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## SHRINKPROOFING WOOL WITH INTERPOLYMERS

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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 polymer is formed in situ on the wool fibers. This is accomplished by serially applying to the wool the complementary agents required to form the desired polymer, 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 containing (1) a diacid chloride and (2) 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 diacid chloride and bischloroformate in water-immiscible solvent. Under these conditions the diamine reacts with the diacid chloride and the bischloroformate almost instantaneously at the interface between the phases, producing in situ on the fibers a high molecular weight, resinous polymer [specifically, a copoly (amide-urethane)] which coats the fibers and renders them shrinkproof. By suitable selection of the complementary reactants other condensation polymers such as copoly (amide-ureas), copoly (urethane-ureas), copoly (ester-urethanes), and

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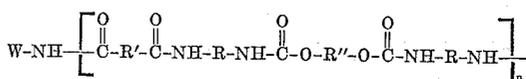
the like can be formed in situ on wool fibers. The polymers formed are insoluble so that the shrinkproofing effect is durable; it is retained even after repeated washings with soap and water or detergent and water formulations. A feature of the invention is that the high molecular weight, resinous polymers are formed in many cases at ordinary (room) temperature, which is in sharp contrast to the much higher temperatures required in the conventional melt condensations used in preparing polyamides, polyurethanes, etc. For example, in the usual preparation of polyamides 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 no 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.

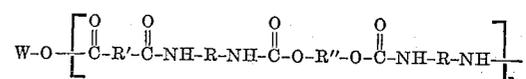
A particular feature of the invention and one that emphasizes its simplicity is that no heat-curing step is required. Following application of the two solutions, the textile merely needs to be rinsed or washed. Then, after drying, it is ready for use or sale.

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.

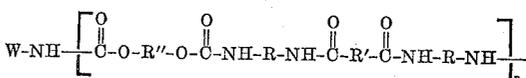
A remarkable feature of the invention is that the polymers formed in situ on the wool fibers are not merely physical coatings; they are chemically bonded to the wool, that is, the added polymer is grafted to the wool. The mechanism by which the graft polymerization occurs is believed to involve a reaction of functional groups on one or the other of the complementary agents with the free amino or hydroxy groups present in the wool molecule, these reactions giving rise to such linkages as amide, ester, urea, urethane, carbonate, etc., which chemically unite the wool with the polymer. Thus the case of a copoly (amide-urethane) grafted to wool through amide, ester, urethane, or carbonate linkages can be postulated by the following idealized formulas:



or

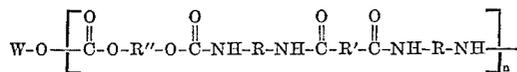


or



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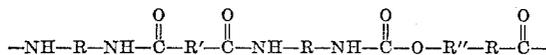
or



In the above formulas, W represents the polypeptide chain of the wool, containing prior to the reaction, free amino ( $-\text{NH}_2$ ) or free hydroxy ( $-\text{OH}$ ) groups. R, R', and R'' are bivalent organic radicals (representing in this case the residues of the diamine, the diacid chloride, and the bischloroformate, respectively) and n represents the number of polymeric repeating units.

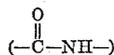
The above formulas are obviously simplified and idealized as the polymer chains may be attached at both their ends to a single wool molecule or they may cross-link together different wool molecules through amide, ester, urethane, or carbonate linkages. The important point from a practical and realistic view is that chemical bonding of the polymers to 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 polymers which are termed interpolymers. The interpolymers produced in accordance with the invention contain in their recurring structural elements at least two different units selected from the category of amide, urethane, urea, ester, and carbonate units, these units being linked together through carbon atoms. The types of different units in the interpolymer are determined by the reactants applied to the wool fabric. In a typical example of the invention, a diamine, a diacid chloride, and a bischloroformate are employed as the reactants to form a copoly (amide-urethane) wherein the recurring structural units have the formula—

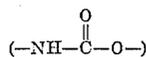


(In the above and following formulas R, R', and R'' represent bivalent organic radicals.)

It will be observed that the above interpolymer contains the amide



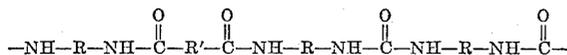
and urethane



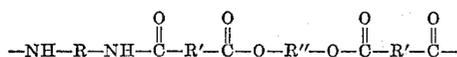
units linked through the bivalent radical R. These units are underlined in the above formula of the interpolymer.

Other illustrative examples of interpolymers which can be produced on wool fibers and grafted thereto in accordance with the invention are given below. The units in point are underlined.

Copoly (amide-urea):



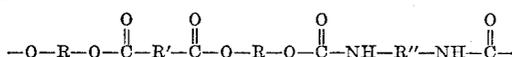
Copoly (amide-ester):



Copoly (urethane-urea):

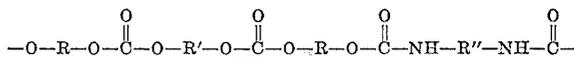


Copoly (ester-urethane):

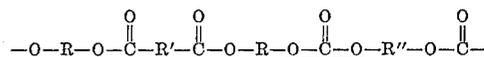


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Copoly (carbonate-urethane):



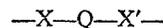
5 Copoly (ester-carbonate):



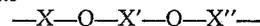
Other possible combinations will be obvious to those skilled in the art, from the above exemplifications. Moreover, the interpolymers need not contain only two different units, they may contain more than two different units as for example terpoly (amide-urethane-urea), terpoly (amide-urea-ester), terpoly (amide-urethane-carbonate), or other combination of the aforesaid amide, urethane, urea, ester, and carbonate units.

