United States Patent

McKillip et al.

[15] **3,640,676**

[45] **Feb. 8, 1972**

[54] **PROCESS FOR SHRINKPROOFING WOOL**

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[22] Filed: **Oct. 10, 1969**

[21] Appl. No.: **865,494**

[52] **U.S. Cl.** ..... **8/127.6**, 8/128, 260/77.5, 260/2 EN, 260/8

[51] **Int. Cl.** **D06m 3/02**

[58] **Field of Search** ..... 8/127.5, 128; 260/77.5 AT, 260/77.5 C, 77.5 CH, 2 EN

[56] **References Cited**

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3,516,781 6/1970 Pensa 8/115.7

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[57] **ABSTRACT**

Linear addition polymers having multiple N, N-ethylene ureido functionality are employed to impregnate a wool or wool-containing substrate to provide a treated substrate exhibiting excellent dimensional stability characteristics.

10 Claims, No Drawings

PROCESS FOR SHRINKPROOFING WOOL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the treatment of wool with a poly-N,N-ethylene urea to impart dimensional stability thereto.

2. Description of the Prior Art

Considerable effort has heretofore been directed toward improving the dimensional stability characteristics of wool. Natural wool is particularly deficient in this regard and it has consequently proven to be a difficult task to ameliorate this shortcoming to the extent whereby only a tolerable degree of shrinkage is experienced after repeated washing operations. The realization of such desideratum, moreover, is complicated by the fact that the unique structure of a natural wool fiber which renders it prone to shrinkage in a washing operation or when subjected to similar environmental conditions also accounts for its overall excellent properties as a textile forming material. Thus, for any effective shrink control method to be useful in a practical sense, it must not deleteriously alter the various desirable characteristics imparted to a fabric by the wool fiber such as, hand, appearance, strength, abrasion resistance, pilling resistance and the like.

Two principal types of shrinkproofing methods have evolved in the development of this art. One of such methods is based on the chemical modification of the wool fiber. The other involves the deposition of a polymer onto the fiber surface. The latter method has been accepted as representing the more efficacious approach in that a number of polymer and potentially reactive prepolymer-type treating agents have been made available which are capable of imparting shrinkproofing properties to the wool without substantially altering the structural form of the individual fiber. The polymer deposition method as hitherto practiced, however, generally imparts only a fugitive type of shrinkage resistance to the wool fiber since repeated washings of the fabric will in time cause loosening and washing away of deposited polymer thereby resulting in a progressive loss of the dimensional stability initially acquired in the treating process.

SUMMARY OF THE INVENTION

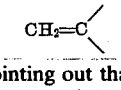
In accordance with this invention, a method is provided for imparting shrinkproof properties to a wool or a wool-containing substrate in either a fibrous or fabric form. Such method comprises impregnating the substrate with a solution or aqueous dispersion of an organic soluble linear copolymer having a plurality of randomly distributed pendant N,N-ethylene ureido groups attached to carbon atoms constituting the polymeric backbone. Upon attaining a desired degree of pickup of the poly-N,N-ethylene urea impregnant, the substrate is heated to effect removal of the solvent or water, as the case may be.

The practice of the present invention results in the deposition of the polymeric treating agent in a manner whereby the polymer is tenaciously bonded to the fiber surface. Thus, the above-mentioned problem associated with the prior art use of polymeric treating agents for imparting shrinkage resistance is obviated. Since wool is a proteinaceous material containing active hydrogen containing groups, the permanent nature of the shrinkproofing method of this invention is largely attributed to the reaction of the aziridinyl groups of the polymeric treating agents of this invention with such active hydrogen groups thereby providing an advantageous degree of grafting of the polymer onto the wool.

The foremost advantage of the present invention over and above the degree and permanency of shrinkproofness imparted to the wool without adversely affecting the physical properties thereof stems from the fact that the contemplated reactive treating agents are preformed addition polymers. Such polymers can therefore be readily formulated so as to be individually suited for the treating application concerned where, in addition to imparting shrinkage resistance to the substrate, it might be desired to achieve a particular supplemental enhancement as, for example, water-repellancy, crease-resistance, flame retardancy, soil release, etc. Still another advantage of the wool shrinking agents of this invention resides in the fact that they possess an unusually high degree of intrinsic stability and thus storage problems are obviated. Moreover, because of such stability characteristics, they can be readily employed in an aqueous emulsion form by wool processors whose plant facilities are primarily adapted for emulsion application practices.

