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## SHRINKPROOFING WOOL WITH POLY-URETHANES

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No Drawing. Filed Mar. 29, 1961, Ser. No. 99,319  
19 Claims. (Cl. 8-123)

(Granted under Title 35, U.S. Code (1952), sec. 266)

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A principal object of this invention is the provision of new methods for shrinkproofing wool. Another object of the invention is the provision of the novel products so produced. Further objects and advantages of the invention will be obvious from the following description wherein parts and percentages are by weight unless otherwise specified.

In the prior art it is suggested that the shrinkage properties of wool can be improved by applying to the wool fibers a high molecular weight polyamide such as polyhexamethylene adipamide or similar polyamide of the nylon type. This is accomplished in the following manner: The selected polyamide is first converted into soluble form, for example, by forming an N-methylol derivative thereof. The N-methylol derivative is applied to the wool and the treated wool is then immersed in hydrochloric acid whereby the N-methylol polyamide is converted to the unsubstituted polyamide. A primary disadvantage of this known process is that it is cumbersome and inefficient because it requires procurement of a pre-formed polyamide, conversion of this to a soluble form, and final reconversion to an insoluble form. Particular trouble is encountered in the last step where extended contact with acid is required to insolubilize the coating of N-methylol polyamide. Unless this acid treatment is complete, the polyamide will remain soluble and be removed from the textile when it is washed.

In accordance with this invention, a pre-formed polymer is not used but a polyurethane is formed in situ on the wool fibers. This is accomplished by serially applying to the wool the complementary agents required to form the polyurethane, these agents—in the preferred modification of the invention—being dissolved in mutually-immiscible solvents. Thus in a typical embodiment of the invention the wool is first impregnated with an aqueous solution of a diamine and then impregnated with a solution of a bischloroformate in a water-immiscible solvent such as carbon tetrachloride. Generally, the solutions are applied in the order given above, however, the reverse order gives good results and it is within the ambit of the invention to apply the solutions in either sequence. By serial application of these solutions to the fabric, each fibrous element is coated with a two-phase system, for example, an inner layer of diamine in water and an outer layer of bischloroformate in water-immiscible solvent. Under these conditions the diamine and bischloroformate react almost instantaneously at the interface between the phases, producing in situ on the fibers a high molecular weight resinous polyurethane which coats the fibers and renders them shrinkproof. The polymer formed is insoluble so that the shrinkproofing effect is durable; it is retained even after repeated washings with soap and water or detergent and water formulations. A feature of the invention is that the high molecular weight resinous polyurethanes are formed at ordinary (room) temperature, which is in sharp contrast to the

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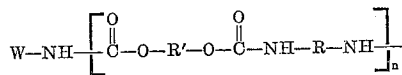
much higher temperatures required in the conventional melt condensations used in preparing polyurethanes. For example, in the usual preparation of these polymers by melt procedures, temperatures of over 200° C. are customarily employed.

As noted above, the treatment in accordance with the invention renders the treated wool essentially shrinkproof so that garments produced from the treated wool may be laundered in conventional soap and water or detergent and water formulations with negligible shrinking or felting. Further, the treated wool or garments prepared therefrom are in the "easy-care" category in that after washing and tumble drying, they are quite free from wrinkles so that they require only a minor amount of pressing. An important point to be stressed is that the shrinkproofing effect is secured without damage to the hand of the fabric. That is, the treated fabric retains its normal hand so that it is useful for all the conventional applications in fabricating garments as is untreated wool. Other items to be mentioned are that the treatment does not cause any degradation of the wool so that there is so significant loss of tensile strength, abrasion resistance, resiliency, elasticity, etc. Moreover, since the polymer is formed in situ on the fibers—in contrast to systems wherein polymers are spread en masse over the face of a fabric—there is substantially no loss of porosity of the fabric. A further item is that the treated wool may be dyed with conventional wool dyes to obtain brilliant level dyeings.

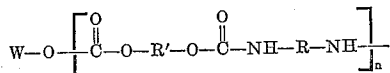
A particular feature of the invention and one that emphasizes its simplicity is that no heat-curing step is required. Following application of the two solutions, the textile merely needs to be rinsed or washed. Then, after drying, it is ready for use or sale.

The invention is applicable to wool in any physical form, for example, bulk fibers, slivers, rovings, yarns, felts, woven textiles, knitted textiles, or even completed garments or garment parts.

