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3,552,910

METHOD OF SHRINKPROOFING A PROTEINACEOUS TEXTILE MATERIAL AND PRODUCT THEREOF

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8 Claims

ABSTRACT OF THE DISCLOSURE

A process for shrinkproofing wool by contacting it with a polyaryl polyisocyanate or a polyaryl polyisocyanate modified by reaction with an alcohol, thio-alcohol, organic acid, amine or amide and then curing the treated wool with water. Desirably, the polyisocyanate is a polymethylene polyphenyl isocyanate or a poly(isocyanatophenyl)methane, applied in an organic solvent and the water cure is effected by immersing the treated wool in warm water.

This invention relates to an improved composition and process for treating wool and more particularly it relates to an improved composition and process for treating wool and similar proteinaceous materials so as to render them substantially shrink proof.

In the past, a great deal of effort has been expended in attempts to develop compositions and processes for treating wool and similar proteinaceous materials so as to render them resistant to shrinking during washing. This has been particularly true in recent years with the advent of various so-called synthetic wools, such as the polyester fibers, or polyacrylic fibers and the like, which materials may be laundered repeatedly without encountering a problem of shrinking.

In general, the prior treatments proposed to shrinkproof wool have involved the uses of materials which form a coating on the wool fibers, thereby minimizing the effect of the overlapping scales of the fiber or of materials which react with and chemically modify the wool fibers themselves, thus modifying or degrading these scales. For the most part, these prior art treatments have not been satisfactory because they have been difficult or expensive to apply or have not had sufficient durability to make the treated fabric substantially permanently shrink resistant. An additional, and perhaps a major disadvantage of these prior art treatments has been that they frequently have an adverse effect on the hand or feel of the fabrics with which they are treated. Thus, wool and similar proteinaceous materials which have heretofore been treated to render them shrinkproof often become hard, and/or stiff and boardy as a result of these treatments. Accordingly, up to the present time, there has not been available a satisfactory process for treating wool and similar proteinaceous fibers to render them substantially permanently shrinkproof.

It is, therefore, an object of the present invention to provide a novel treated wool or similar proteinaceous material, which is substantially permanently shrinkproof.

A further object of the present invention is to provide an improved process for treating wool and other protein-

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aceous materials so as to render them substantially permanently shrinkproof, which process is easily and economically carried out.

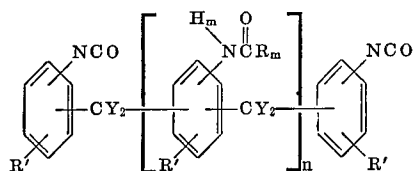
These and other objects of the present invention will become apparent to those skilled in the art from the description which follows.

Pursuant to the above objects, the present invention includes a process for treating a proteinaceous material which comprises contacting the proteinaceous material with a polymerizable treating solution comprising a polyaryl polyisocyanate containing at least three aryl groups and an average of at least three isocyanate groups, a portion of which isocyanate groups may be modified by reaction with an alcohol, thioalcohol, organic acid, amine or amide, and, thereafter, curing the thus-contacted material with water. The proteinaceous materials, such as proteinaceous textiles, treated in accordance with this process are found to be durably shrink resistant, even after repeated washings in hot water. Additionally, the hand or feel of the thus-treated fabric is generally found to be substantially unchanged from that of the untreated material.

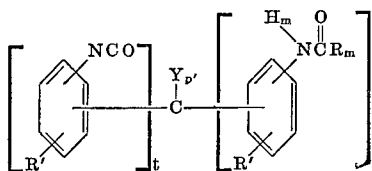
More specifically, in the practice of the present invention, the proteinaceous materials to be treated are proteinaceous textile materials, and particularly proteinaceous textiles which undergo shrinking during normal laundering operations. These textile materials may be in various forms, including yard goods, as well as various finished articles, such as articles of clothing, including coats, sweaters, socks, shirts, trousers, skirts, and the like. Of the numerous proteinaceous materials of which such articles may be made, the process of the present invention has been found to be particularly applicable in the treatment of wool. Accordingly, hereinafter, primary reference will be made to wool as being the preferred proteinaceous material. This is not, however, to be taken as a limitation on the present invention as other proteinaceous materials which are subject to shrinkage may also be advantageously treated by the present process, including fabrics made of alpaca, angora, camel hair, cashmere, huarizo, lama, misti, mohair, suri, vicuna and the like. Additionally, the process of the present invention is not limited to the treatment of wool or other proteinaceous materials in the form of yard goods or finished articles, but may in many instances also be utilized in treating these materials in the fiber or yarn form. It is to be further appreciated that the proteinaceous materials treated may be admixed with other non-proteinaceous materials as in various fiber blends with synthetics or other natural fiber materials or they may be in the form of a so-called "multiply" fabric wherein the proteinaceous fabric is bonded to a fabric of some other material, such as acetate, rayon, nylon, and the like. The treatment of this latter type material has been found to be particularly advantageous in that such materials when treated are found to be substantially wrinkle-free after washing, thereby providing a "wash and wear" wool.