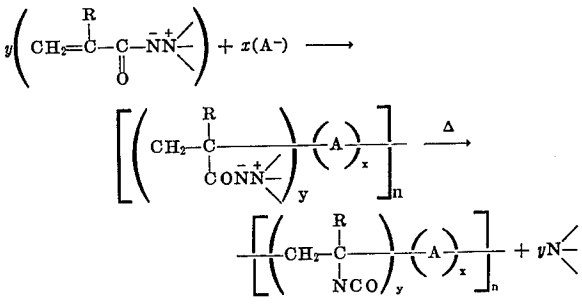
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polymeric treating agents useful in the practice of this invention can be broadly defined as the products obtained by the reaction of an ethylenimine with certain aliphatic polyisocyanates. The applicable polyisocyanates are those resulting from the thermolysis of the corresponding polyaminimides derived by the addition polymerization of tertiary amine acrylimide and a monomer copolymerizable therewith. The manner in which these polyisocyanates can be prepared and converted to the corresponding poly-N,N-ethylene ureas is illustrated in the following reaction schematic wherein R of the amine is hydrogen, halogen or methyl and wherein A represents a compound containing a polymerizable

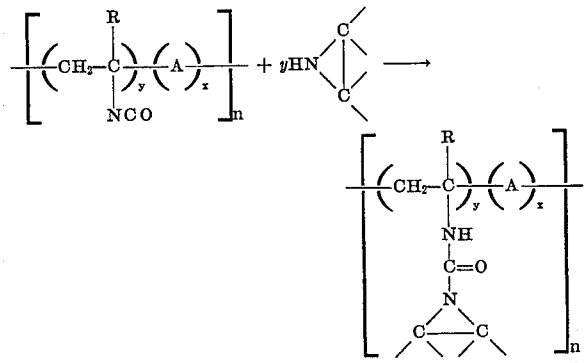


grouping. It warrants pointing out that the formula given for the resultant polymers is meant to indicate only the statistical distribution of the respective comonomer residues and not that they are necessarily structurally arranged in the way shown.

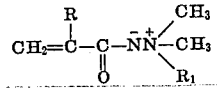
(I)



(II)



As is to be noted from the overall reaction schematic presented hereinabove, the base starting compound for obtaining the polyisocyanates from whence the shrinkproofing agents of this invention are derived is a tertiary amine acrylimide. Particularly exemplary of such compounds are those having the following formula:

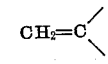


wherein R is hydrogen, halogen, or methyl, and R_1 is methyl or a lower hydroxy alkyl.

Amine acrylimides of the type depicted above can be conveniently prepared by reacting an acrylate, preferably one having a lower alkyl substituent in the ester group, with an unsymmetrical disubstituted hydrazine, e.g., 1,1-dimethyl hydrazine, and a lower alkylene oxide such as, for example, ethylene oxide. In accordance with this method, an applicable variation thereof consists of initially reacting the alkylene oxide with the hydrazine, whereupon the resultant hydroxy aminimine can be reacted with the acrylate in a separate step. Further details relative to the above procedures are set forth in copending application Ser. No. 703,554 filed Feb. 7, 1968, now U.S. Pat. No. 3,485,806.

An alternate way for producing suitable amine acrylimides consists of an in situ method wherein the vinyl ester, trimethyl hydrazinium salt and a strong base such as sodium methoxide, are reacted in t-butanol. As indicated, this method is known in the art.

The next step in obtaining the treating agents contemplated herein consists of copolymerizing the amine acrylimide with an active-hydrogen free comonomer containing a polymerizable



group. The applicable comonomers accordingly embrace a host of vinyl and vinylidene compounds.