A remarkable feature of the invention is that the polymers formed on the wool fibers are not merely physical coatings; they are chemically bonded to the wool, that is, the added polymer is grafted onto the wool. The mechanism by which the graft polymerization occurs is believed to involve a reaction of functional groups on the bischloroformate with the free amino or hydroxy groups present in the wool molecule, these reactions giving rise to such linkages as urethane or carbonate, which chemically unite the wool with the polymer. Thus the products of the invention can be postulated by the following idealized formulas:



or

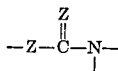


In the above formulas, W represents the polypeptide chain of the wool, containing prior to the reaction, free amino (—NH<sub>2</sub>) or free hydroxy (—OH) groups. R and R' are bivalent organic radicals (representing in this case the residues of the diamine and bischloroformate, respectively) and n represents the number of polyurethane repeating units.

The above formulas are obviously simplified and idealized as the polyurethane chains may be attached at both their ends to a single wool molecule or they may cross-link together different wool molecules through urethane or carbonate linkages. The important point from a practical and realistic view is that chemical bonding of the polyurethane to the wool has been demonstrated and the

theoretical nature of the mechanism of bonding is not of real concern to the invention.

It will be evident from the description herein that the invention is of great latitude and versatility and can be employed for forming on and grafting to wool fibers a wide variety of condensation polymers, particularly and preferably those condensation polymers wherein the recurring structures contain at least one urethane group, that is, a group of the structure



wherein Z is sulphur or oxygen.

#### General Considerations

In the practice of the invention, selection is first made of the appropriate complementary agents—herein termed Component A and Component B—required to form the desired polymer on the wool fibers. The interrelationship between the nature of the agents to be used as Components A and B and the type of polymer produced is explained in detail below in connection with the various modifications of the invention. However, it is apropos to mention at this point that Component A may be a diamine or a mixture of different diamines and Component B may be a bischloroformate or a mixture of different bischloroformates. Since components A and B may be selected to form any desired type of urethane polymer, these components may be aptly termed as complementary organic polyurethane-forming intermediates. They may further be appropriately designated as fast-reacting or direct-acting because they form the resinous polyurethanes rapidly and directly on contact without requiring any after-treatments, such as treatment with curing agents, oven cures, etc.

Having selected the desired Components A and B, these are formed into separate solutions for application to the wool to be treated. An essential consideration in the preferred modification of the invention is that the solvents used in the respective solutions of Components A and B be substantially mutually immiscible so that a liquid-liquid interface will be set up between the two solutions on the wool fibers. Thus, for example, Component A is dissolved in water and Component B is dissolved in benzene, carbon tetrachloride, toluene, xylene, ethylene dichloride, chloroform, hexane, octane, petroleum ether or other volatile petroleum distillate, or any other inert water-immiscible solvent. The two solutions are then applied to the wool serially, that is, the wool is treated first with one solution then with the other. The order of applying the solutions is not critical. Generally, the solution of Component A is applied first and the solution of Component B is applied next; however, the reverse order gives good results and it is within the ambit of the invention to apply the solutions in either sequence.

The solutions may be applied to the wool in any desired way as long as they are applied serially. A preferred method involves immersing the wool in one solution, removing excess liquid as by use of squeeze rolls, immersing the wool with the second solution, again removing excess liquid, rinsing the treated fabric in water and then drying it. Conventional apparatus consisting of tanks, padding rolls, squeeze rolls and the like are generally used in applying the respective solutions. The amount of each solution applied to the textile may be varied by altering the residence time in the solutions, the pressure exerted by the squeeze rolls and by varying the concentration of the active materials in the respective solutions. To decrease carry-over of the solvent from the first treating solution to the second solution, the wool after its immersion in the first solution may be subjected to drying conditions such as a current of warm air to concentrate the solution carried by the wool.

As noted above, a critical factor in the preferred form of the invention is that the complementary-agents—Com-

