl sulphate.

EXAMPLE 5

A rayon staple fabric is impregnated with an aqueous liquor which contains, per liter, about 200 grams of the 40 percent aqueous dispersion of a copolymer described in example 2 as well as about 330 grams of the emulsion of the reaction product having isocyanate groups described below. The fabric is then squeezed off until its increase in weight amounts of about 100 percent, and dried at about 110° C. for about 5 minutes.

The advantageous effects obtained on the fabric treated in the manner described and stored at room temperature for about 5 days are evident from the following table:

	Dry creasing angle		Wet creasing angle	
	i a	b	a	b
Untreated fabric	102°	110°	50°	61°
Fabric treated according to the invention	140°	157°	147°	153°

The above-mentioned emulsion of the reaction product containing isocyanate groups was prepared as follows:

About 1,000 grams of a branched polypropylene glycol, which was prepared by the propoxylation of trimethylolpropane and has a molecular weight of about 3,750, an —OH number of about 45 and an acid number <0.5, were heated with about 135 grams of hexamethylene-diisocyanate for about 2 hours to about 110° C. and subsequently about 1 hour to about 130° C. An emulsion was then prepared from about 300 grams of the resultant reaction product whose content of free isocyanate groups amounts to 2.9 percent, about 300 grams of ethyl acetate and about 400 grams of water with the addition of about 5 grams lauryl sulphate.

EXAMPLE 6

A woolen fabric is impregnated with an aqueous liquor which contains, per liter, about 200 grams of the aqueous dispersion of a copolymer described in example 2 as well as about 200 grams of the emulsion of a reaction product having isocyanate groups described below. The fabric is then squeezed off until its increase in weight amounts to about 100 percent and dried at about 110° C. for about 10 minutes.

The abrasion resistance (repenning) of the fabric treated in the manner described and stored at room temperature for about 4 days amounts to about 1,020 revolutions, whereas the abrasion resistance of the untreated fabric amounts only to about 210 revolutions. The woolen fabric does not tend to felting when washed in a boiling soda alkaline solution; shrinkage is considerably diminished as can be seen from the following table:

	Shrinkage	
a		b
Untreated woolen fabric	18.7%	12.6%
Woolen fabric treated according to the invention	3.1%	1.2%

Pleatings are retained even after repeated washing.

The above-mentioned emulsion of the reaction product containing isocyanate groups was prepared as follows:

About 3,000 grams of the branched polypropylene glycol described in example 4 were heated to about 110° C. with about 535 grams of hexamethylene diisocyanate for about 2 hours. An emulsion was then prepared from about 500 grams of the resultant reaction product, whose content of free isocyanate groups amounts to 3.9 percent, about 100 grams of ethyl acetate and about 400 grams of water with the addition of about 5 grams of lauryl sulphate.

EXAMPLE 7

Silk crape and silken knitted fabric are treated in the manner described in example 6.

The advantageous effects obtained on the textile materials thus treated and stored at room temperature for about 5 days are evident from the following table:

	Dry creasing angle		Wet creasing angle		Abrasion resistance (repenning)
A. Silk crepe	a	b	a	b	
1. Untreated	140°	151°	82°	62°	60 revs.
2. Treated according to the invention	164°	170°	148°	146°	210 revs.
3. Untreated and washed in a soda alkaline solution	148°	157°	93°	88°	—
4. Treated according to the invention and washed in a soda alkaline solution	175°	171°	156°	144°	—washed
B. Silk knitted fabric					
1. Untreated	143°	148°	112°	131°	40 revs.
2. Treated according to the invention	160°	165°	163°	151°	220 revs.
3. Untreated and washed in a soda alkaline solution	138°	141°	115°	132°	—
4. Treated according to the invention and washed in a soda alkaline solution	152°	160°	152°	160°	—

EXAMPLE 8

A mixed fabric consisting of about 70 parts of cotton and about 30 parts of fibers of polyterephthalic acid glycol ester are impregnated with an aqueous liquor which contains per liter about 100 grams of the 40 percent aqueous dispersion of a copolymer described in example 2 and about 100 grams of the emulsion of a reaction product having isocyanate groups described in example 6. The fabric is then squeezed off until its increase in weight amounts to about 100 percent and dried at about 110° C. for about 10 minutes.

