United States Patent

Schafer et al.

[15] **3,653,957**

[45] **Apr. 4, 1972**

[54] TEXTILE FIBER MATERIAL TREATED WITH A FINISHING COMPOSITION

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[22] Filed: **Dec. 18, 1968**

[21] Appl. No.: **784,934**

[30] **Foreign Application Priority Data**

Sept. 25, 1968 Germany ..... P 17 94 221.1

[52] **U.S. Cl.** ..... **117/141,** 117/138.8 F, 117/138.8 N, 117/138.8 UA, 117/161 KP

[51] **Int. Cl.** **B32b 27/04,** D06m 3/02, C09d 3/60

[58] **Field of Search** ..... 117/141, 161 KP, 150, 138.8 F, 117/138.8 N, 138.8 UA; 8/128, 127.6; 260/77.5 AP, 77.5 AT

[56] **References Cited**

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FOREIGN PATENTS OR APPLICATIONS

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[57] **ABSTRACT**

Textiles with improved handle, produced by applying a mixture of (A) a reaction product having isocyanate groups and (B) a reaction product of a hydroxy compound and an aliphatic monoisocyanate, wherein (B) can optionally be alkylated or further reacted with an isocyanate prior to mixing with (A).

3 Claims, No Drawings

TEXTILE FIBER MATERIAL TREATED WITH A FINISHING COMPOSITION

This invention relates to a textile finishing process which comprises impregnating textile materials with reaction products having free or blocked isocyanate groups wherein finishing of the textiles with the isocyanate products occurs in the presence of a softening agent comprising a reaction product of a hydroxy-containing compound and an aliphatic monoisocyanate or the alkylation product thereof.

It has been known to finish fiber materials, especially textiles, by treatment with reaction products bearing free or blocked isocyanate groups which have been produced by reacting organic compounds having at least two active hydrogen atoms and a molecular weight of 500 to 10,000 to 10,000 with polyisocyanates. The treatment is carried out, for example, from organic solvents or from an aqueous solution. Through this treatment the finished textile will attain an increased abrasion resistance, an improved crease behavior and decreased inclination to pilling. Articles made of wool can be finished felt-free by the process which is described in British Pat. Nos. 1,097,516 and 1,062,564. The sorption behavior and the dyeing characteristics of the textiles are generally not deteriorated by this finishing process; however, the handle is deteriorated since the textiles exhibit an undesirable full and hard handle. It has been proposed to eliminate the undesirable handle by employing conventional textile softening agents, e.g., reaction products of fatty acids with polyamines or alkylamines, but these agents do not give a soft handle when the textile finish employs reaction products bearing isocyanate groups. A subsequent treatment to soften the textiles is possible, but it requires an additional work process, adding time and expense to the process. It has further been proposed to use paraffin oil with finishes comprising reaction products bearing free isocyanate groups, but the said oil, while improving handle, deteriorates when applied in high quantities — more than 10 percent based on the reaction product — other effects, for example, the felt-free effect desired when treating woolen articles. Because of these adverse effects, no optimum softening effect can be achieved by use of paraffin oil with the subject finish compositions.

It is therefore a primary object of this invention to devise a process for producing textiles finished with reaction products containing isocyanate groups, which textiles have improved handle.

It is another object of this invention to produce a finishing composition comprising a reaction product containing isocyanate groups and a softening agent which does not adversely affect other properties of the textiles.

These objects and others will become apparent from the following disclosure with preferred embodiments presented by way of illustrative examples.

It has been found that fiber materials finished with reaction products (A) having free or blocked isocyanate groups, such as those produced from a mixture of:

1. organic compounds having at least two active hydrogen atoms and a molecular weight of 500 to 10,000, and

2. polyisocyanates can be finished to feel exceptionally soft to the touch if the finishing treatment is carried out in the presence of reaction products (B) from:

3. compounds bearing at least one hydroxyl group, preferably of a molecular weight of 500 to 3,000, and

4. aliphatic monoisocyanates or the alkylation products of (B).