ponent A and Component B—are serially applied to the textile dispersed in solvents which are substantially mutually immiscible. The nature of the solvents is of no consequence as long as they are essentially inert and possess the above-stated property of substantial immiscibility. Usually volatile solvents are preferred as they may be removed from the treated textile by evaporation. However, non-volatile solvents can be used, in which case they may be removed from the product by extraction with suitable volatile solvents therefor or washed out with soap and water or detergent and water formulations. In many cases the ingredients of Component A are soluble in water and may thus be applied to the textile in aqueous solution. In such case the solvent for Component B may be any inert, essentially water-immiscible organic solvent. Typical illustrative examples thereof are benzene, toluene, xylene, carbon tetrachloride, ethylene dichloride, chloroform, hexane, octane, petroleum ether or other volatile petroleum fraction. It is, however, not essential that Component A be employed in aqueous solution. Thus, one may utilize a system of two essentially immiscible organic solvents, Component A being dispersed in one solvent and Component B in the other. As an example, Component A may be dispersed in 2-bromoethyl acetate and Component B dispersed in benzene. Another example involves using formamide, dimethylformamide, or diethylformamide as the solvent for Component A and using n-hexyl ether as the solvent for Component B. A further example involves a system of adiponitrile as the solvent for Component A and ethyl ether as the solvent for Component B. Examples of other pairs of solvents which are substantially immiscible with one another and which may be used for preparing the solutions of the respective reactants are 2-bromoethyl acetate and n-hexyl ether, ethylene glycol diacetate and n-hexyl ether, adiponitrile and n-butyl ether, adiponitrile and carbon tetrachloride, benzonitrile and formamide, n-butyl ether and formamide, di-N-propyl aniline and formamide, isoamyl sulphide and formamide, benzene and formamide, butyl acetate and formamide, benzene and nitromethane, n-butyl ether and nitromethane, carbon tetrachloride and formamide, dimethyl aniline and formamide, ethyl benzoate and formamide.

Moreover, the solvents used for Component A may contain hydroxy groups. Because amine groups are so much more reactive than hydroxy groups, there will be little if any interference by reaction of the hydroxy groups of the solvent with the active agents of Component B, particularly if the solutions of the reactants are at ordinary temperatures. In such event, then, solvent pairs of the following types may be employed: Diethylene glycol monomethyl ether and n-hexyl ether, diethylene glycol monoethyl ether and n-hexyl ether, 2-ethylhexanol and adiponitrile, isoamyl alcohol and adiponitrile, glycerol and acetone, capryl alcohol and formamide, ethylene glycol and benzonitrile, diacetone alcohol and di-N-propylaniline, 2-ethylhexanol and formamide, triethylene glycol and benzyl ether.

The concentration of active materials (Component A and Component B) in the respective solutions is not critical and may be varied widely. Generally, it is preferred that each of the pair of solutions contains about from 1 to 20% of the respective active component. In applying the process of the invention, enough of the respective solutions are applied to the wool to give a polymer deposit on the fibers of about 1 to 10%. Such amounts provide a substantial degree of shrinkproofing with no significant reduction in hand of the wool. Greater amounts of polymer may be deposited on the fibers if desired but tend to change the natural hand of the wool. Also, thicker deposits are likely to contain substantial amounts of non-grafted polymer. The relative amounts of Component A and Component B applied to the wool may be varied as desired for individual circumstances. Generally, it is preferred to apply the components in

equimolar proportions, that is, the amounts are so selected that there are the same number of functional groups provided by Component A as provided by the functional groups of Component B.

It is often desirable to add reaction promoters or catalysts to either of the solutions of Components A or B in order to enhance reaction between the active agents. For example, it is desirable to add to either of the solutions, preferably to the solution of Component A, a sufficient amount of alkaline material to take up the HCl formed in the reaction. For such purpose one may use a tertiary amine such as pyridine, dimethyl aniline, or quinoline or an alkali-metal hydroxide, or, more preferably, an alkaline material with buffering capacity such as sodium carbonate, sodium bicarbonate, trisodium phosphate, borax, etc. Another plan which may be used involves supplying the diamine in excess so that it will act both as a reagent and as an HCl-acceptor. The reaction of Components A and B may also be catalyzed by addition of such agents as tributyl tin chloride, stannous tartrate, ferric chloride, titanium tetrachloride, boron trifluoride-diethyl ether complex, or tin salts of fat acids such as tin laurate, myristate, etc.

Where one of the solutions of the reactants contains water as the solvent, it is often desirable to incorporate a minor proportion of a surface-active agent to aid in dispersing the reactant and to assist in penetration of the solution into the textile. For this purpose one may use such agents as sodium alkyl (C<sub>8</sub>-C<sub>18</sub>) sulphates, the sodium alkane (C<sub>8</sub>-C<sub>18</sub>) sulphonates, the sodium alkyl (C<sub>8</sub>-C<sub>20</sub>) benzene sulphonates, esters of sulphosuccinic acid such as sodium dioctylsulphosuccinate, and soaps, typically sodium salts of fat acids. Emulsifying agents of the non-ionic type are suitable, for example, the reaction products of ethylene oxide with fatty acids, with polyhydric alcohols, with partial esters of fatty acids and polyhydric alcohols or with alkyl phenols, etc. Typical of such agents are a polyoxyethylene stearate containing about 20 oxyethylene groups per mole, a polyoxyethylene ether of sorbitan monolaurate containing about 16 oxyethylene groups per mole, a distearate of polyoxyethylene ether of sorbitol containing about 40 oxyethylene groups per mole, iso-octyl phenyl ether of polyethylene glycol, etc. Generally, only a small proportion of surface-active agent is used, on the order of 0.05 to 0.5%, based on the weight of the solution. In addition to, or in place of the surface-active agent, a supplementary solvent may be added to the primary solvent (water) in quantity sufficient to disperse the active reactant. For such purpose one may employ acetone, or other inert volatile solvent, particularly one that is at least partially miscible with water. It is evident that the solutions of Components A and B need not necessarily be true solutions; they may be colloidal solutions, emulsions, or suspensions, all these being considered as solutions for the purposes of the present invention.