Generically, the interpolymers produced in accordance with the invention may be described as interpolymers wherein the recurring structures contain at least two different units of the category amide, urethane, urea, ester, and carbonate, these units being linked through carbon atoms. These interpolymers can thus be designated by the formulae

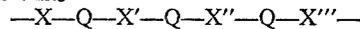
25 2 different units



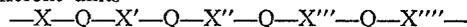
3 different units



30 4 different units

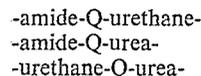


5 different units



wherein X, X', X'', X''', X'''' represent the different units (amide, urethane, urea, ester, or carbonate) and Q represents the divalent radicals linking the units together. It will be evident from the following description that the values of Q (as well as the values of X, X' etc.) will depend on the nature of the reactants chosen for forming the interpolymers. As disclosed below, these reactants may be chosen from a wide variety of categories so that generically Q represents a bivalent organic radical. More specifically, and preferably, the reactants are chosen so that Q represents a bivalent hydrocarbon radical or a bivalent hydrocarbon radical interrupted by internal ether ( $-\text{O}-$ ) linkages. In an especially preferred modification of the invention, the reactants are chosen so that Q represents bivalent hydrocarbon radicals containing at least two carbon atoms.

Generally, excellent results are obtained with the interpolymers containing two different units and among these the ones which provide particularly good shrinkproofing effects with low levels of interpolymer deposits are those of the types



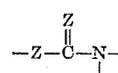
Also, these nitrogenous units are generally more easily formed than the oxygen-containing units (ester and carbonate).

The units with which the invention is concerned are understood to have the following configurations:

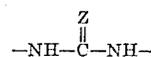
65 Amide



Urethane



70 Urea

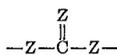


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Ester



Carbonate



wherein Z is oxygen or sulphur.

## 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 produce the desired interpolymer. The interrelationship between the nature of the agents to be used as Components A and B and the type of interpolymer produced are explained in detail below in connection with the different modifications of the invention. However, it is apropos to mention at this point that in general, Component A may be a diamine, a diol, or a mixture of a diamine and a diol. Dependent on the materials selected for Component A, Component B may be a diacid chloride, a bischloroformate, a diisocyanate, or mixtures of these classes of compounds. Since the aim in every case is to produce an interpolymer, the selection of materials must include this proviso: Taken together, Components A and B must include reagents of at least three classes. For example, if Component A includes both a diamine and a diol then Component B may represent any one of the classes of diacid chlorides, bischloroformates, or diisocyanates. A typical example in this area would be to use a mixture of a diamine and a diol as Component A and a diacid chloride as Component B, whereby the resin eventually formed would be a copoly (amide-ester). If, however, Component A is a diamine (or a diol) then Component B would need to include at least two reagents of different class, for instance, a diacid chloride and a bischloroformate, a diacid chloride and a diisocyanate, or other combinations of any two or more of the group diacid chlorides, bischloroformates, and diisocyanates. A typical example in this area would be to use a diamine as Component A and a mixture of diacid chloride and diisocyanate as Component B, whereby the resin eventually formed would be a copoly (amide-urea). The guiding factors involved in the selection of materials for Components A and B to produce a desired interpolymer will be evident to those skilled in the art from the above general description and the detailed information set forth herein-after.

Since Components A and B may be selected to form any desired type of condensation interpolymer, these components may be aptly termed as complementary organic condensation interpolymer-forming intermediates. They may further be appropriately designated as fast-reacting or direct-acting because they form the resinous interpolymers 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

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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—Component 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.

In cases where Component A is a diamine and/or a diol in the form of its alkali-metal salt, the solvents therefor may contain hydroxy groups. Because amine, alcoholate, and phenolate 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, in cases where the system involves reaction between a diamine (or a diol) and a diacid chloride or a bischloroformate it is desirable to add to either of the solutions 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 in instances where Component A includes a diamine and Component B includes a diacid chloride or bischloroformate, 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. Such catalysts are particularly useful to promote reaction between (1) diols and (2) diisocyanates, diacid chlorides, and bischloroformates.

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 ( $C_8-C_{18}$ ) sulphates, the sodium alkane ( $C_8-C_{18}$ ) sulphonates, the sodium alkyl ( $C_8-C_{20}$ ) 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 ac-

tive 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. Also, where the agents used include a diol as such (in contrast to the alkali salt thereof) it is preferable to heat the second solution as the polymerization rates with the diols are generally unsatisfactory at room temperature.