As compounds (3) bearing at least one hydroxyl group, which are suitable for the production of softeners to be used according to the invention, the following species are illustrative: aliphatic and cycloaliphatic alcohols with one to 22 carbon atoms and their alkylene oxide addition products; diols such as ethylene glycol and propylene glycol, polyalkylene ether, diols, such as polyethylene, polypropylene, polybutylene and polyhexylene glycols; polyols such as propane triol or trimethylol propane; polyalkylene ether polyols such as the reaction products of alkylene oxides, especially of ethylene and propylene oxide with polyols or polyether thioether diols

which can be obtained by condensation of thiodiglycol with itself or with sulfur-free polyols; polyesters, as can be obtained, for example, from aliphatic dicarboxylic acids, such as succinic acid, adipic acid, sebacic acid or maleic acid, and polyalcohols, such as ethylene glycol, diethylene glycol, propylene glycol, butane diol and neopentyl glycol. Preferably, polyalkylene ether polyols, for example, polyalkylene ether triol, such as the addition products of ethylene oxide or propylene oxide to trimethylol propane, are suitable.

As monoisocyanates (4), the following compounds are illustrative of suitable reactants: aliphatic isocyanates with carbon chains of C_4–C_{22}, preferably, however, C_{14}–C_{18}, such as myristyl isocyanate or stearyl isocyanate.

Compounds (1) bearing at least two active hydrogen atoms, preferably in the form of hydroxyl groups, and of a molecular weight of 500 to 10,000, include polyethylene, polypropylene, polybutylene or polyhexylene diols; furthermore, polyesters which can be obtained from aliphatic dicarboxylic acid, such as succinic acid, adipic acid, sebacic acid or maleic acid, and polyalcohols, such as ethylene glycol, diethylene glycol, propylene glycol, butane diol and neopentyl glycol. Also, polyether thioether diols which are obtained through condensation of thiodiglycol can be used.

Compounds (2) are preferably aliphatic and cycloaliphatic diisocyanates, such as tetramethylene diisocyanate, hexamethylene diisocyanate, 1,4-cyclohexane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, as well as 2,4- and 2,6-hexahydrotoluylene diisocyanate, which are herein considered as polyisocyanates. Furthermore, aromatic diisocyanates, such as p-phenylene diisocyanate and 2,4- or 2,6-toluylene diisocyanate, as well as triisocyanate, such as the reaction product of the formula:

$$OCN—(CH_2)_6—N\,[-CONH—(CH_2)_6—NCO]_2,$$

obtainable from 3 moles hexamethylene diisocyanate and 1 mole water, are suitable.

The reaction of the compounds (3) bearing hydroxyl groups with the monoisocyanates (4) takes place, for example, at temperatures of 50°–130° C., preferably at 80°–110° C. The hydroxyl groups of the compounds (3) can be reacted partially or completely with the isocyanates (4). The reaction of the compounds (3) bearing hydroxyl groups can also take place in such a manner that one reacts partially in a first step with monoisocyanates (4) and in a second step the remaining hydroxyl groups are brought to react with polyisocyanates in such a manner that they will result in compounds with free isocyanate groups. For example, polyalkylene ether triols, as obtained by addition of propylene oxide to trimethylol propane, can be reacted in the first stage with stearyl isocyanate at one- or two-thirds of their content of hydroxyl groups. The remaining one- or two-thirds of the residual hydroxyl groups can be reacted in a second stage with hexamethylene diisocyanate.

Likewise, the reaction of the compounds (3) bearing the hydroxyl groups can be carried out in the first stage with long-chain aliphatic isocyanates, such as myristyl or stearyl isocyanate, up to two-thirds of the hydroxyl groups, the remaining portion of hydroxyl groups being brought to react with short-chain aliphatic isocyanates, such as methyl, ethyl, propyl isocyanate or methoxymethyl or methoxyethyl isocyanate. But it is also possible to react the remaining hydroxyl groups with aromatic isocyanates, such as phenyl isocyanate or cyclohexyl isocyanate.