Ordinarily, the treatment of the wool with the solutions of the complementary agents is carried out at room temperature as at such temperature the polymerization takes place very rapidly, that is, in a matter of a minute or less. If, however, a higher rate of polymerization is desired—as in continuous operation on long lengths of cloth—the second solution may be kept hot, for example, at a temperature up to around 150° C.

As has been explained above, in the preferred modification of the invention the solutions of Components A and B—the complementary condensation polymer-forming intermediates—are serially applied to the wool in the form of mutually-immiscible solutions to provide a liquid-liquid interface between the solutions as they are serially laid onto the fibers. In a less preferred modification of the invention, a system is used which utilizes a solid-liquid interface. Such a system is established in the following way: The wool is first impregnated with a solution of one of the complementary agents—for example, Com-

ponent A—dispersed in an inert volatile solvent. The wool is then subjected to drying as by subjecting it to a current of hot air. The wool fibers which are now covered with a deposit of the first component in a solid state, are then impregnated with the complementary agent—Component B, in this case, dispersed in an inert, preferably volatile solvent. In this way the fibers are layered with a superposed system of solid Component A and a solution of Component B. Under these conditions polymerization takes place rapidly forming the polymer in situ on the fibers and grafted thereto. In this system it is not essential that the respective solvents be immiscible. Thus, for example, Component A may be applied in water solution and Component B in a water-miscible solvent such as dioxane or acetone. A typical example of practicing this modification involves immersing the wool in an aqueous solution of a diamine and an HCl-acceptor, removing the wool from the solution, squeezing it through rolls to remove excess liquid, subjecting it to a draft of hot air until the wool is dry to the touch (about 10–20% moisture in the impregnated wool) and then immersing the wool in a solution of a bischloroformate dissolved in an inert, volatile solvent. The wool is then removed from this second bath, squeezed through rollers to remove excess water, rinsed, and dried in air. Although this system is operative, it is not a preferred technique because the polymerization at the solid-liquid interface is slower and less uniform in degree of polymerization and the degree of shrinkproofing afforded to the wool per unit weight of polymer formed on the fibers is less than with the system of mutually-immiscible solutions.

#### COMPONENTS A AND B

As noted briefly above, the selection of Components A and B depends on the type of polymer desired to be formed on the wool fiber and grafted thereto. Typical examples of compounds which can be employed as Component A in a practice of the invention are described below.

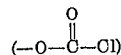
As the diamine one may employ any of the aromatic, aliphatic, or heterocyclic compounds containing two primary or secondary amine groups, preferably separated by at least two carbon atoms. The diamines may be substituted if desired with various non-interfering (non-functional) substituents such as ether radicals, thioether radicals, tertiary amino groups, sulphone groups, fluorine atoms, etc. Typical compounds in this category are listed below merely by way of illustration and not by way of limitation: Ethylene diamine, trimethylene diamine, tetramethylene diamine, hexamethylene diamine, octamethylene diamine, decamethylene diamine, N,N'-dimethyl-1,3-propanediamine, 1,2-diamino-2-methylpropane, 2,7-diamino-2,6-dimethyloctane, N,N'-dimethyl-1,6-hexanediamine, 1,4-diamino cyclohexane, 1,4-bis (aminomethyl) cyclohexane, 2,2'-diaminodiethyl ether, 2,2'-diaminodiethyl sulphide, bis (4-aminocyclohexyl) methane, N,N'-dimethyl - 2,2,3,3,4,4 - hexafluoropentane - 1,5 - diamine, ortho-, meta-, or para-phenylene diamine, benzidine, xylylene diamine, m-toluyene diamine, ortho-tolidine, piperazine, and the like. If desired, mixtures of different diamines may be used. It is generally preferred to use aliphatic alpha, omega diamines, particularly of the type



wherein  $n$  has a value of 2 to 12, preferably 6 to 10.

Typical examples of compounds which can be employed as Component B in a practice of the invention are described below.