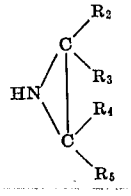
An exemplary enumeration of suitable vinyl and vinylidene compounds for copolymerizing with the amine acrylimide include: the vinyl halides, e.g., vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene chloride, etc., including the vinyl pseudo halides, e.g., acrylonitrile and methacrylonitrile; the unsymmetrical dialkyl substituted ethylenes, e.g., isobutylene, isooctene, isooctadecene, the alpha olefins, e.g., 1-butene, 1-hexene, 1-octene, 1-dodocene, 1-hexadecene, 1-octadecene; the vinyl ethers, e.g., methyl-, ethyl-, propyl-, butyl-, isobutyl-, lauryl-, and stearyl vinyl ether; the vinyl esters, e.g., vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl stearate, etc.; the aromatic vinyl compounds, e.g., styrene, alpha methyl styrene, chloro-styrene, vinyl toluene and vinyl naphthalene; the vinyl derivatives of heterocyclic compounds, e.g., vinyl pyridine, N-vinyl pyrrolidine, N-substituted N-vinyl piperidine and the N-vinyl oxazolidones; acrylamide and the N-substituted acrylamides; the acrylates, halo- and methacrylates, e.g., ethyl acrylate, butyl chloro acrylate, hexyl acrylate, decyl acrylate, stearyl acrylate, behenyl acrylate, methyl methacrylate, octyl methacrylate, lauryl methacrylate, eicosyl methacrylate; the vinyl ketones, e.g., methyl vinyl ketone, hexyl vinyl ketone, lauryl vinyl ketone, etc.; esters of alpha, beta-ethylenically unsaturated polycarboxylic acids, e.g., dimethyl maleate, dibutyl fumarate, dimethyl itaconate, etc.; ethylenically unsaturated fatty acids, dimers and trimers thereof, e.g., oleic acid, linoleic acid, etc.; vinyl silanes, vinyl trifluoroacetate, 2,2,2, trifluoroethyl acrylate, etc. The various comonomers can be used singly or in combination with one another.

The copolymerization of the amine acrylimide with the vinyl or vinylidene comonomer can be carried out in bulk, in solution, or in an aqueous medium. Solution polymerization is preferred insofar as a solution of the poly-N,N-ethylene urea represents the preferred form for wool treating in accordance with this invention. A variety of organic solvents can be utilized for this purpose. Both aliphatic and aromatic solvents as well as mixtures thereof with a polar solvent are applicable. Aromatics such as benzene, toluene, xylene, etc., and combinations thereof with a polar solvent; e.g., a lower alkanol, are preferred. Because of the relative stability of the aminimide grouping, elevated temperatures of as high as 100° C. can be used in carrying out copolymerization without extensive isocyanate formation. Polymerization temperatures in excess of 100° C. may be employed; however, some rearrangement of the aminimide grouping to isocyanate will occur, either to isopropenyl isocyanate or the isocyanate on the polymer backbone.

The copolymerization can be effected by heating alone, but is preferably initiated by the use of a conventional radical forming catalyst. In some instances, it is desirable to use the free radical forming catalyst in combination with a reducing agent or promoter. Such techniques are well understood in the polymerization art. The ratio of amine acrylimide to the comonomer or comonomers copolymerizable therewith can vary extensively depending in the main upon the particular use application envisioned for the final poly-N,N-ethylene urea product. Likewise, the polymerization can be carried out or comonomers appropriately selected to produce an ultimate polymer of any desired length.

Upon obtaining the polyaminimide as outlined above, the pendant aminimide groups thereof are thermally rearranged to isocyanate groups. Thermolysis of the polyaminimide can be effected simply by heating an organic solution thereof at a temperature of between about 120° and 200° C. and more preferably from about 120° and 150° C. In the rearrangement of the aminimide group to an isocyanate group, a tertiary amine is evolved. Accordingly, facilitating the removal of the tertiary amine is desirable. This can be accomplished by codistilling a fraction of the evolved amine with the solvent employed in preparing the polyaminimide in accordance with the preferred method. The extent of conversion of the aminimide groupings can be followed by noting the reduction of the infrared spectrum band at 1,580 $cm.^{-1}$ and the corresponding increase of the isocyanate band at 2,270 $cm.^{-1}$ or by wet analysis of isocyanate content. Substantially complete conversion of the aminimide groups to isocyanate groups can be readily achieved in this manner. On the other hand, the extent of conversion can be controlled to retain a degree of aminimide functionality if such is desired.

The final step in preparing the treating agents useful in the practice of this invention consists of reacting the thermolyzed aminimide, i.e., the resultant aliphatic polyisocyanate, with an ethylenimine of the formula:



wherein R_2, R_3, R_4 and R_5 are either hydrogen, aryl or alkyl. An enumeration of representative ethylenimines for reaction with the polyisocyanate is as follows: ethylenimine, 2-methyl-ethylenimine, 2-ethyl-ethylenimine, 2,2-dimethyl-ethylenimine, 2,3-dimethyl-ethylenimine, 2,2,3-trimethyl-ethylenimine, 2,2-dimethyl-3-propyl-ethylenimine, 2-butyl-ethylenimine, 2,3-dipropyl-ethylenimine, 2-phenyl-ethylenimine, 2,3-diphenyl-ethylenimine, 2-ethyl-2-phenyl-ethylenimine, 2-ethyl-2-phenyl-3-methyl-ethylenimine, 2-propyl-2-phenyl-ethylenimine, 2-tolyl-ethylenimine, 2-xylyl-ethylenimine, etc. The preferred imines are ethylenimine and 2-methyl-ethylenimine.