As polymeric reaction products (A) bearing free isocyanate groups which are used for finishing textile materials, for example, to make wool non-felting, should be mentioned for instance the compounds described in German published application No. 1,265,113. These reaction products are made from compounds bearing hydroxyl groups with a molecular weight of 500 to 3,000 and polyisocyanates.

Compounds (A) which have blocked isocyanate groups and with which the softeners of this invention are used are described, for example, in British Pat. No. 1,058,800. As a

blocking agent the following, for example, are suitable: oximes, such as methylethylketoxime, cyclohexanonoxime, acetophenoxime, dimethylketoxime, butyraldoxime, as well as imines, such as ethyleneimine, propyleneimine and 2-methylethyleneimine, alcohols, such as methanol, ethanol, propanol and secondary amines, such diethylamine, morpholine, and dibutylamine.

The above-mentioned reaction products (A) carrying blocked or, preferably, free isocyanate groups, can be applied from organic solvents or aqueous dispersions to finish textiles. If aqueous liquors are used, it is of advantage if the reaction products (A) bearing isocyanate groups are employed together with aqueous dispersions of polymers or copolymers (C) based on vinyl or divinyl compounds.

The polymers or copolymers (C) can be formed from monomers, such as ethylene, propylene, vinyl chloride, vinyl acetate, vinyl ether, additionally styrene or divinyl benzene, butadiene, isoprene or chloroprene and alpha, beta-unsaturated carboxylic acids, such as acrylic acid and methacrylic acid, as well as their nitriles, esters and amides.

As component (C), polymers or copolymers which have groups capable of reaction with isocyanates are preferred. For example, those polymers or copolymers which are produced from acrylic acid, methacrylic acid, their hydroxyalkyl esters or amides or which can be obtained if one copolymerizes N-methylolacrylamide, N-methylolmethacrylamide or their derivatives prepared by the reaction with alcohols containing at least one other functional group, with other olefinic unsaturated compounds.

The application of the reaction products (A), (B) to the textile material can be made from organic solutions, for example, from perchloroethylene or from aqueous liquors, e.g., emulsions.

In aqueous emulsions the alkylation products of (B) are advantageously used. For example, the reaction product (B) of a polyalkylene ether triol of a molecular weight of 3,000, produced from propylene oxide and trimethylol propane, can be reacted with stearyl isocyanate in such a manner that all available hydroxyl groups are brought to react. The reaction product obtained is now reacted further with a methylation agent, such as dimethyl sulfate and alkali, for example, sodium hydroxide, at preferably 50° to 60° C. The product thus obtained can be processed into an aqueous emulsion in the usual manner with the addition of sodium salts of paraffin sulfonic acids, advantageously in mixture with nonionic emulsifiers, such as benzylhydroxybiphenyl polyglycol ether.

The treatment of the textile materials with the reaction product (B) and the reaction product (A), preferably bearing free isocyanate groups but also for (A) bearing blocked isocyanate groups, preferably takes place from organic solvents, such as perchlorethylene, by submerging the textile material in the solution, followed by centrifuging or wringing to remove excess treatment solution. Subsequently, the solvent is removed, for example, with the aid of hot air, for example, air at 80°–110° C.

Treatment of the textile material according to the invention using finishes bearing free isocyanate groups can also be accomplished from an aqueous liquor by submerging and wringing or centrifuging the textile material. In this case, the reaction product from (1) and (2), preferably bearing free isocyanate groups, can be emulsified in water with the sodium salt of a paraffin sulfate. The aqueous emulsion can be mixed with the aqueous dispersion of a polymer or copolymer based on vinyl compounds (C), mentioned above; then aqueous emulsions of novel softeners according to this invention, are added to this aqueous liquor.

The aqueous liquors can likewise contain catalysts, for example, zinc acetate, which speed up the reactions of the isocyanate groups. The textile material treated with the aqueous liquors is dried, as with the organic solvent treatment, with air heated to 80°–120° C., or other removal steps.

In applying the softeners, it is also possible to spray the combined reaction product (A) and softener (B) from organic solvents or from aqueous liquors onto the textile material.

After the heat treatment of the finished textile material with hot air, one can follow this up with a damping step or steam treatment at 100°–105° C. The damping process can be coupled with shaping of the textile material.