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, Component 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 diacid chloride and 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. In general, Component A may be a diamine, a diol, or a mixture of a diamine and a diol; Component B may be a diacid chloride, a bischloroformate, a diisocyanate, or a mixture of two or more of these classes of compounds. 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, fluoride 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-toluylene 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



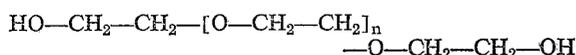
wherein  $n$  has a value of 2 to 12, preferably 6 to 10.

As the diol one may employ any of the aliphatic, aromatic, or heterocyclic compounds containing two hydroxy groups, preferably separated by at least two carbon atoms. The diols may be substituted if desired with various non-interfering (non-functional) substituents such as ether groups, sulphone groups, tertiary amine groups, thioether groups, fluoride atoms, etc. Typical compounds which may be used are listed below merely by way of illustration and not limitation: Ethylene glycol, diethylene glycol, 2,2-dimethyl propane-1,3-diol, propane-1,3-diol, butane-1,4-diol, hexane-1,6-diol, octane-1,8-diol, decane-1,10-diol, dodecane-1,12-diol, butane-1,2-diol, hexane-1,2-diol, 1-O-methylglycerol, 2-O-methyl glycerol, cyclohexane-1,4-diol, hydroquinone, resorcinol, catechol, bis(parahydroxyphenyl) methane, 1,2-bis(parahydroxyphenyl) ethane, 2,2-bis(parahydroxyphenyl) propane, 2,2-bis(parahydroxyphenyl) butane, 4,4'-dihydroxybenzophenone, naphthalene-1,5-diol, biphenyl-4,4'-diol, 2,2-bis(3-methyl-4-hydroxyphenyl) propane, 2,2-bis(3-isopropyl-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-dibromophenyl) propane, etc. If desired, mixtures of different diols may be used. It is also within the purview of the invention, though less preferred, to use the compounds containing more than two hydroxy groups as for example, glycerol, diglycerol, hexanetriol, pentaerythritol, etc. Moreover, it is within the spirit of the invention to utilize the sulphur analogues of the diols. Thus, for example, instead of using the compounds containing two hydroxy groups one can use the analogues containing either (a) two —SH groups or (b) one —SH group and one —OH group.

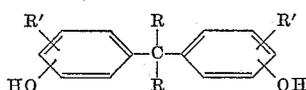
Among the preferred compounds are the aliphatic diols, for example, those of the type:



wherein  $n$  has a value from 2 to 12. Another preferred category of aliphatic compounds are the polyethylene glycols, i.e.:



wherein  $n$  has a value from zero to 10. A preferred category of aromatic diols are the bisphenols, that is, compounds of the type



wherein R—C—R represents an aliphatic hydrocarbon group containing 1 to 12 carbon atoms and R' represents hydrogen or a lower alkyl radical. In this category especially preferred compounds are 2,2-bis(parahydroxyphenyl) propane, often designated as bisphenol-A; 2,2-bis(3-methyl-4-hydroxyphenyl)propane; 2,2-bis(3-isopropyl-4-hydroxyphenyl) propane; and brominated derivatives of bisphenol A, such as 2,2-bis(4-hydroxy-dibromophenyl) propane.

The diols are employed as such or in the form of their alkali-metal salts, that is, as alcoholates or phenolates, depending on whether the diols are aliphatic or aromatic. The alkali-metal derivatives are preferred as they will react with the active agents of Component B at room temperature. With the diols, as such, temperatures above room temperature are generally required to promote reaction with their complements in Component B. In such case proper temperature for the reaction can be achieved by holding the second solution into which the textile is immersed, at about 50 to 150° C. It is obvious that the solvent selected for the second solution will need to be one which has a boiling point above the temperature selected, or, in the alternative, a pressurized system can be used to maintain the solvent in the liquid phase.

In the modification of the invention wherein water is used as the solvent for Component A (a diol in this case) and Component B is dispersed in a water-immiscible, inert solvent, it is preferred to use aromatic diols in their salt (phenolate) form. This affords several distinct advantages. Thus the alkali-metal phenolates are quite soluble in water, they are relatively stable in aqueous solution (in contrast to the alcoholates), and they will react at room temperature with diacid chlorides, bis-chloroformates, or diisocyanates so that no heating is required.