In treating the proteinaceous materials so as to make them shrink resistant, the material is impregnated with a solution which comprises, as the essential shrinkproofing component, a polyaryl polyisocyanate compound, either as such or modified by reaction with an alcohol, thioalcohol organic acid, amine or amide. Suitable compounds

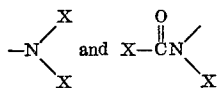
may be characterized generally as being selected from the group consisting of



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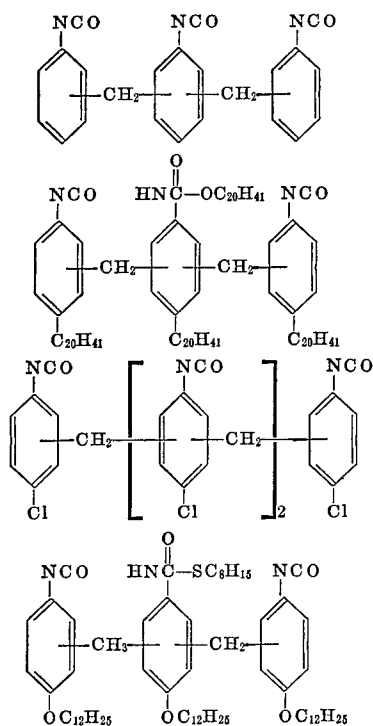


wherein n is a number having an average value of at least 1 and is generally from 1 to 4; t is a number from 2 to 4; p is a number from 0 to 2; p is 0 or 1; $t+p$ has an average value of at least 3 and is generally from 3 to 4; $t+p+p'$ is 4; m is a number from 0 to 1; R' is selected from the group consisting of halogen, hydrogen, alkyl and alkoxy; y is selected from the group consisting of hydrogen, alkyl and phenyl; R is selected from the group consisting of OX , SX , X ,

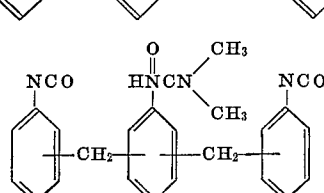
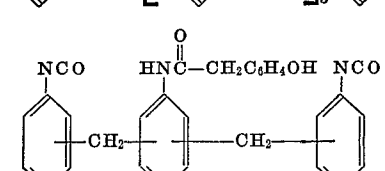
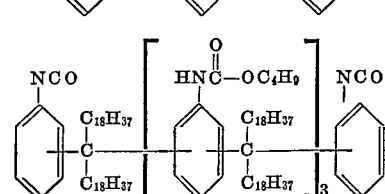
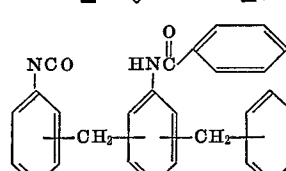
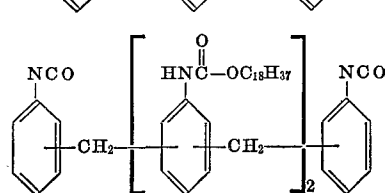
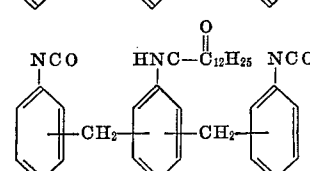
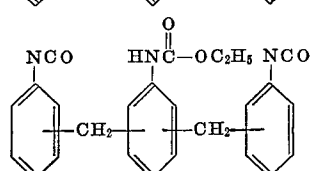
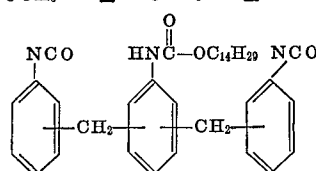
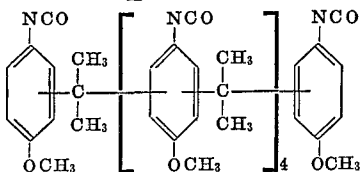
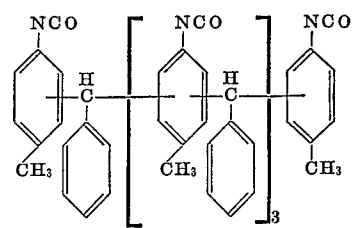


and X is selected from the group consisting of hydrogen, alkyl, alkylphenol, alkylphenoxyalkoxy and phenyl.

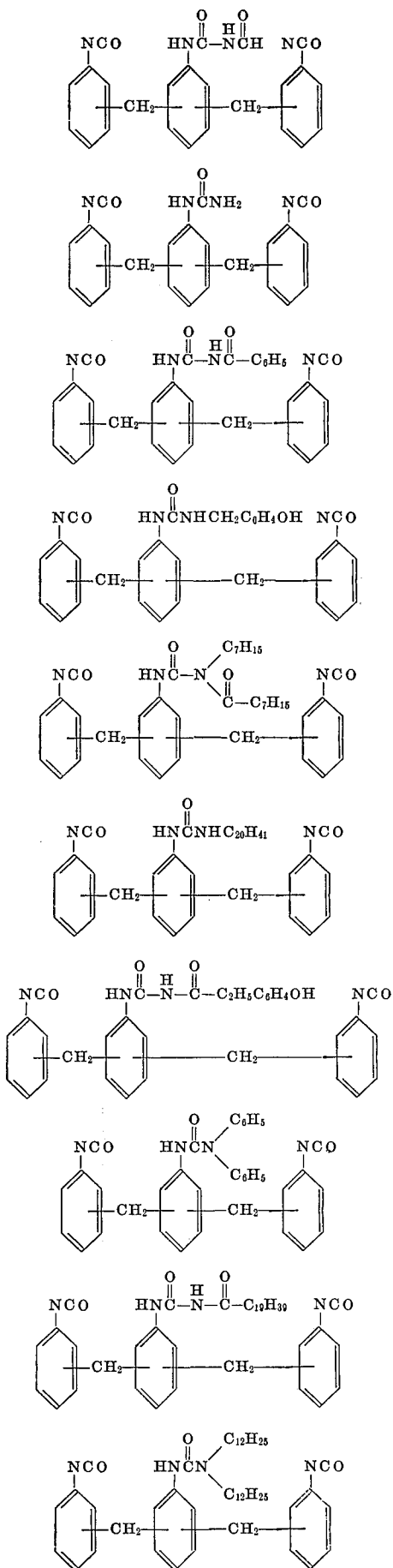
Desirably in the compounds used, as characterized by the above generic formulas, the alkyl groups, either as such or in an alkylphenoxy or alkoxy group contain from about 1 to 20 carbon atoms and preferably from about 4 to 20 carbon atoms. Additionally, the term "halogen," as used in the formula, is intended to include chlorine, fluorine, bromine and iodine. Exemplary of specific compounds falling within the generic formulas given hereinabove are the following:



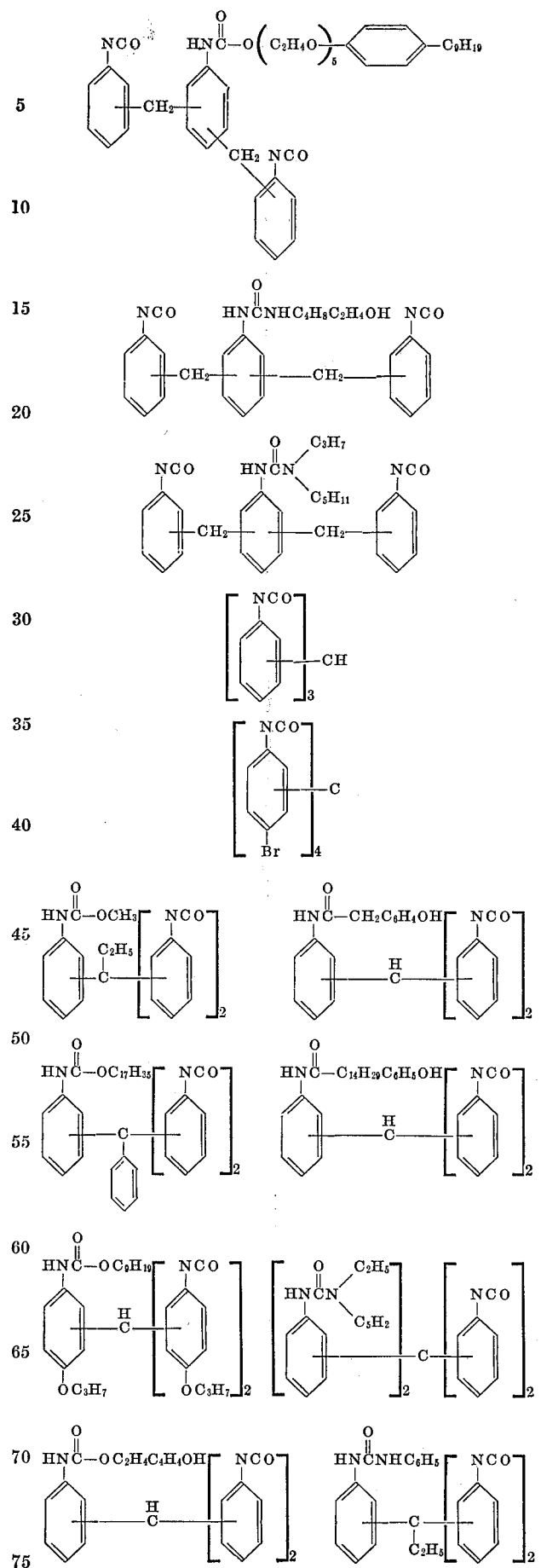
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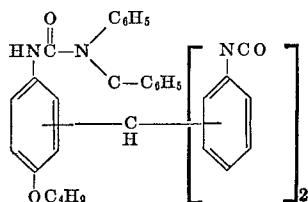
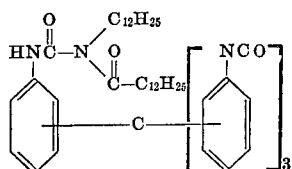
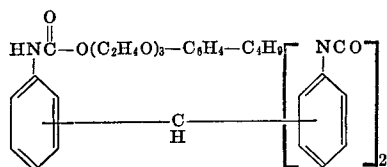
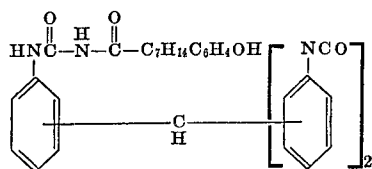
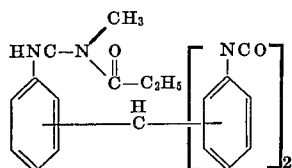
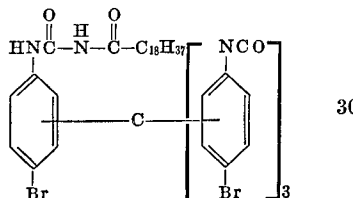
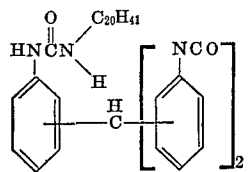
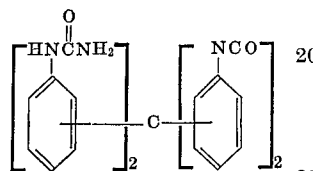
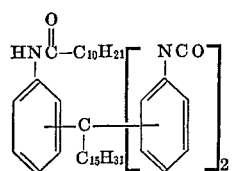
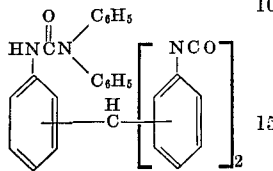
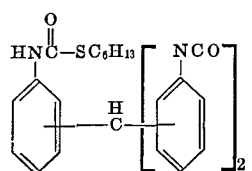
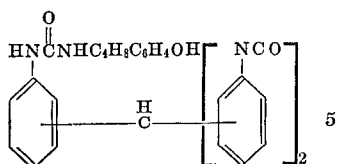
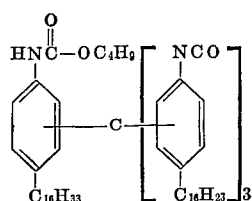
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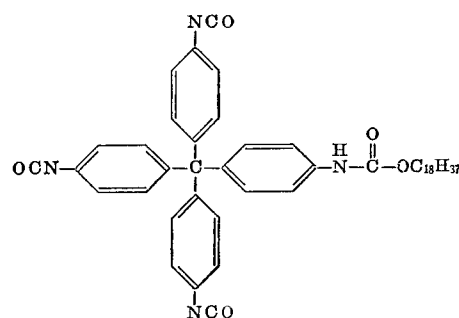
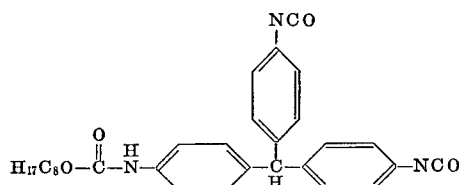
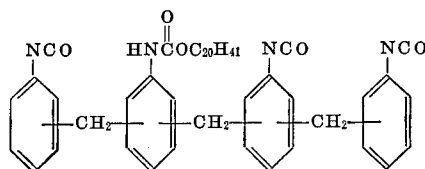
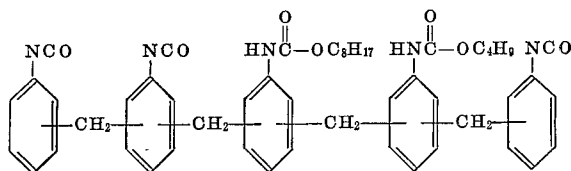
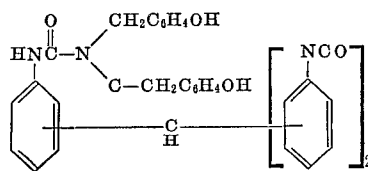
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It is to be appreciated that similar compounds, other than those which have been specifically set forth hereinabove, may be utilized as shrinkproofing agents in the process of the present invention. Additionally, the shrinkproofing compositions used may be a mixture of one or more of the above compounds or other similar compound which fall within the generic formulas which have been given. Often, such mixtures will be the natural result of the preparation of the compositions, which preparations may give a statistical distribution of the possible products. Such mixtures may be mixtures of various polymethylene polyphenyl isocyanates, mixtures of various poly(isocyanato phenyl) methanes, or mixtures of both polymethylene poly-