The polyisocyanate is preferably reacted with the selected ethylenimine in a stoichiometric ratio, i.e., 1 mole of the ethylenimine per equivalent of the isocyanate (NCO) content of the copolymer. Applicable temperature conditions range from about room temperature to 50° C. It is preferred to react the ethylenimine with the polyisocyanate in an organic solution of the latter. Suitable solvents for this purpose are those enumerated hereinabove in connection with the preferred manner for carrying out copolymerization.

Reaction of the ethylenimine with the polyisocyanate in the foregoing manner results, as indicated hereinbefore, in the conversion of the pendant isocyanate groups to N,N-ethylene ureido groups. The resultant products which are useful as shrinkproofing agents in contemplation of the practice of this invention contain a N-N-ethylene ureido content or moiety of

from about 0.1–50 percent and more preferably, from about 0.5–10 percent based on the weight of the final product. While polymers containing substantially in excess of the former exemplary range represent effective shrinkproofing agents, any improvements realized with respect to shrinkage resistance and permanency are not ordinarily economically warranted. The polyisocyanate from whence the corresponding poly-N,N-ethylene urea is obtained can be formulated so as to provide the desired N,N-ethylene ureido content by appropriately adjusting the ratio of amine acrylimide to the comonomer(s) in preparing the copolymer, all as described hereinabove.

The method for treating a wool substrate with the poly-N,N-ethylene urea in accordance with the preferred mode, commonly referred to as a padding procedure, involves immersing the substrate into an organic solution of the polymer to accomplish a desired degree of pickup of the polymer by the substrate following the wringing thereof to remove excess solution. The amount of pickup can be conveniently controlled by appropriately adjusting the solids content of the impregnating solution. The preferred amount of pickup is from about 1–20 percent based on the weight of the substrate. The solids content of the treating solution for realizing such amounts of deposition will generally be in the order of from about 1–40 percent. Thereafter, the impregnated substrate is dried to effect removal of the solvent. Applicable drying temperatures employing the preferred solvents range from about 100° to 150° C.

As indicated previously, the primary objective of this invention is to provide a method for imparting a highly permanent degree of shrink resistance to wool in the sense that the wool can be subjected to repeated washings. Not only is this objective realized but additionally the treated wool can be dry cleaned without materially affecting the degree of dimensional stability that is imparted thereto by the treating process. This represents an especially unique feature of the present invention. Moreover, the effect upon such stability of the treated wool by a dry cleaning operation can be held to a minimal value by either washing the stabilized substrate before dry cleaning or aging the substrate under ambient condition for 12 hours to 3 days before dry cleaning.

While the foregoing description of the invention has been mainly presented in terms of treating wool, it is apparent that the substrate can be a blend or a mixture with other natural fibers such as cotton and mohair or with synthetic fibers such as the polyamide, polyester, polyolefin, and acrylic fibers. In general, for optimum textile properties, the foregoing blends customarily contain an appreciable portion of the wool fiber generally over 30 percent by weight or more commonly 60 percent or higher. The substrates, moreover can take the form of thread, yarn, woven or knitted fabric and garments.

The following working examples illustrate the best mode contemplated for carrying out the present invention. As indicated, these examples are given primarily by way of illustration and accordingly, any enumeration of detail set forth therein is not to be construed as limiting the invention except as such limitations appear in the appended claims. All parts are parts by weight unless otherwise noted.

EXAMPLE I

This example illustrates the preparation of three exemplary polymeric wool shrinkproofing agents useful in the practice of this invention and outlines the results obtained in shrinkproofing wool and wool-containing cloths with organic solutions thereof.