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

As the diacid chloride one may employ any of the aliphatic, aromatic, or heterocyclic compounds containing two carbonylchloride (—COCl) groups, preferably separated by at least two carbon atoms. The diacid chlorides may be substituted if desired with non-interfering (non-functional) substituents such as ether groups, thioether groups, sulphone groups, etc. Typical examples of compounds in this category are listed below merely by way of illustration and not limitation: Oxalyl chloride, maleyl chloride, fumaryl chloride, malonyl chloride, succinyl chloride, glutaryl chloride, adipyl chloride, pimelyl chloride, suberyl chloride, azeloyl chloride, sebacoyl chloride, cyclohexane-1,4-biscarbonyl chloride, phthalyl chloride, isophthalyl chloride, terephthalyl chloride, 4,4'-biphenyl-dicarbonyl chloride,  $\beta$ -hydromuconyl chloride, i.e., ClCO—CH<sub>2</sub>—CH=CH—CH<sub>2</sub>—COCl, diglycollic acid chloride, i.e., O(CH<sub>2</sub>—COCl)<sub>2</sub>, higher homologues of this compound as O(CH<sub>2</sub>—CH<sub>2</sub>—COCl)<sub>2</sub>, dithiodiglycollic acid chloride, diphenylolpropanediacetic acid chloride, i.e., (CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>COCl)<sub>2</sub>, and the like. If desired, mixtures of different diacid chlorides may be used. It is also evident that the sulphur analogues of these compounds may be used and are included within the spirit of the invention. Thus, instead of using compounds containing two —COCl groups one may use compounds containing one —CSCI and one —COCl group or compounds containing two —CSCI groups. Moreover, although the diacid chlorides are preferred as they are reactive and relatively inexpensive, the corresponding bromides and iodides may be used.

As the diacid chloride, it is generally preferred to use the aliphatic compounds containing two carbonylchloride groups in alpha, omega positions, particularly those of the type:

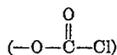


wherein  $n$  has a value from 2 to 12. Another preferred

## 11

category includes the compounds of the formula  $\text{ClCO}-\text{A}-\text{COCl}$  (where A is the benzene or cyclohexane radical), especially para-substituted compounds such as terephthalyl and hexahydroterephthalyl chlorides.

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

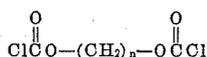


preferably separated by at least two carbon atoms. The bischloroformates may be substituted if desired with non-interfering (non-functional) substituents such as sulphone groups, ether groups, thioether groups, etc. Typical examples of compounds in this category are listed below merely by way of illustration and not limitation:

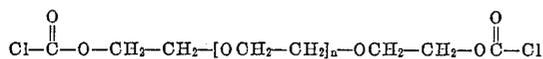
ethylene glycol bischloroformate,  
diethylene glycol bischloroformate,  
2,2-dimethyl propane 1,3-diol bischloroformate,  
propane-1,3-diol bischloroformate,  
butane-1,4-diol bischloroformate,  
hexane-1,6-diol bischloroformate,  
octane-1,8-diol bischloroformate,  
decane-1,10-diol bischloroformate,  
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.

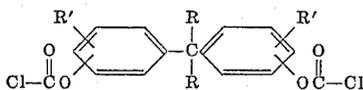
Among the preferred compounds are the aliphatic bischloroformates, for example, those of the type:



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

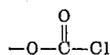


wherein  $n$  has a value from zero to 10. A useful category of aromatic bischloroformates are the bisphenol chloroformates, that is, compounds of the type:



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.

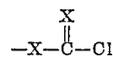
It is also evident that the sulphur analogues of the bischloroformates may be used and such are included within the spirit of the invention. Thus, instead of using the compounds containing two



groups one may use any of the compounds containing the

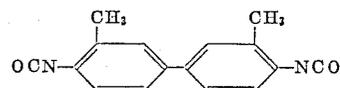
## 12

sulphur analogues of these groups, for example, the compounds containing two groups of the formula

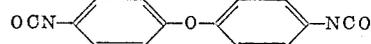


wherein one X is sulphur and the other is oxygen or wherein both X's are sulphur. Moreover, although the bischloroformates are preferred because they are reactive and relatively inexpensive, it is not essential that they contain chlorine and one may use the corresponding bisbromoformates or bisiodoformates.

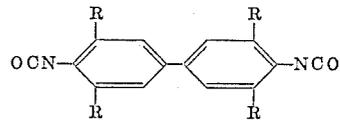
As the diisocyanate one may employ any of the aliphatic, aromatic, or heterocyclic compounds containing two isocyanate ( $-\text{NCO}$ ) groups, preferably separated by at least two carbon atoms. The diisocyanates may be substituted if desired with non-interfering (non-functional) substituents such as ether groups, thioether groups, sulphone groups, etc. Typical examples of compounds in this category are listed below merely by way of illustration and not limitation: Ethylene diisocyanate, propylene diisocyanate, butylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, decamethylene diisocyanate, cyclohexylene diisocyanate, bis(2-isocyanatoethyl) ether, bis(2-isocyanatoethyl) ether of ethylene glycol, *o*-phenylene diisocyanate, *m*-phenylene diisocyanate, *p*-phenylene diisocyanate, tolylene-2,4-diisocyanate, tolylene-2,6-diisocyanate, 3,3'-ditolylene-4,4'-diisocyanate, i.e.,



diphenyl ether-4,4'-diisocyanate, i.e.,

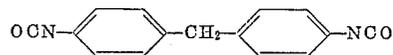


3,5,3',5'-bixylylene-4,4'-diisocyanate, i.e.,



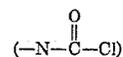
(R is  $-\text{CH}_3$ )

diphenylmethane-4,4'-diisocyanate, i.e.,

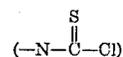


biphenylene diisocyanate, 3,3'-dimethoxy-biphenylene-4,4'-diisocyanate, naphthalene diisocyanates, polymethyl