phenyl isocyanates and poly(isocyanatophenyl)methanes.

In preparing the impregnating solutions for use in the method of the present invention, the shrinkproofing component as has been described is dispersed or dissolved in a suitable solvent. Although any solvent, in which the isocyanate material will dissolve without decomposition may be used, in many instances, the aromatic organic solvents, such as benzene, toluene, xylene, and the like, are preferred. Additionally, halogenated aliphatic solvents, such as trichloroethylene, perchloroethylene, carbon tetrachloride, methylene chloride, and the like, have also been found to be extremely useful. The solvents may be classified generally as benzene, substituted benzenes containing 1-3 lower alkyl groups of 1-6 carbon atoms each and halogenated lower alkyls containing 1-6 carbon atoms and 1-8 halogens. The shrinkproofing component is dispersed or dissolved in the solvent in an amount sufficient to provide the desired resin add-on on the proteinaceous material when the material is impregnated with the solution. Concentrations within the range of about 0.5 to about 50% by weight of the solvent composition are typical, but in many instances, higher concentrations are also suitable, up to the maximum solubility of the isocyanate material in the solvent used. Typical of such higher concentrations which may be used are those of 80 to 90% by weight of the solvent composition, or even higher, in those instances where the isocyanate material used is miscible in substantially all proportions with the solvent.

In preparing the impregnating solution for use in the present method, when using an unmodified polyisocyanate, such as polymethylene polyphenylisocyanate or tris(isocyanatophenyl)methane, the polyisocyanate material is dissolved in the solvent in an amount sufficient to provide the desired concentration in the impregnating solution. Where a modified polyisocyanate material is used, the unmodified polyisocyanate may be dissolved in several times its own weight of solvent and to this mixture the modifying material, such as an alcohol, thioalcohol, organic acid, amine, or amide is added, in an amount sufficient to react with the unmodified polyisocyanate and effect the modification desired. Additionally, if desired, the reaction mixture may also contain a suitable catalyst, such as a polyalkyl amine. Typically, the amount of modifying agent added is sufficient to react with from about 5% to about 70% of the isocyanate groups present, and preferably is sufficient to react with from about 10% to 35% of the isocyanate groups. The amount of modifier used is such that in the resulting modified isocyanate there are at least two unmodified isocyanate groups.

Once reaction is substantially complete, additional solvent may be added to the reaction mixture to obtain the impregnating solution having the desired concentration. Alternatively, of course, the modified polyisocyanates may be prepared separately and thereafter dissolved in the solvent in appropriate amounts to form the impregnating solution, as is done with the unmodified polyisocyanate.