The quantities in which the softeners to be used in accordance with the invention are applied may fluctuate within wide limits; generally speaking, quantities of 5–60 percent by weight and preferably 30–50 percent by weight, based on the reaction product (A) bearing the isocyanate groups, have proven suitable.

The reaction product (A) bearing the isocyanate groups to be applied to the textile material is applied in a quantity of, for example, 0.5–15 percent by weight of the textile material, and preferably 1–6 percent by weight. The polymers or copolymers (C) prepared from vinyl compounds are used in quantities of preferably 10–50 percent by weight of the reaction product (A) bearing the isocyanate groups.

The process according to the invention will be used preferably for the finishing of wool and fiber material containing wool. Beyond that, the process can likewise be used for the finishing of silk, of fibers on a cellulose base, synthetic fibers, such as superpolyamides and urethanes, polyacrylonitrile as well as polyester fibers and cellulose tri- and 2.5 acetates, or leather.

It will be seen that in some cases (3) is the same as (1) since the compounds (1) naturally include compounds wherein the two active hydrogen atoms are in hydroxyl groups and wherein the molecular weight ranges from 500 to 3,000. For ease in understanding such a case where (3) is the same as (1) is illustrated in the examples.

The following examples are presented by way of nonlimiting illustration of the invention.

EXAMPLE 1

1,000 g. of a branched polyether of medium molecular weight (3,000 ± 200) and an OH number of 56 ± 3, produced from propylene oxide and trimethylol propane, are reacted with 295 g. of stearyl isocyanate for 2 ½hours at 80° C. and for 1 hour at 110° C. to yield Reaction Product B_1.

3,000 g. of the above-mentioned polyether are heated with 535 g. of a hexamethylene diisocyanate for 2 hours to 110° C., and subsequently another 1 ½hours to 130°–140° C., yielding Reaction Product (A).

Knitted parts made of wool are treated in a liquor which contains 5 g. of the reaction product (B_1) and 8 g. of the reaction product (A) per liter of perchloroethylene. For this purpose, the knitted parts are impregnated at about25° C. for 4 minutes in a rotation drum with the treatment solution. Subsequently, the excess treatment solution is pumped off and through the movement of the drum the take up of treatment solution by the knitted parts is limited to about 350 percent by weight. Then the solvent is removed with the help of hot air (90° C.) and the knitted parts are treated for 60 seconds with steam (101° C.) after a storage time of 24 hours.

The knitted parts treated in this manner have a very good soft handle and are no longer inclined to felt during the washing process. The following data in the "Cubex" Test show the favorable influence of the treatment of the wool described on its characteristics:

TESTED ACCORDING TO IWS [1] SPECIFICATION 7A

Percent felt shrinkage: 30 minutes, +4.1%; Area: 60 minutes, −2.7%.

[1] International Wool Secretariat.

EXAMPLE 2

1,000 g. of a partially branched polyether of medium molecular weight (2,500 ± 150) and with an OH number of 56 ± 3, produced from propylene oxide, propylene glycol and trimethylol propane, are reacted with 295 g. of stearyl iso-

cyanate for 2 ½hours at 80° C. and another 1 hour at 110° C., yielding Reaction Product B_2.

Knitted parts made of wool are treated analogously to the process described in Example 1 with 5 g. of the reaction product ($B_2$and 8 g. of the reaction product (A) from Example 1 per liter of perchloroethylene. The knitted parts made of wool treated in this manner show a soft, loose handle and the following behavior in the "Cubex" Test:

TESTED ACCORDING TO IWS SPECIFICATION 7A

Percent felt shrinkage: 30 minutes, +1.6%; Area: 60 minutes, −3.3%.

EXAMPLE 3

1,000 g. of a branched polyether of medium molecular weight (3,000 ± 200) and with an OH number of 56 ± 3, produced from propylene oxide and trimethylene propane, are reacted with 240 g. of myristyl isocyanate for 2 hours at 80° C. and another 1 hour at 110° C., yielding Reaction Product B_3.