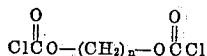
As the bischloroformate one may use any of the aliphatic, aromatic, or heterocyclic compounds containing two chloroformate groups



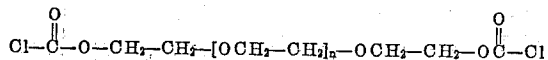
preferably separated by at least two carbon atoms. The

bischloroformates may be substituted if desired with non-interfering (non-functional) substituents such as sulphone groups, ether groups, thioether groups, etc. Typical examples of compounds in this category are listed below merely by way of illustration and not limitation: Ethylene glycol bischloroformate, diethylene glycol bischloroformate, 2,2-dimethyl propane 1,3-diol bischloroformate, propane-1,3-diol bischloroformate, butane-1,4-diol bischloroformate, hexane-1,6-diol bischloroformate, octane-1,8-diol bischloroformate, decane-1,10-diol bischloroformate, butane-1,2-diol bischloroformate, hexane-1,2-diol bischloroformate, 2-methoxyglycerol-1,3-bischloroformate, glycerol-1,2-bischloroformate, glycerol-1,3-bischloroformate, diglycerol bischloroformate, hexanetriol bischloroformate, pentaerythritol bischloroformate, cyclohexane-1,4-diol bischloroformate, hydroquinone bischloroformate, resorcinol bischloroformate, catechol bischloroformate, bischloroformate of 2,2-bis(parahydroxyphenyl) propane, bischloroformate of 2,2-bis(parahydroxyphenyl) butane, bischloroformate of 4,4'-dihydroxybenzophenone, bischloroformate of 1,2-bis(parahydroxyphenyl) ethane, naphthalene-1,5-diol bischloroformate, biphenyl-4,4'-diol bischloroformate, etc. If desired, mixtures of different bischloroformates may be used.

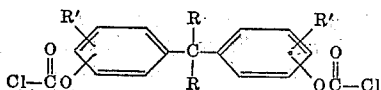
Among the preferred compounds are the aliphatic bischloroformates, for example, those of the type:



wherein  $n$  has a value from 2 to 12. Another preferred category of compounds are the bis-chloroformates derived from polyethylene glycols, e.g.,

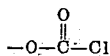


wherein  $n$  has a value from zero to 10. A useful category of aromatic bischloroformates are the bisphenol chloroformates, that is, compounds of the type:

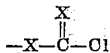


wherein  $\text{R}-\text{C}-\text{R}$  represents an aliphatic hydrocarbon group containing 1 to 12 carbon atoms and  $\text{R}'$  is hydrogen or a low alkyl radical.

It is also evident that the sulphur analogues of the bischloroformates may be used and such are included within the spirit of the invention. Thus, instead of using the compounds containing two



groups one may use any of the compounds containing the sulphur analogues of these groups, for example, the compounds containing two groups of the formula

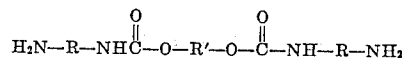


wherein one X is sulphur and the other is oxygen or wherein both X's are sulphur. Moreover, although the bischloroformates are preferred because they are reactive and relatively inexpensive, it is not essential that they contain chlorine and one may use the corresponding bisbromoformates or bisiodoformates.

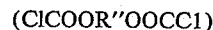
Numerous variations of the basic procedure herein described will suggest themselves to those skilled in the art in the application of the invention without departing from the fundamentals of the invention. Some of these variations are explained below.

If desired, one may prepare a prepolymer containing internal urethane units and terminal amino groups. Such prepolymers can be prepared, for example, in known manner by reacting a molar excess of diamine with a bischloroformate. The prepolymer would then be used as Component A while for Component B one would use a bis-

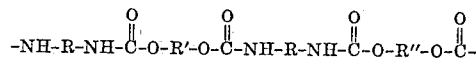
chloroformate. A typical example of procedure in this area would be to use as Component A a prepolymer of the type



and to use as Component B a bischloroformate



thus to produce a polymer containing repeating units of the type



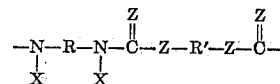
(In these formulas, R, R', and R'' represent bivalent organic radicals.)

In the alternative, one may prepare a prepolymer containing internal urethane units and external



groups. Such a prepolymer used as Component B in conjunction with a diamine as Component A would yield a polyurethane similar to that shown above.

It is evident from the foregoing description that there is a very wide choice available in the selection of the complementary agents (diamine and bischloroformate) so that generically the polyurethanes deposited on the wool and grafted thereto will contain repeating units of the type



wherein R and R' are bivalent organic radicals; Z represents an oxygen or sulphur atom; and the x's taken separately represent two hydrogen atoms or two monovalent organic radicals, or, taken together the x's represent a single bivalent organic radical which links the two nitrogen atoms to which they are attached.