The proteinaceous material, such as a wool textile material, may be impregnated with the polymerizable shrinkproofing solution prepared as indicated hereinabove, using any convenient means. For example, the wool may be immersed or padded in the treating solution and the fabric then passed through squeeze rolls to remove excess solution. If desired, the treating solution may be applied to the material by spraying, rather than by immersion. Other suitable application techniques, as are known to those in the art, may also be used. After the proteinaceous materials have been impregnated with the solution, they are preferably dried so as to remove the solvent from the material. Desirably, the impregnation is carried out so that the treated proteinaceous material has a resin add-on within the range of about 1 to about 15% by weight of the material. Higher resin add-on than 15%, e.g., 40 to 50%, may be attained in some in-

stances although, generally, it has not been found that such higher add-ons appreciably improve the shrink resistance which is obtained. Generally, it has been found that resin add-ons appreciably less than 15%, e.g., 0.1 to 5% are often sufficient to provide durable shrinkproofing of the proteinaceous materials. Typically, the treating solution is maintained at a temperature within the range of about 10° centigrade to the boiling point of the solvent used, e.g., 120° centigrade for perchloroethylene, and preferably is within the range of about 20° centigrade to about 30° centigrade during the impregnation step. Thereafter, the impregnated material is dried, preferably in an oven, at a temperature within the range of about 20° centigrade to the boiling point of the solvent used, with temperatures within the range of about 65° centigrade to about 125° centigrade being preferred.

Following the impregnation and drying of the proteinaceous material, the thus-treated fabric is then cured in water. Although various techniques may be utilized in effecting this water cure, the treated proteinaceous material is preferably immersed in water and maintained in the water until the curing is complete.

It has been found that the time to effect the desired cure of the polyisocyanate material with which the proteinaceous textile is impregnated varies with the temperature at which the cure is effected. Accordingly, it is desirable that the water used is at an elevated temperature, temperatures within the range of about 40° centigrade to about 100° centigrade being typical, with temperatures within the range of about 80° centigrade to about 94° centigrade being preferred. When carrying out the water cure at these temperatures, curing times within the range of about 1 hour to about 1 minute are typical, with times of 30 minutes to 2 minutes being preferred. It is to be appreciated, that where the length of curing time is not an important factor, the water cure of the polyisocyanate impregnant may be carried out at room temperature, i.e., about 20° centigrade. Under such conditions, the curing time may be as long as several days, e.g., 48 hours. There is, however, some indication that the full shrinkproofing effectiveness of the polyisocyanate compositions may not be attained when the water cure is carried out under these low temperature conditions. Moreover, it has been found that low temperature curing techniques, and particularly those carried out below about 75° centigrade, may not impart to the treated fabric the desired degree of durability to dry cleaning solvents, such as trichloroethylene. In many instances, after curing under these conditions, dry cleaning of the fabric may remove appreciable quantities of the cured shrinkproofing material so that after a subsequent laundering, shrinkage may occur. Additionally, it has been found that in some instances water in vapor form may be used to effect the cure of the treated fabric. Accordingly, low temperature curing techniques are generally not preferred. It is to be further appreciated, that if desired, the water cure of the polyisocyanate impregnant may be effected by substantially saturating the impregnated proteinaceous material with water and thereafter, completing the polymerization or cure of the polyisocyanate by heating the water-wet, substantially saturated material at an elevated temperature. In such processes, curing temperatures within the range of about 66° centigrade to about 177° centigrade for periods of about 30 minutes to about 1 minute are typical, with temperatures within the range of about 107° to about 135° centigrade for periods of 10 minutes to about 3 minutes being preferred. After the water cure of the impregnated textile material has been completed, the material is then dried to remove any water which may remain. Frequently, where the later described curing process is used, i.e., water impregnation of the treated fabric, followed by heating at an elevated temperature, the curing and drying of the fabric is effected substantially simultaneously.

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It has been found that in many instances the water used to carry out the polymerization or cure of the polyisocyanate impregnated in the textile material is desirably slightly alkaline. Typical pH values for the curing water are within the range of about 7.5 to 9. Where the pH of the curing water is below these values, it may be adjusted by adding thereto an alkaline material, such as an alkali metal bicarbonate. Additionally, if desired, the curing water may also contain small amounts of a suitable wetting agent, to insure more thorough and rapid wetting of the impregnated material. Typical wetting agents which may be used are nonionics, such as the polyalkylene ethers and anionics such as alkyl aryl sulfonates and sulfates. These materials are typically present in amounts within the range up to about 1% by weight of the treating water, amounts within the range of about 0.05 to about 0.2% being preferred.

As has been indicated hereinabove, the process of the present invention may be carried out on proteinaceous materials in various forms, including yard goods, finished articles, such as sweaters and the like, as well as on the unspun fiber or the yarn itself. It has been found that proteinaceous textile materials, such as wool, which have been treated in accordance with this process consistently show an area shrinkage of less than about 5%, with area shrinkages within the range of about 1 to 3% being typical. Moreover, it has been found that the shrink resistance is retained by the treated fabric even after numerous washings in hot water and that the hand and feel of the treated materials are not substantially different from those of untreated material. Additionally, the shrink-proof finish is durable to dry cleaning and is found to impart dimensional stability to the fabric. It also facilitates dyeing and improves dye fastness.