polyphenyl isocyanates, etc. It is also evident that the sulphur analogues of these compounds may be used and such are included within the spirit of the invention. Thus for example, instead of using the compounds containing two  $-\text{NCO}$  groups one may use their their analogues containing either two  $-\text{NCS}$  groups or one  $-\text{NCO}$  group and one  $-\text{NCS}$  group. Another point to be made is that it is within the spirit of the invention to utilize the derivatives which yield the same products with compounds containing active hydrogen as do the isocyanates. Particular reference is made to the biscarbamyl chlorides which may be used in place of the diisocyanates. Thus one may use any of the above-designated compounds which contain carbamyl chloride groups



or their sulphur analogues



in place of the isocyanate groups.

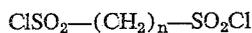
Among the preferred compounds are the aliphatic diisocyanates, for example, those of the type



wherein  $n$  has a value from 2 to 12. Other preferred compounds are the toluene diisocyanates, xylene diisocyanates, and diphenylmethane-4,4'-diisocyanate which may also be termed methylene-bis(*p*-phenylisocyanate).

There has been set forth above a comprehensive disclosure of the preferred types of complementary agents, that is, diamines, diols, diacid chlorides, bischloroformates, diisocyanates, and their equivalents. Although it is preferred to use these agents for optimum results, they are by no means the only compounds which may be used. The invention in its broadest aspect includes the application of many other types of complementary agents which have the ability to form condensation interpolymers when applied to wool by the disclosed procedures. Various examples are thus set forth of other types of compounds which may be used.

By substituting disulphonyl chlorides for the diacid chlorides, interpolymers may be formed which contain sulphonamide groups. A typical example in this category involves applying to the wool an aqueous solution of a diamine, followed by applying to the wool a solution containing a disulphonyl chloride and a bischloroformate dissolved in a water-immiscible solvent such as benzene or carbon tetrachloride. In this way there will be formed on and grafted to the wool a copoly (sulphonamide-urethane). Any of the diamines and bischloroformates described above can be used in this technique together with a disulphonyl chloride such as benzene-1,3-disulphonyl chloride, biphenyl-4,4'-disulphonyl chloride, toluene disulphonyl chlorides or aliphatic compounds such as those of the formula—



wherein  $n$  has a value from 2 to 12. An alternative to this plan is to use a disulphonyl chloride and a diisocyanate as Component B in conjunction with a diamine as Component A to form copoly (sulphonamide-ureas) on the wool.

In another plan, an aqueous solution of a diol—preferably in the form of its alkali-metal salt—is first applied to the wool, followed by application of a disulphonyl chloride and a bischloroformate dissolved in an inert, essentially water-immiscible solvent whereby to form a copoly (sulphonate-carbonate) on the wool. For this purpose one may use any of the diols, bischloroformates, and disulphonyl chlorides exemplified above. A variant of this procedure is to use the corresponding dithiol in place of the diol, thus to form a copoly (thiolsulphonate-thiolcarbonate).

An alternative to the diacid chlorides is the use of mixed anhydrides of the corresponding dicarboxylic acids with monobasic acids such as trifluoroacetic acid, dibutylphosphoric acid, or the like. Such mixed anhydrides may be employed, for example, in Component B in the same manner as described for the diacid chlorides.

Another plan is to use as Component A a mixture of a diamine and a compound such as urea, thiourea, biuret, dithiobiuret, or guanidine. Such a mixture used in conjunction with a diacid chloride or disulphonyl chloride as Component B would form on the wool fibers such interpolymers as copoly (amide-urea), copoly (amide-thiourea), copoly (sulphonamide-urea), and the like.

Having now described the types of compounds which may be used as Components A and B, we will next explain how these compounds may be selected in various combinations to form the preferred types of interpolymers in situ on wool fibers and grafted thereto.

*Embodiment I.—Component A: Diamine.*—In this embodiment of the invention a diamine is used as Component A. Various interpolymers may then be deposited on wool and grafted thereto by appropriate selection of the ingredients of Component B. Typical examples of the alternatives which may be employed are given below.

## EMBODIMENT I—COMPONENT A: DIAMINE

Component B	Interpolymer formed
5 Diacid chloride and bischloroformate... Diacid chloride and diisocyanate..... Bischloroformate and diisocyanate..... Diacid chloride, bischloroformate, and diisocyanate.	Copoly (amide-urethane). Copoly (amide-urea). Copoly (urethane-urea). Terpoly (amide-urethane-urea).