POLYMER A

Into a suitable reaction vessel of approximately 5 gallon capacity equipped with a stirrer and reflux condenser were charged 0.465 lb. of 1,1-dimethyl-1-(2-hydroxypropyl) amine methacrylimide (DHA), 2.88 lb. butyl acrylate and 17.84 lb. xylene. With stirring and under a nitrogen blanket, the charged ingredients were heated to 190°–195° F. and 0.08 lb. of azobisisobutyronitrile (VAZO) added. A solution of 8.64 lb. butyl acrylate and 8.92 lb. xylene was slowly added to the reaction vessel at an approximate rate of 1,000 ml. per 5 minutes. Following the addition of each 1,000 ml. portion of the butyl acrylate solution, an additional charge of DHA in the amount of 0.155 lb. was accomplished resulting in a total amount thereof added in such incremental manner of 1.4 lb. After the addition of one-half of the butyl acrylate solution was accomplished as indicated, an additional 0.08 lb. of VAZO was added. Following the completion of the addition of the monomers as aforesaid, the reactor contents were held for 2 hours at 200° F. The nonvolatile or solids content of the completed polymer was 31.1 percent.

The reaction vessel was then equipped with a receiver and the polymer solution thermolyzed. Thermolysis was carried out at the reflux temperature (pot temperature 140° C.) thereby resulting in the codistillation of xylene and N,N-dimethyl β-hydroxypropyl amine liberated in the course of the thermolysis reaction. The solids content of the reaction vessel was maintained relatively constant by the continuous addition of makeup xylene. Thermolysis under these conditions was continued for about 4 hours. The completed polymer solution exhibited an isocyanate content (NCO) of 2.2 percent by weight and contained 35 percent by weight solids.

The thermolyzed polymer solution was cooled to room temperature and 1.1 equivalents of ethylenimine based on the NCO content of the solution was added. The reaction mixture was stirred for 1 hour.

POLYMER B

Into a suitable reaction vessel equipped with a stirrer and reflux condenser were charged 230 parts butyl acrylate, 28.3 parts trimethylamine methacrylimide and 516.6 parts xylene. With stirring and under nitrogen atmosphere, the reactor contents were heated to 80° C. and 4 parts of VAZO added. By the application of cooling, the resultant exotherm was held to 96° C. The reaction mixture was cooled to 90° C. and maintained thereat for 2 hours. The solids content of the completed polymerization reaction mixture was 33 percent.

The reaction vessel was equipped with a receiver and the polymer solution thermolyzed following the procedure outlined above in the preparation of polymer A. After about 6 hours holding at the reflux temperature, the polymer solution exhibited an isocyanate content of 2.05 percent by weight and contained 43.5 percent by weight solids.

The thermolyzed polymer solution then reacted with ethylene amine as described in the preparation of polymer A.

POLYMER C

Into a suitable reaction vessel equipped with a stirrer and reflux condenser were charged 186 parts of DHA, 768 parts butyl acrylate, 258 parts vinyl acetate and 2,000 parts xylene. With stirring and under a nitrogen blanket, the reactor contents were heated to 80° C. and 16 parts VAZO added. The resultant exotherm was controlled to 110° C., the polymerization reaction mixture was cooled to 95° C. and held thereat for 1½ hours at which time an additional 2 parts of VAZO were added. Heating at 90°–95° C. was continued for an additional 1½ hours providing a polymer solution containing 33 percent solids.

The resultant polymer solution was thermolyzed following the procedure outlined above. After 4 hours, the polymer solution exhibited a NCO content of 1.78 percent and contained 40.8 percent solids. The thermolyzed solution was then reacted with ethylenimine in the same manner as employed in the preparation of the foregoing polymers of this example.

WOOL TREATING

Wool treating solutions were prepared from polymers A, B and C by further diluting each with xylene. The respective solutions were then padded on the various types of wool cloth indicated in table I below to achieve a level of dry weight

pickup of 10 percent. Following padding and wringing, the impregnated cloths were dried at 110° C. for 15 minutes in a forced air oven.

An area measuring 8 inches ×8 inches (aligned with the warp and filler, respectively) was marked on each dried cloth sample and the samples were then washed once. The conditions utilized in the initial washing and drying procedure are noted below. This preliminary washing is equivalent to the relaxation shrinkage normally imparted to a wool fabric by the wool fabricator to compensate for the stretching occurring in the weaving operation. Such relaxation shrinkage is customarily effected by immersing the wool cloth in water containing 0.1 percent of a nonionic wetting agent at 140° F. for 30 minutes. Following immersion, the cloth is static or press dried. Typically, the foregoing relaxation procedure results in an area shrinkage of about 15 percent.