In order that those skilled in the art may better understand the present invention and the manner in which it may be practiced, the following specific examples are given. It is to be understood that these examples are illustrative of the invention and are not intended to be limitations thereon. In these examples, unless otherwise indicated, temperatures are in degrees centigrade, parts and percentages are by weight and shrinkages are given as percent change from an untreated, unwashed control.

EXAMPLE 1

A textile treating solution was prepared by dissolving a commercial polymethylene polyphenylisocyanate having a viscosity of 250 centipoises at 25° centigrade and an NCO equivalent weight of 133.5 in benzene to form a solvent solution containing about 7% by weight of the polyisocyanate. Wool fabric was padded through this solution so as to impregnate the fabric and thereafter, the fabric was dried in an oven at a temperature of about 40° C. The treated wool was then immersed in water, which was at a temperature of about 60° C. for a period of ten minutes, the pH of the water having been adjusted to about 8 with sodium bicarbonate and the water additionally containing 0.1% by weight of a polyalkylene ether nonionic wetting agent. The resin add-on on the fabric was found to be about 6.7%. Thereafter, a rectangle measuring 250 by 300 millimeters was marked on the wool fabric and the treated fabric was washed for 5 hours in an aqueous solution of a commercial detergent at a temperature of about 60° centigrade using a standard home agitator type washing machine. The fabric was then removed from the wash solution, dried, and the change in the area of the marked rectangle was measured. Using this procedure, it was determined that the treated fabric had an area shrinkage of only 3.4%, as compared to an untreated wool fabric which showed an area shrinkage of greater than 60%.

EXAMPLE 2

The procedure of Example 1 was repeated with the exception that the solvent solution prepared was a trichlo-

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roethylene solution containing 4% by weight of the polyisocyanate. The fabric treated with this solution had a resin add-on of 6.7% and gave an area shrinkage of only 3.2% after being subjected to the cure conditions and to the 5 hour wash, as in Example 1.

EXAMPLE 3

The procedure of Example 1 was repeated with the exception that the treating solutions used were benzene solutions containing 1, 4, and 7% by weight respectively, of tris(isocyanatophenyl)methane. The fabrics treated with these solutions had resin add-ons of 3.0, 6.4 and 11.6% respectively, and gave area shrinkages after the five hour washing of 3.2, 2.0 and 2.3%, respectively.

EXAMPLE 4

A textile treating composition was prepared by dissolving 50 parts of the polymethylene polyphenylisocyanate, as used in Example 1, in 100 parts of toluene. To this solution were added 20 parts of 1-octadecanol, and 0.5 parts of triethylamino catalyst. The resulting solution was stirred for a period of about 30 minutes while the temperature was maintained below about 40° centigrade. At the end of this time, it was found that all of the alcohol had reacted with the isocyanate to form an alcohol substituted polyisocyanate containing 0.2 moles of alcohol per mole equivalent of NCO group. Thereafter, additional toluene was added to the reaction product to obtain a diluted treating solution containing about 6% by weight of the alcohol substituted polyisocyanate. This treating solution was padded onto a wool fabric, as in Example 1, and the treated fabric was dried. This material was then immersed in water at room temperature, the water containing 0.1% sodium bicarbonate and 0.1% of the nonionic wetting agent of Example 1. A wet pickup on the treated fabric of about 100% was obtained and the wet fabric was then heated for five minutes at a temperature of about 120° centigrade to effect curing and drying of the fabric and obtain a resin add-on of 3.7%. Thereafter, the fabric was washed for five hours at 60° centigrade, and dried as in Example 1, and at the end of this time the area shrinkage of the fabric was found to be 1.3% and the fabric had a Gurley stiffness value of 33 milligrams.

EXAMPLE 5

Additional treating solutions were formulated, using the procedure of Example 4 with the exception that five, fifteen and thirty parts by weight of the alcohol were used. The resulting alcohol substituted polyisocyanates formed contained 0.05, 0.15 and 0.30 mole of alcohol per mole equivalent of NCO. Wool fabric was treated with impregnating solutions containing 6% of these products and the treated fabric was cured and washed, as in Example 4. The area shrinkages obtained were 2.8%, 2.1% and 1.0%, respectively and the Gurley stiffness values were 46, 36 and 31 milligrams, respectively.

EXAMPLE 6

The procedure of Example 4 was repeated with the exception that the alcohol used was 1-octanol in an amount of 9.6 parts by weight. The resulting alcohol modified polyisocyanate contained 0.2 mol of alcohol per mol equivalent of NCO. After curing and washing the treated wool fabric as in Example 4, the area shrinkage obtained was 4.53%.

EXAMPLE 7

The procedure of Example 4 is repeated with treating solutions prepared by using the modifiers and polyisocyanates in the amounts shown in the following table. In each instance, the reaction temperatures and catalyst amounts are varied as necessary to obtain the indicated reaction products. With all of these treating solutions, the wool treated had an area shrinkage of less than about 10%. It is to be noted that in Section II of the table, the

polyisocyanate used is a 20% by weight solution of the isocyanate:

blend was 3.3% and that of the wool-nylon blend was 5.6%.