10 As noted hereinabove, in this embodiment (I) of the invention, it is necessary that Component B include at least two of the classes of bifunctional compounds. Thus Component B may be a mixture of diacid chloride and bischloroformate or a mixture of diacid chloride and diisocyanate or a mixture of bischloroformate and diisocyanate or a mixture of diacid chloride, bischloroformate and diisocyanate. The relative amounts of these reactants of different class may be varied depending on the character of the interpolymer to be produced. For example, in using a mixture of diacid chloride and bischloroformate as Component B, the proportion of amide to urethane groups in the interpolymer may be increased by increasing the proportion of diacid chloride used in the mixture. In many cases it is preferred to employ the reagents in equimolar proportions, thus to provide an interpolymer having an equal number of different units. For example, by using an equimolar mixture of a diacid chloride and a bischloroformate as Component B, the resulting interpolymer will contain substantially equal number of amide and urethane units. However, the use of equimolar mixtures is by no means critical and one may use any mixture containing 10 to 90% (molar basis) of the reagent of one class and the remainder (90 to 10%) of the reagents of the other classes.

15 Numerous variations in procedure will suggest themselves to those skilled in the art in the application of Embodiment I of this invention, without departing from the fundamentals of the invention. Some of these variations are explained below.

20 If desired, one may prepare a prepolymer containing internal amide (or urethane or urea) units and terminal amino groups. Such prepolymers can be prepared, for example, by reacting in known manner a molar excess of diamine with a diacid chloride, bischloroformate, or diisocyanate. The prepolymer would then be used as Component A while for Component B one would use any one of the reagents (diacid chloride, bischloroformate or diisocyanate) which was not used in preparing the prepolymer. Thus, taking into account the variation in the internal units of the polymer, the following alternatives are among those possible:

## COMPONENT A—PREPOLYMER CONTAINING INTERNAL AMIDE UNITS AND TERMINAL AMINO GROUPS

Component B	Interpolymer formed
55 Bischloroformate..... Diisocyanate.....	Copoly (amide-urethane). Copoly (amide-urea).

## COMPONENT A—PREPOLYMER CONTAINING INTERNAL URETHANE UNITS AND TERMINAL AMINO GROUPS

Component B	Interpolymer formed
65 Diacid chloride..... Diisocyanate.....	Copoly (urethane-amide). Copoly (urethane-urea).

## COMPONENT A—PREPOLYMER CONTAINING INTERNAL UREA UNITS AND TERMINAL AMINO GROUPS

Component B	Interpolymer formed
70 Diacid chloride..... Bischloroformate.....	Copoly (urea-amide). Copoly (urea-urethane).

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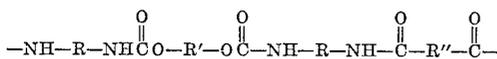
A typical example of procedure in this area would be to use as Component A a prepolymer of the type



and to use as Component B a diacid chloride



thus to produce an interpolymer containing amide and urethane units of the type



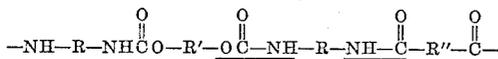
A typical example of procedure in this area would be to use as Component A a prepolymer of the type



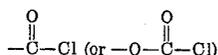
and to use as Component B a diacid chloride



thus to produce an interpolymer containing amide and urethane units of the type

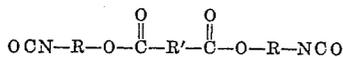


This principle of using prepolymers could be applied in other ways as well. For example, a diol could be condensed in known manner with an excess of diacid chloride (or bischloroformate) to produce a prepolymer containing internal ester (or carbonate) units and terminal

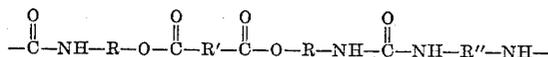


units. This prepolymer used as Component B in conjunction with a diamine as Component A would yield interpolymers containing (a) ester and amide units or (b) carbonate and amide units.

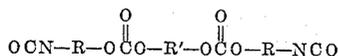
Another variation is to employ as Component B a bifunctional compound having an appropriate disposition of internal units (amide, urethane, urea, ester, or carbonate) and terminal groups ( $-\text{COCl}$ ,  $-\text{OCOC}$ , or  $-\text{NCO}$ ). For example, by using as Component B a compound containing internal ester units and terminal isocyanate groups of the formula



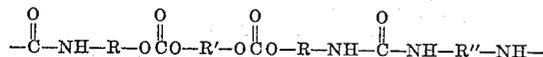
and using  $\text{H}_2\text{N}-\text{R}''-\text{NH}_2$  as Component A one could deposit on the wool fibers a copoly (ester-urea) containing recurring units of the type



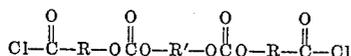
Another example of this system is to use as Component B a compound containing internal carbonate units and terminal isocyanate groups, having the formula



This compound used in conjunction with  $\text{H}_2\text{N}-\text{R}''-\text{NH}_2$  as Component A would yield a copoly (carbonate-urea) containing recurring units of the type



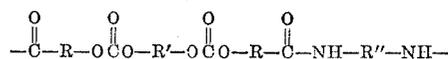
A further example of this system is to employ as Component B a compound containing internal carbonate units and terminal carbonyl chloride groups, having the formula



This compound used in conjunction with  $\text{H}_2\text{N}-\text{R}''-\text{NH}_2$

16

as Component A will yield a copoly (carbonate-amide) containing recurring units of the type



This embodiment (I) of 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 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 Accelerotor is described in the American Dyestuff Reporter, vol. 45, p. 685, September 10, 1956.