In the preferred modifications of the invention, Z is oxygen; R and R' represent bivalent hydrocarbon radicals or bivalent hydrocarbon radicals interrupted by internal ether ( $-\text{O}-$ ) linkages and x is hydrogen. In the especially preferred modifications of the invention, the reactants are so chosen that R and R' represent bivalent hydrocarbon radicals containing at least two carbon atoms.

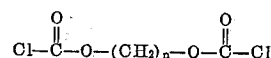
Coming under special condition particularly because of the exceptionally high shrink resistance imparted with a very small proportion of polyurethane, are the use of the following materials as the complementary agents.

Component A: Xylylene diamines or aliphatic alpha, omega diamines, particularly those of the type



wherein  $n$  has a value from 6 to 10.

Component B: Ethylene glycol bischloroformate, diethylene glycol bischloroformate, or the aliphatic alpha, omega bischloroformates, particularly those of the type



wherein  $n$  has a value from 2 to 10.

Typical examples are the conjoint use of (A) metaxylylene diamine or hexamethylene diamine and (B) ethylene glycol bischloroformate, diethylene glycol bischloroformate, or hexane-1,6-diol bischloroformate.

#### Examples

The invention is further demonstrated by the following illustrative examples.

*Standard shrinkage test.*—The tests for shrinkage referred to below were conducted in the following way: The wool samples were milled at 1700 r.p.m. for 2 minutes at 40–42° C. in an Accelerotor with 0.5% sodium

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oleate solution, using a liquor-to-wool ratio of 50 to 1. After this washing operation the samples were measured to determine their area and the shrinkage was calculated from the original area. With this washing method, samples of control (untreated) wool gave an area shrinkage of 47%. The Accelerator is described in the American Dyestuff Reporter, vol. 45, p. 685, Sept. 10, 1956.

## EXAMPLE 1

A. A solution was prepared containing 2% of metaxylylene diamine in water.

B. A solution was prepared containing 3% of ethylene glycol bischloroformate in benzene.

A sample of wool cloth was immersed in solution A for 30 seconds, run through squeeze rolls to remove excess liquid, immersed for 30 seconds in solution B, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air at room temperature. The treated wool had a polyurethane resin uptake of 1.6% and on washing exhibited an area shrinkage of 10.7%. These results are tabulated below, together with the shrinkage of the untreated wool sample:

Polyurethane resin deposited on wool, percent	Area shrinkage, percent
1.6-----	10.7
None (control)-	47.0

## EXAMPLE 2

The procedure of Example 1 was repeated using as solution A 3% ethylene glycol bischloroformate in benzene and as solution B, a 4% solution of hexamethylene diamine in water. The following results were obtained:

Polyurethane resin deposited on wool, percent	Area shrinkage, percent
1-----	7.8
None (control)-	47.0

## EXAMPLE 3

The process of Example 1 was repeated using as solution A 4% hexamethylene diamine in water and as solution B, a 3% solution of ethylene glycol bischloroformate in carbon tetrachloride. The following results were obtained:

Polyurethane resin deposited on wool, percent	Area shrinkage, percent
2.5-----	11.6
None (control)-	47.0

## EXAMPLE 4

The process of Example 1 was repeated using as solution

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A 4% hexamethylene diamine in water and as solution B, a 3% solution of diethylene glycol bischloroformate in carbon tetrachloride. The following results were obtained:

Polyurethane resin deposited on wool, percent	Area shrinkage, percent
4.0-----	3.0
None (control)-	47.0

## EXAMPLE 5

The process of Example 1 was repeated using as solution A 2% hexamethylene diamine in water and as solution B, a 3% solution of diethylene glycol bischloroformate in carbon tetrachloride. The following results were obtained:

Polyurethane resin deposited on wool, percent	Area shrinkage, percent
2.8-----	4.0
None (control)-	47.0

## EXAMPLE 6

The process of Example 1 was repeated using as solution A 2% metaxylylene diamine in water and as solution B, a 3% solution of diethylene glycol bischloroformate in benzene. The following results were obtained:

Polyurethane resin deposited on wool, percent	Area shrinkage, percent
0.1-----	22.6
None (control)-	47.0

## EXAMPLE 7

A. A series of solutions were prepared containing 4% hexamethylene diamine (or 4% metaxylylene diamine), 4% Na<sub>2</sub>CO<sub>3</sub>, and 0.1% of a commercial wetting agent (the iso-octyl phenyl ether of polyethylene glycol) in water.