Knitted goods made of wool are treated according to Example 1 with 5 g. of the reaction product (B_3) and 8 g. of the reaction product (A) from Example 1 per liter of perchloroethylene. The knitted goods treated in this manner have a soft handle and good non-felting properties as to be seen from the following data obtained in the "Cubex" Test:

TESTED ACCORDING TO IWS SPECIFICATION 7A

Percent felt shrinkage: 30 minutes, −0.1%; Area: 60 minutes, −4.0%.

EXAMPLE 4

A fabric made of wool is submerged in a liquor which contains 5 g. of the reaction product (B_1) described in Example 1 and 25 g. of the reaction product (A) described in Example 1 per liter of perchloroethylene. The fabric is wrung out (up to about 115 percent of absorption of liquor) and subsequently it is freed of this solvent with hot air (100° C.). The fabric treated in this manner shows a very good soft handle and good nonfelting properties, as the following data show:

Percent shrinkage after 5 machine washings at 60° C.: Warp, −1.2%; Weft, −1.0%; Appearance of the goods, open, not felted.

EXAMPLE 5

1,000 g. of a partially branched polyether of medium molecular weight (2,500 ± 150) and an OH number of 56 ± 3, produced from propylene oxide, propylene glycol and trimethylol propane, are reacted with 240 g. of myristyl isocyanate for 2 hours 80° C. and another one hour at 110° C., yielding Reaction Product B_4.

A fabric made of wool is treated according to Example 1 with 5 g. of the reaction product (B_4) and 25 g. of the reaction product (A) from Example 1 per liter of perchloroethylene. The fabric treated in this manner has a soft handle and a good behavior in regard to being free of felt during washing, as the following data show:

Percent shrinkage after 5 machine washings at 60° C.: Warp, −2.0%; Weft, −1.3%; Appearance of the goods, open, not felted.

EXAMPLE 6

1,000 g. of a branched polyether of medium molecular weight (3,000 ± 200) and an OH number of 56 ± 3, produced from propylene oxide and trimethylol propane, are reacted with 98.3 g. of stearyl isocyanate for 2 hours at 90° C. and an additional 1 ½hours at 110° C., yielding Reaction Product B_5.

Knitted fabric made of wool is treated with 2 g. of the reaction product (B_5) and 16 g. of the reaction product (A) from Example 1 per liter of perchloroethylene. The knitted fabric made of wool is submerged for 4 minutes in the treatment solution and is wrung out to 110 percent by weight of liquor absorption. Subsequently, the solvent is removed by hot air (100° C.). The knitted parts made of wool treated in this manner have a soft, smooth handle and good nonfelting properties, as shown by the following data:

TESTED ACCORDING TO IWS SPECIFICATION 7A

Percent felt shrinkage: 30 minutes, +5.1%; Area: 60 minutes, −1.8%.

EXAMPLE 7

1,000 g. of a partially branched polyether of medium molecular weight (2,500 ± 150) and with an OH number of 56 ± 3, produced from propylene oxide, propylene glycol and trimethylol propane, are reacted with 196.6 g. of stearyl isocyanate at 100° C. for 3 hours. Subsequently, this is cooled down to 40° C., mixed with 29 g. of propyl isocyanate by portions and still left for 4 ½hours at 40°–45° C., yielding Reaction Product B_6.

A fabric made of 55 percent wool and 45 percent polyester fibers (polyethylene terephthalate) is submerged in a solution which contains, per liter of the perchloroethylene, 8 g. of the reaction product (B_6) and 20 g. of the reaction product (A) of Example 1. The fabric is wrung out (up to an increase in weight of approximately 95 percent) and the solvent is removed with hot air (100°–110° C.). The fabric has a soft feel and has very good effects with regard to being free of felt, as shown by the following data:

Percent shrinkage after 5 machine washings at 60° C.: Warp, −0.5%; Weft, −0.4%; Appearance of the goods, open, not felted.