The petroleum solvent referred to in the examples was a commercial hydrocarbon mixture having the following characteristics: 96% aromatics, 1% paraffins, 3% naphthenes; specific gravity 0.87; boiling range 314–362° F.

The commercial wetting agent referred to in the examples was Triton X-100—isoctylphenyl ether of polyethylene glycol.

The toluene diisocyanate referred to in Examples 6 and 7 was toluene 2,4-diisocyanate.

#### Example 1.—Copoly (Amide-Urethane)

Component A: Diamine.

Component B: Diacid chloride and bischloroformate.

A sample of wool cloth was immersed for 30 seconds in a solution containing 4 g. hexamethylene diamine and 8 g.  $\text{Na}_2\text{CO}_3$  per 100 ml. water and 0.1% of a commercial wetting agent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, then immersed for 30 seconds in a solution containing 1.5 ml. sebacyl chloride and 1.5 ml. hexane-1,6-diol bischloroformate per 100 ml. petroleum solvent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air.

The following results were obtained:

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
2.8	4.0

#### Example 2.—Copoly (Amide-Urethane)

Component A: Diamine.

Component B: Diacid chloride and bischloroformate.

A sample of wool cloth was immersed for 30 seconds in a solution containing 4 g. hexamethylene diamine and 8 g.  $\text{Na}_2\text{CO}_3$  per 100 ml. water and 0.1% of a commercial wetting agent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, then immersed for 30 seconds in a solution containing 1.5 ml. sebacyl chloride and 1.5 ml. diethylene glycol bischloroformate per 100 ml. benzene. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air.

The following results were obtained:

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
4.0	2.0

## Example 3.—Copoly (Amide-Urethane)

Component A: Mixture of diamines.  
Component B: Diacid chloride and bischloroformate.

A sample of wool cloth was immersed for 30 seconds in a solution containing 2 g. hexamethylene diamine and 2 ml. meta-xylylene diamine per 100 ml. water and 0.1% of a commercial wetting agent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, then immersed for 30 seconds in a solution containing 1.5 ml. sebacyl chloride and 1.5 ml. hexane-1,6-diol bischloroformate per 100 ml. petroleum solvent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air.

The following results were obtained:

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
3.1	14.4

## Example 4.—Copoly (Amide-Urea)

Component A: Diamine.  
Component B: Diacid chloride and diisocyanate.

A sample of wool cloth was immersed for 30 seconds in a solution containing 4 g. hexamethylene diamine and 8 g. Na<sub>2</sub>CO<sub>3</sub> per 100 ml. water and 0.1% of a commercial wetting agent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, then immersed for 30 seconds in a solution containing 1.5 ml. sebacyl chloride and 1.5 g. methylene bis (p-phenylisocyanate) per 100 ml. benzene. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air.

The following results were obtained:

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
3.3	5.9

## Example 5.—Copoly (Amide-Urea)

Component A: Diamine.  
Component B: Diacid chloride and diisocyanate.

A sample of wool cloth was immersed for 30 seconds in a solution containing 4 g. metaxylylene diamine and 8 g. Na<sub>2</sub>CO<sub>3</sub> per 100 ml. water and 0.1% of a commercial wetting agent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, then immersed for 30 seconds in a solution containing 1.5 ml. sebacyl chloride and 1.5 g. methylene bis (p-phenylisocyanate) per 100 ml. benzene. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air.

The following results were obtained:

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
3.5	1.0

## Example 6.—Copoly (Amide-Urea)

Component A: Diamine.  
Component B: Diacid chloride and diisocyanate.

A sample of wool cloth was immersed for 30 seconds in a solution containing 4 g. hexamethylene diamine and 8 g. Na<sub>2</sub>CO<sub>3</sub> per 100 ml. water and 0.1% of a commercial wetting agent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, then immersed for 30 seconds in a solution containing 1.5 ml. sebacyl chloride and 1.5 ml. toluene diisocyanate per 100 ml. benzene. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air.

The following results were obtained.

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
4.0	4.0

## Example 7.—Copoly (Urethane-Urea)

Component A: Diamine.  
Component B: Bischloroformate and diisocyanate.

A sample of wool cloth was immersed for 30 seconds in a solution containing 4 g. hexamethylene diamine and 8 g. Na<sub>2</sub>CO<sub>3</sub> per 100 ml. water and 0.1% of a commercial wetting agent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, then immersed for 30 seconds in a solution containing 1.5 ml. toluene diisocyanate and 1.5 ml. hexane-1,6-diol bischloroformate per 100 ml. benzene. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air.

The following results were obtained:

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
3.5	5.0

## Example 8.—Copoly (Urethane-Urea)

Component A: Diamine.  
Component B: Bischloroformate and diisocyanate.

A sample of wool cloth was immersed for 30 seconds in a solution containing 4 ml. meta-xylylene diamine and 8 g. Na<sub>2</sub>CO<sub>3</sub> per 100 ml. water and 0.1% of a commercial wetting agent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, then immersed for 30 seconds in a solution containing 1.5 g. methylene bis (p-phenylisocyanate) and 1.5 ml. hexane-1,6-diol bischloroformate per 100 ml. benzene. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air.