B. Another series of solutions were prepared containing 3% 1,6-hexanediol bischloroformate in benzene or carbon tetrachloride.

Wool cloth was treated with the solutions in the following manner: The cloth was immersed in solution A for a predetermined time, squeezed to remove excess liquid, immersed for a predetermined time in solution B, squeezed to remove excess liquid, rinsed in water, and dried in air.

The conditions used and the results obtained are tabulated below:

Run	First treating solution	Second treating solution	Time of immersion in each solution, Sec.	Resin uptake on wool, percent	Area shrinkage, percent
1-----	4% hexamethylene diamine, 4% Na <sub>2</sub> CO <sub>3</sub> , 0.1% of the iso-octyl phenyl ether of polyethylene glycol in water.	3% 1,6-hexanediol bischloroformate in benzene.	60	5.4	0
2-----	do	do	30	2.4	0
3-----	do	3% 1,6-hexanediol bischloroformate in CCl <sub>4</sub> .	30	4.6	1.0
4-----	4% metaxylylene diamine, 4% Na <sub>2</sub> CO <sub>3</sub> , 0.1% of the iso-octyl phenyl ether of polyethylene glycol in water.	3% 1,6-hexanediol bischloroformate in benzene.	30	4.4	3.0
5 (Control)-					47.0

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This application is a continuation-in-part of our co-pending application Ser. No. 98,718, filed March 27, 1961, entitled Shrinkproofing Wool With Polymers, wherein is disclosed the broad concept of grafting condensation polymers—particularly polyamides—to wool. Said application is a continuation-in-part of the following applications: Serial No. 90,604, filed February 20, 1961, entitled Shrinkproofing of Wool With Polyamides (which in turn is a continuation-in-part of Ser. No. 22,651, filed Apr. 15, 1960); Serial No. 83,848, filed January 19, 1961, entitled Shrinkproofing of Wool With Polyurethanes; Serial No. 85,438 filed January 27, 1961, entitled Shrinkproofing of Wool With Polyureas; Serial No. 88,232, filed February 9, 1961, entitled Shrinkproofing of Wool With Polyesters; and Serial No. 88,233, filed February 9, 1961, entitled Shrinkproofing of Wool with Polycarbonates. Of the applications referred to above, the following have been abandoned: Ser. No. 22,651, Ser. No. 83,848, Ser. No. 85,438, Ser. No. 88,232, Ser. No. 88,233, and Ser. No. 90,604.

Attention is called to the fact that the present application is one of a series of applications filed by us generally concerned with shrinkproofing wool wherein various types of condensation polymers are formed on and grafted to the wool fibers. Polyurethanes are the subject of the present application; polyureas are the subject of Serial No. 100,476, filed April 3, 1961; polyesters are the subject of Serial No. 101,599, filed April 7, 1961; polycarbonates are the subject of Serial No. 102,323, filed April 11, 1961; interpolymers are the subject of Serial No. 109,229, filed May 10, 1961. Condensation polymers broadly and polyamides specifically are the subjects of the parent application referred to above, of which this application is a continuation-in-part.

Although the present invention finds its greatest field of utility in the shrinkproofing of wool and is peculiarly adapted for such use because of a combination of important factors—including the advantages that a high degree of shrink resistance is imparted with a minor amount of polymer, that the shrinkproofing treatment does not significantly impair the hand of the wool, that the treatment does not impair other desirable fiber characteristics such as tensile strength, elasticity, porosity, etc., that the polymer is grafted to the wool molecules so that the shrinkproofing effect is exceedingly durable and is retained even after long wear and repeated laundering—it is evident that the invention may be extended to other areas. Thus the principles of the invention may be extended to forming polymers in situ on other substrates besides wool, particularly substrates of a fibrous structure. Typical examples of such materials are animal hides, leather; animal hair; cotton; hemp; jute; ramie; flax; wood; paper; synthetic cellulosic fibers such as viscose, cellulose acetate, cellulose acetate-butyrate; casein fibers; polyvinyl alcohol-protein fibers; aliginic fibers; glass fibers; asbestos; and organic non-cellulosic fibers such as poly(ethylene glycol terephthalate), polyacrylonitrile, polyethylene, polyvinyl chloride, polyvinylidene chloride, etc. Such applications of the teachings of the invention may be for the purposes of obtaining functional or decorative effects such as sizing, finishing, increasing gloss or transparency, increasing water-repellancy, increasing adhesion or bonding-characteristics of the substrates with rubber, polyester resins, etc. It is not claimed that in such extensions of our teachings shrinkproofing would be attained nor that graft polymers would be produced. However, it might be expected that graft polymers would be formed with proteinous substrates such as animal hair, animal hides, and the like.