Modifier	Amount of modifier, parts	Polyisocyanate	Amount of polyisocyanate, parts	Mols of modifier per mole equiv. of NCO
Section I:				
A..... 1-hexanethiol.....	8.7	Polymethylene-polyphenylisocyanate.....	50	0.2
B..... 1-decanoic acid.....	19	do.....	50	0.3
C..... Benzoic acid.....	4.5	do.....	50	0.1
D..... Heptyl amine.....	8.5	do.....	50	0.2
E..... Didecyl amine.....	55	do.....	50	0.5
F..... 4-(4-hydroxyphenyl) butyl amine.....	12	do.....	50	0.2
G..... Formamide.....	12	do.....	50	0.7
H..... Benzamide.....	13.4	do.....	50	0.3
I..... N-heptylheptamide.....	17.8	do.....	50	0.2
Section II:				
J..... 1-licosanol.....	30	tris(Isocyanatophenyl)methane.....	185	1
K..... p-hydroxyphenylethanol.....	14	do.....	920	0.2
L..... 1-pentanethiol.....	11	do.....	368	0.5
M..... p-Hydroxyphenyltetradecanoic acid.....	7	do.....	19	2
N..... Diphenyl amine.....	2	do.....	184	0.1
O..... Licosanyl amine.....	3	do.....	46	0.4
P..... N-phenyl benzamide.....	2	do.....	28	0.67
Q..... N-decyl dodecamide.....	3.5	do.....	37	0.5

EXAMPLE 8

The procedure of Example 1 was repeated using a treating solution containing 4.0% by weight of the polymethylene polyphenylisocyanate, as described in Example 1 and benzene. The treating solution was applied to a pair of worsted wool trousers which, after curing as in Example 1, were given five home launderings. The percentages of linear shrinkage which resulted from these washings, measured at the length of the leg, and the waist, and the width at the crotch, were 0.7, 2.5, and 0, respectively.

EXAMPLE 9

The procedure of the preceding example was repeated using a treating solution containing 3% by weight of the polymethylene polyphenyl isocyanate and benzene. This treating solution was applied to a wool knit sweater and the thus-applied polyisocyanate material was cured, using the procedure of Example 1. After ten home washings, the sweater showed the following linear shrinkages:

	Percent
Width	-0.2
Arm length	2.2
Back length	3.6
Band	0

It is to be noted, that the minus value given for the percentage of linear shrinkage indicates that there was a slight stretching of the sweater at that point, rather than a shrinkage.

EXAMPLE 10

The procedure of Example 1 was repeated, using two treating solutions, one containing 3.7% by weight of the polymethylene polyphenylisocyanate and the second containing 2.4% by weight of the polymethylene polyphenylisocyanate. The first solution was used to treat a 55-45 percent blend of "Dacron"¹ polyester fiber and wool while the second was used to treat a 70-30 percent blend of wool and nylon. After curing, as in Example 1, both of the treated fabrics were washed for 5 hours at 60 degrees centigrade. Following these washings, it was found that the area shrinkage of the "Dacron" polyester fiber-wool

EXAMPLE 11

Using the procedure and treating solution of Example 1, a number of wool fabric samples were impregnated and were then cured, using different water temperatures and immersion times. Thereafter, the cured samples were extracted for 30 minutes in boiling trichloroethylene and then were washed for 10 hours at 60 degrees centigrade. Using this procedure, the following area shrinkages were obtained in these samples:

Sample:	Percent resin add-on before cure	Cure conditions		Percent resin add-on after TCE extraction	Percent area shrinkage
		Water temperature, ° C.	Time, minutes		
A.....	4.2	27	10	1.71	40
B.....	4.8	27	30	2.74	21
C.....	5.7	49	30	5.60	3.6
D.....	4.5	71	10	3.67	2.13
E.....	4.3	71	30	4.33	2.53
F.....	3.8	93	10	3.72	3.45
G.....	4.3	93	30	2.68	3.7

EXAMPLE 12

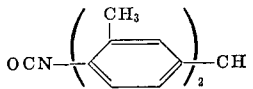
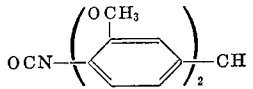
Using the procedure and composition of Example 1, a bonded wool-acetate fabric was impregnated, cured and washed for 1 hour at 60° centigrade, as in Example 1. Thereafter, the washed fabric was hung on a line and allowed to dry. After drying, the bonded fabric was found to be substantially wrinkle free and showed an area shrinkage of 1.5%.

EXAMPLE 13

The procedure of Example 1 was repeated using different isocyanate materials at varying concentrations. These materials are similar to isocyanate materials of the present invention and are included to show the improvement obtained by the use of the materials of the present invention, containing at least two NCO groups. In each instance, the wool fabric impregnated with these treating solutions was cured and dried, and the area shrinkage was determined,

¹ Registered trademark of E. I. du Pont de Nemours.

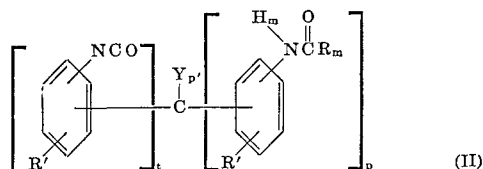
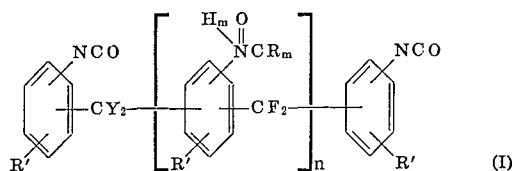
as in Example 1. Using this procedure, the results obtained were as follows:

Sample:	Isocyanate used	Concentration of treating solution, percent	Percent resin add-on	Percent area shrinkage
A	CH ₃ (CH ₂) ₁₁₋₁₆ NCO	1	4.1	73.6
B	Same as above	4	7.5	73.3
C	do.	7	11.2	71.2
D	Hexamethylene diisocyanate	1	2.4	72.8
E	do.	4	5.1	71.6
F	do.	7	7.2	71.0
G		1	6.1	53.8
H	Same as above	4	7.0	12.11
I		1	1.9	61.2
J	Same as above	4	2.4	45.2
K	do.	7	14.6	66.7
L	Toluene diisocyanate	1	2.5	73.6
M	do.	4	6.6	69.7
N	do.	7	10.8	66.4
O	di(Isocyanatophenyl)methane	1	0.9	59.0
P	do.	4	5.5	21.5

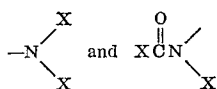
While there have been described various embodiments of the invention, the compositions and methods described are not intended to be understood as limiting the scope of the invention, as changes therewithin are possible and it is intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. A method of shrinkproofing a proteinaceous textile material which comprises (a) contacting the proteinaceous material to be treated with a polymerizable treating solution comprising a polyaryl polyisocyanate having the formula:



wherein n is a number having an average value of at least 1 and is generally from 1 to 4; t is a number from 2 to 4; p is a number from 0 to 2; p' is 0 or 1; $t+p$ has an average value of at least 3 and is generally from 3 to 4; $t+p+p'$ is 4; m is 0 or 1; R' is selected from the group consisting of halogen, hydrogen, alkyl and alkoxy; Y is selected from the group consisting of hydrogen, alkyl and phenyl; R is selected from the group consisting of OX , SX , X ,



and X is selected from the group consisting of hydrogen, alkyl, alkylphenol, alkylphenoxyalkoxy and phenyl; and

(b) thereafter curing the thus-contacted material with water.

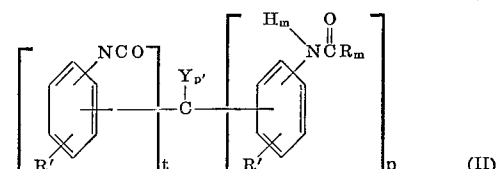
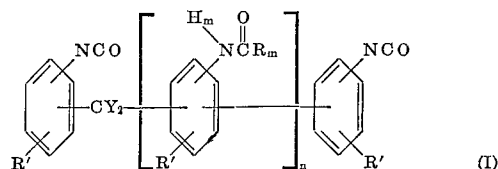
2. The method as claimed in claim 1 wherein the isocyanate groups on the polyaryl polyisocyanate in excess of two are modified by reaction with an aliphatic alcohol containing from about 4 to about 20 carbon atoms.

3. The method as claimed in claim 1 wherein the polyisocyanate is contained in the treating solution in an amount within the range of about 1 to about 50% by weight of the solution.

4. The method as claimed in claim 3 wherein the water curing of the impregnated proteinaceous textile material is effected by immersing the impregnated proteinaceous textile material in water at a temperature within the range of about 40° C. to about 100° C. for a period of from about 1 hour to about 1 minute.

5. The method as claimed in claim 3 wherein the water cure is effected by impregnating the polyisocyanate treated proteinaceous textile material with water and, thereafter, heating the thus-water impregnated material at a temperature within the range of about 66° to about 177° C. for a time within the range of about 30 minutes to about 1 minute.

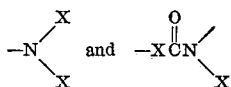
6. A proteinaceous textile material containing a shrinkproofing amount of a polyaryl polyisocyanate having the formula:



wherein n is a number having an average value of at least 1 and is generally from 1 to 4; t is a number from 2 to 4; p is a number from 0 to 2; p' is 0 or 1; $t+p$ has an average

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value of at least 3 and is generally from 3 to 4; $t+p+p'$ is 4; m is 0 to 1; R' is selected from the group consisting of halogen, hydrogen, alkyl and alkoxy; Y is selected from the group consisting of hydrogen, alkyl and phenyl; R is selected from the group consisting of OX , SX , X ,



and X is selected from the group consisting of hydrogen, alkyl, alkylphenol, alkylphenoxyalkoxy and phenyl; which polyaryl polyisocyanate has been cured with water.

7. The proteinaceous textile material as claimed in claim 6 wherein the water curing of the polyisocyanate with which the proteinaceous textile material is impregnated is effected by immersing the impregnated material in water at a temperature within the range of about 40° C. to about 100° C. for a period of about 1 hour to about 1 minute.

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8. The proteinaceous textile material as claimed in claim 6 wherein the water cure of the polyisocyanate with which the material is impregnated is effected by impregnating the polyisocyanate treated material with water and, thereafter, heating the water-impregnated material at a temperature within the range of about 66° C. to about 177° C. for a period of about 30 minutes to about 1 minute.

References Cited

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15 RICHARD D. LOVERING, Primary Examiner

U.S. Cl. X.R.

8—128

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,552,910 Dated January 5, 1971

Inventor(s) George M. Wagner et al.

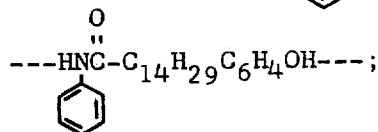
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, lines 5 and 10: number formulas as --- (I) and (II) ---;

line 15: correct "] " to read ---]_p ---.

Column 4, line 50: correct formula " " to read ---  ---.

Column 6, line 50: correct formula "  HNC(=O)-C₁₄H₂₉C₆H₅OH " to read



Column 14, line 59: correct "Exmaple" to read ---Example---

Claim 1: correct " NCR_m " to read ---  NCR_m ---;

Signed and sealed this 4th day of May 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER,
Commissioner of Patents