The relaxed wool samples of this example were thereupon subjected to a cycle of five washings, dried and then measured for area shrinkage. Five sequences of this type were carried out to provide the test data (accumulative basis) given in table I. Each laundering cycle consisted of 15 minutes washing of a 4 pound load in a household automatic washer (reversing agitator type) employing a normal wash setting, medium water level and a water temperature of 120°–130° F. Sixty grams of commercial heavy duty detergent composition were added for each washing cycle. Drying was accomplished in a household tumbler-type dryer for 20 minutes at 140°–178° F.

The results obtained in this series of washing tests are outlined in the following table I:

TABLE I

Test Run No.	Polymer	Type cloth	Relaxation shrinkage, percent	Percent shrinkage after— 5 washes	10 washes	25 washes
1	A	WF-LW	7.6	0.8	1.4	1.7
2	A	WF-TW	2.8	1.7	1.5	1.9
3	A	W/PE-TW	8.0	3.0	3.0	3.0
4	B	WF-LW	5.0	1.6	1.6	1.6
5	C	WF-LW	4.4	1.1	1.9	1.9

NOTE.—WF-LW=wool flannel, loose weave; WF-TW=wool flannel, tight weave; W/PE-TW=wool-polyester blend (65/35) tight weave.

EXAMPLE II

This example serves to illustrate the use of the shrinkproofing agents of this invention in aqueous emulsion form for treating wool cloth.

Into a conventional mixing vessel were charged 210 parts of tap water. An electrically driven stirrer fitted with an impeller blade was immersed into the water and the stirring speed adjusted to provide a moderately deep vortex. Polymer A solution of example I containing 3 percent of a conventional emulsifier was poured at a uniform rate into the vortex of the mixing vessel. The amount of polymer solution added in this manner was 57 parts. Total addition time was approximately 3 minutes.

A loose weave wool flannel cloth was padded from the resultant emulsion to give a 150 percent weight pickup, yielding upon drying a 10 percent by weight polymer add-on. One sample of the impregnated cloth (designated sample A) was dried and cured on a frame for 5 minutes at 150° C. in a forced air oven and another sample (designated sample B) was dried under the same conditions for 10 minutes. Each cloth sample was then washed once to achieve relaxation shrinkage and then tested identically as described in example I. The results obtained are set forth in the following table II:

TABLE II

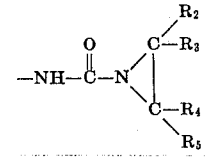
Sample	Relaxation shrinkage %			
A	6.5	0.8	1.3	2.1
B	2.7	1.8	2.3	2.8

We claim:

1. A process for treating a wool or wool-containing substrate to impart dimensional stability thereto which comprises impregnating said substrate with a solution or aqueous dispersion of a linear addition copolymer having a plurality of randomly distributed pendant N,N-ethylene ureido groups attached to carbon atoms constituting the backbone thereof and drying the impregnated substrate.

2. A process in accordance with claim 1 wherein said carbon atoms of the addition copolymer are tertiary carbon atoms.

3. A process in accordance with claim 2 wherein said pendant N,N-ethylene ureido groups correspond to the structural formula:



where R_2, R_3, R_4 and R_5 are either hydrogen, phenyl or an alkyl group containing from one to four carbon atoms.

4. A process in accordance with claim 3 wherein the R_2, R_3 and R_4 substituents of the pendant N,N-ethylene ureido groups of said addition copolymer are each hydrogen and the R_5 substituent is either hydrogen or methyl.

5. A process in accordance with claim 4 wherein said addition copolymer contains from about 0.1–50 weight percent of the N,N-ethylene ureido moiety.

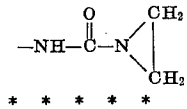
6. A process in accordance with claim 4 wherein the weight percent of the N,N-ethylene ureido moiety is from 0.5–10 percent.

7. A process in accordance with claim 6 wherein the amount of the addition copolymer deposited is from about 1–2 percent based on the weight of the substrate.

8. A process in accordance with claim 7 wherein said substrate is in the form of a woven or knit fabric.

9. A process in accordance with claim 8 wherein the comonomeric residue units of said copolymer which are devoid of N,N-ethylene ureido substituents are derived via addition polymerization from a comonomer selected from the group consisting of a C_1—C_{22} alkyl acrylate, a C_1—C_{22} methacrylate, a vinyl ester and mixtures thereof.

10. A process in accordance with claim 9 wherein the pendant N,N-ethylene ureido groups of said addition copolymer correspond to the structural formula:



* * * * *