Having thus described the invention, what is claimed is:

1. A process for shrinkproofing wool without significant impairment of its hand, which comprises serially impregnating wool with two solutions, one solution containing a diamine dispersed in water, the other solution containing a bischloroformate dispersed in an inert, vola-

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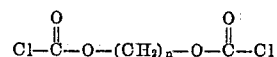
tile, essentially water-immiscible solvent, the said diamine and bischloroformate reacting to form in situ on the wool fibers a resinous polyurethane.

2. The process of claim 1 wherein the diamine has the formula:



wherein  $n$  has a value from 6 to 10.

3. The process of claim 1 wherein the bischloroformate has the formula:



wherein  $n$  has a value from 2 to 10.

4. The process of claim 1 wherein the diamine is hexamethylene diamine.

5. The process of claim 1 wherein the diamine is metaxylylene diamine.

6. The process of claim 1 wherein the bischloroformate is ethylene glycol bischloroformate.

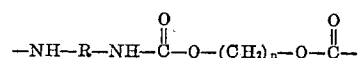
7. The process of claim 1 wherein the bischloroformate is diethylene glycol bischloroformate.

8. The process of claim 1 wherein the bischloroformate is 1,6-hexanediol bischloroformate.

9. A process for shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one containing a diamine in a first solvent, the other containing a bischloroformate in a second solvent, the first and second solvents being substantially mutually immiscible, the said diamine and bischloroformate reacting to form in situ on the wool fibers a resinous polyurethane.

10. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a polyurethane formed in situ thereon and chemically bonded to the wool.

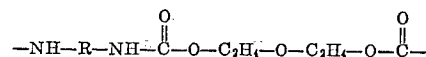
11. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a polyurethane formed in situ thereon and chemically bonded to the wool, said polyurethane containing recurring structural groups of the formula—



wherein R is the bivalent radical  $-(\text{CH}_2)_m-$  in which  $m$  has a value from 6 to 10 and  $n$  has a value from 2 to 10.

12. The product of claim 11 wherein R represents the metaxylylene radical.

13. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a polyurethane formed in situ thereon and chemically bonded to the wool, said polyurethane containing recurring structural groups of the formula—



wherein R is the bivalent radical  $-(\text{CH}_2)_m-$  in which  $m$  has a value from 6 to 10.

14. The product of claim 13 wherein R is the metaxylylene radical.

15. A process for treating a fibrous material which comprises applying serially to said material in interfacial relationship, a pair of complementary direct-acting organic polyurethane-forming intermediates.

16. A process for treating a fibrous material which comprises serially applying to said material a pair of complementary direct-acting organic polyurethane-forming intermediates in separate phases of limited mutual solubility.

17. A process for treating a fibrous material which comprises serially distributing on the surface of the fibrous elements of said material a pair of complementary direct-acting organic polyurethane-forming intermediates in superposed phases of limited mutual solubility, the said

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intermediates reacting under such conditions to form a polymer in situ on said fibrous elements.

18. A process for treating wool which comprises distributing on the surface of the wool fibers a pair of complementary direct-acting organic polyurethane-forming intermediates in superposed liquid phases of limited mutual solubility, said intermediate reacting rapidly under said conditions to form a polymer in situ on said fibrous elements and grafted thereto.

19. A process for treating a fibrous material which comprises serially impregnating a fibrous material with two solutions, one solution containing one member of a pair of complementary direct-acting, organic, polyurethane-forming intermediates in a first solvent, the other solution containing the complementary member of said pair of complementary direct-acting, organic, polyurethane-forming intermediates in a second solvent, said first

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and second solvents being substantially mutually immiscible, the said pair of intermediates reacting rapidly under said conditions to form in situ on the fibers a resinous polyurethane.

## References Cited in the file of this patent

## UNITED STATES PATENTS

2,522,338	Angus et al. -----	Sept. 12, 1950
2,526,948	Himel -----	Oct. 24, 1950
2,537,064	Kropa et al. -----	Jan. 9, 1951
2,565,259	Nyquist et al. -----	Aug. 21, 1951
2,644,773	Hammer et al. -----	July 7, 1953
2,684,305	Quinlivan -----	July 20, 1954
2,696,448	Hammer et al. -----	Dec. 7, 1954
2,862,836	Oosterhout -----	Dec. 2, 1958
2,866,722	Gensel et al. -----	Dec. 30, 1958
2,929,737	Tischbein -----	Mar. 22, 1960