The advantageous effects obtained on the fabric treated in the manner described and stored at room temperature for about 5 days are evident from the following table:

	Dry creasing angle		Wet creasing angle	
	a	b	a	b
1. Untreated	120°	93°	108°	123°
2. Treated according to the invention	143°	157°	148°	150°
3. Untreated and washed in a soda alkaline solution	92°	88°	126°	131°
4. Treated according to the invention and washed in a soda alkaline solution	150°	142°	153°	148°

Fabrics made from fibers of polyterephthalic acid glycol ester or polycaprolactam or mixed fabrics made from equal parts of fibers of polyacrylonitrile and polyterephthalic acid glycol ester are treated in the same manner.

The advantageous effects obtained on the fabrics thus treated and stored at room temperature for about 5 days are evident from the following table:

	Dry creasing angle		Wet creasing angle		Abrasion resistance (repenning)
	a	b	a	b	
A. Fabrics made from fibers of polyterephthalic acid glycol ester					
1. Untreated	135°	146°	140°	148°	530 revs.
2. Treated according to the invention	168°	165°	163°	164°	1060 revs.
3. Untreated and washed in a soda alkaline solution	154°	158°	140°	143°	—
4. Treated according to the invention and washed in a soda alkaline solution	170°	165°	162°	166°	—
B. Fabrics made from fibers of polycaprolactam					
1. Untreated	64°	66°	44°	62°	220 revs.
2. Treated according to the invention	170°	170°	147°	167°	530 revs.
3. Untreated and					

washed in a soda	72°	83°	87°	86°	—
4. Treated according to the invention and washed in a soda alkaline solution	180°	180°	165°	168°	—
C. Mixed fabrics made from polyacrylonitrile and polyterephthalic acid glycol ester					
1. Untreated	140°	155°	132°	142°	380 revs.
2. Treated according to the invention	170°	171°	152°	157°	720 revs.
3. Untreated and washed in a soda alkaline solution	145°	157°	135°	140°	—
4. Treated according to the invention and washed in a soda alkaline solution	172°	175°	163°	160°	—

It is to be understood that any other suitable vinyl compound, isocyanato terminated compound, textile material or the like could have been used in the foregoing examples provided that the teachings of this disclosure are followed since the examples are given for the purpose of illustration.

Although the invention has been described in considerable detail for the purpose of illustration, it is to be understood that variations can be made by those skilled in the art without departing from the spirit of the invention and scope of the claims.

What is claimed is:

1. An aqueous composition consisting essentially of water and about 5 to 70 percent by weight of a mixture of (a) about 0.25 to about 4 parts by weight of a polymer prepared from a vinyl monomer and containing groups capable of reacting with isocyanate groups and (b) about 1 part by weight of a free isocyanate group containing reaction product of a compound of molecular weight 500–6,000 having at least two hydroxyl groups with a stoichiometric excess of an organic polyisocyanate.

2. The composition of claim 1 wherein the component having at least two hydroxyl groups is a polyhydric polyalkylene ether or a polyhydric polyester having a molecular weight of 800 to 3,500 and a hydroxyl number of 30 to 250.

3. The composition of claim 1 wherein the organic polyisocyanate is an aliphatic or cycloaliphatic diisocyanate.

4. A method for finishing textile material comprising treating a textile material with an aqueous liquor consisting essentially of water and about 5 to 70 percent by weight of a mixture of (a) about 0.25 to about 4 parts by weight of a polymer prepared from a vinyl monomer and containing groups capable of reacting with isocyanate groups and (b) about 1 part by weight of a free isocyanate group containing reaction product of a compound of molecular weight 500–6,000 having at least two hydroxyl groups with a stoichiometric excess of an organic polyisocyanate, and drying the treated textile material.

5. The method of claim 4 wherein the treated and dried textile material is submitted to the further step of storage at room temperature.

6. The method of claim 4 wherein the textile material is selected from the group consisting of cotton, regenerated cellulose, wool, silk, polyamide, polyurethane, polyester, polycarbonate, polyacrylonitrile and polypropylene.

7. The method of claim 4 wherein the drying is accomplished at 80° to 110° C.

8. The textile material prepared by the process of claim 4.

9. A method for finishing textile materials comprising treating a textile material with an aqueous liquor consisting essentially of water and an amount effective to impart improved physical properties to the textile material when coated thereon of a mixture of (a) about 0.25 to about 4 parts by weight of a polymer prepared from a vinyl monomer and containing groups capable of reacting with isocyanate groups and (b) about 1 part by weight of a free isocyanate group containing reaction product of a compound of molecular weight 500–6,000 having at least two hydroxyl groups with a stoichiometric excess of an organic polyisocyanate, and drying the treated textile material.

10. The textile material prepared by the process of claim 9.

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