EXAMPLE 8

1,000 g. of a partially branched polyether of medium molecular weight (2,500 ± 150) and with an OH number of 56 ± 3, produced from propylene oxide, propylene glycol and trimethylol propane, are reacted with 196.6 g. of stearyl isocyanate at 100° C. for 3 hours. Subsequently, this is cooled to 40° C. and mixed by portions with 41.7 g. of cyclohexyl isocyanate. The reaction mixture is reacted for an additional 4 hours at 50°–55° C., yielding Reaction Product B_7.

A fabric made of synthetic superpolyamide fibers is treated with a perchloroethylene solution which, per liter, contains 5 g. of the reaction product (B_7) and 10 g. of the reaction product (A) from Example 1. The fabric is submerged for 2 minutes in the treatment solution and it is wrung out to approximately 65 percent addition in weight. The organic solvent is removed with air (130° C.). The fabric (a) treated in this way shows, in comparison to a treatment with only 10 g. of the reaction product (A) from Example 1 per liter of perchloroethylene (b), a soft, smooth feel and a considerably improved creasing behavior.

EXAMPLE 9

1,000 g. of a branched polyether of medium molecular weight (3,000 ± 150) and an OH number of 56 ± 3, produced from propylene oxide, propylene glycol and trimethylol propane are reacted with 196.6 g. of stearyl isocyanate at 110° C. for 3 hours. Subsequently, this is mixed with 28 g. of hexamethylene diisocyanate and treated another 2 ½hours at 110° C., yielding Reaction Product B_8.

A fabric made from 45 percent wool and 55 percent polyacrylonitrile fibers is treated with a solution from perchloroethylene which contains, per liter, 10 g. of the reaction product (B_8) and 15 g. of the reaction product (A) from Example 1. The fabric is submerged in the treatment solution and is wrung out to about 85 addition of weight. The organic solvent is removed with hot air (120° C.). The fabric treated in this manner has a smooth, soft feel and a good behavior with regard to being free of felt in the case of washing processes.

EXAMPLE 10

260 gg. of the reaction product (B_1), described in Example 1, are mixed with 25.2 g. of dimethyl sulfate and are heated for 20 minutes at 50° C. Then 8 g. of sodium hydroxide, dissolved in 70 g. of water, is added by portions and is heated at 50° C. for 30 minutes more. The reaction product obtained is mixed by stirring with 2 g of benzyl-hydroxy-biphenyl-polyglycol ether, and 80 g. of a 20 percent aqueous solution of the sodium salt of a paraffinic sulfonic acid is added. After a further addition of 555 g. of water, an emulsion (Emulsion I) is then prepared in the customary manner.

An emulsion (Emulsion II) is prepared from 500 g. of the reaction product (A) described in Example 1 and having free isocyanate groups, and 100 g. of ethyl acetate, in the customary manner, with 600 g. of water, which contains 5 g. of the sodium salt of a paraffinic sulfonic acid.

A fabric made of wool is treated with an aqueous liquor which contains 100 g. of emulsion (II), 25 g. of a 40 percent aqueous dispersion of a copolymerizate (C) consisting of 80 parts acrylic acid butyl ester, 10 parts styrene and 10 parts acrylamide, 0.5 g. of zinc acetate and 40 g. of aqueous emulsion (I), per liter of said liquor. The fabric is submerged in the treatment liquor and is wrung out to about 100 percent addition by weight. It is then dried with air (110° C.) for 15 minutes. The fabric treated in this manner has a soft, smooth feel and a good behavior with regard to being free of felt after washing processes.

What is claimed is:

1. A textile fiber material which has been treated with a composition consisting of a finishing quantity of

A. an isocyanate group containing reaction product of

1. an organic compound containing at least two active hydrogen atoms and having a molecular weight of 500 to 10,000; and

2. a polyisocyanate; and

B. 5–60 percent by weight based on the weight of (A) of a softener consisting of the reaction product of

3. an organic compound containing at least one hydroxyl group; and

4. an aliphatic monoisocyanate having 14–18 carbon atoms.

2. The fiber of claim 1 wherein (4) is selected from the group myristyl monoisocyanate and stearyl monoisocyanate.

3. Fibers of claim 1 wherein the fibers are at least in part wool.

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