The following results were obtained:

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
4.6	7.8

**Embodiment II.—Component A: Diol.**—In this embodiment of the invention a diol is used as Component A. Various interpolymers may then be deposited on wool fibers by appropriate selection of the ingredients of

Component B. Typical examples of the alternatives which may be employed are given below:

## EMBODIMENT II—COMPONENT A: DIOL

Component B	Interpolymer formed
Diacid chloride and bischloroformate.....	Copoly (ester-carbonate).
Diacid chloride and diisocyanate.....	Copoly (ester-urethane).
Bischloroformate and diisocyanate.....	Copoly (carbonate-urethane).
Diacid chloride, bischloroformate, and diisocyanate.	Terpoly (ester-carbonate-urethane).

As noted hereinabove, the objects of Embodiment II of the present invention are attained by using as Component B a mixture of diacid chloride and bischloroformate or a mixture of diacid chloride and diisocyanate or a mixture of bischloroformate and diisocyanate or a mixture of diacid chloride, bischloroformate, and diisocyanate. It is evident that with regard to Component B of this embodiment, the same considerations are applicable as in Embodiment I described above.

That is, all the information set forth above in describing the compounds suitable for use as Component B of Embodiment I, the proportions of these compounds, the conditions of reaction, etc., is equally applicable in the present embodiment.

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

If desired, one may prepare a prepolymer containing internal ester (or carbonate or urethane) units and terminal hydroxy groups. Such prepolymers can be prepared for example, by reacting in known manner a molar excess of diol with a diacid chloride, bischloroformate, or diisocyanate. The prepolymer would then be used as Component A while for Component B one would use any one of the reagents (diacid chloride, bischloroformate, or diisocyanate) which was not used in preparing the prepolymer. Thus, taking into account the variation in the internal units of the prepolymer, the following alternatives are among those possible:

## COMPONENT A—PREPOLYMER CONTAINING INTERNAL ESTER UNITS AND TERMINAL HYDROXY GROUPS

Component B	Interpolymer formed
Bischloroformate.....	Copoly (ester-carbonate).
Diisocyanate.....	Copoly (ester-urethane).

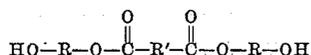
## COMPONENT A—PREPOLYMER CONTAINING INTERNAL CARBONATE UNITS AND TERMINAL HYDROXY GROUPS

Component B	Interpolymer formed
Diacid chloride.....	Copoly (carbonate-ester).
Diisocyanate.....	Copoly (carbonate-urethane).

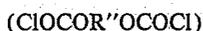
## COMPONENT A—PREPOLYMER CONTAINING INTERNAL URETHANE UNITS AND TERMINAL HYDROXY GROUPS

Component B	Interpolymer formed
Diacid chloride.....	Copoly (urethane-ester).
Bischloroformate.....	Copoly (urethane-carbonate).

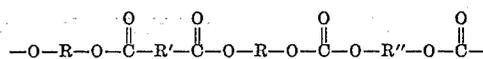
A typical example of this procedure in this area would be to use as Component A a prepolymer of the type:



and to use as Component B, a bischloroformate



to produce an interpolymer having elements of the structure:



The principle of using prepolymers could be applied in other ways as well. For example, a diol could be condensed in known manner with an excess of diacid chloride and bischloroformate to produce a prepolymer containing terminal



groups and/or terminal



groups. This prepolymer used as Component B in conjunction with a diol as Component A would yield an interpolymer containing both ester and carbonate units.

This embodiment (II) of the invention is further demonstrated by the following illustrative examples.

The shrinkage tests referred to in the example were carried out as described above in the paragraph entitled "Standard shrinkage test." The control (untreated) wool used in these experiments had an area shrinkage of 47%.

The commercial wetting agent referred to in the examples was Triton X-100-isooctylphenyl ether of polyethylene glycol.

The petroleum solvent referred to in the examples was a commercial hydrocarbon mixture having the following characteristics. 96% aromatics, 3% naphthenes, 1% paraffins; specific gravity 0.87; boiling range 314-362° F.

## Example 9.—Copoly (Ester-Carbonate)

Component A: Diol.

Component B: Diacid chloride and bischloroformate.

A sample of wool cloth was immersed for 60 seconds in a solution containing 10 g. of 2,2-bis (4-hydroxy-dibromophenyl) propane per 100 ml. water, with addition of sufficient sodium hydroxide to dissolve the bisphenol, and 0.1% of a commercial wetting agent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, then immersed for 60 seconds in a solution containing 1.5 ml. sebacyl chloride and 1.5 ml. hexane-1,6-diol bischloroformate per 100 ml. petroleum solvent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air.

The following results were obtained:

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
4.9	26.9

## Example 10.—Copoly (Ester-Carbonate)

Component A: Diol.

Component B: Diacid chloride and bischloroformate.

A sample of wool cloth was immersed for 60 seconds in a solution containing 5 g. of 2,2-bis (3-methyl-4-hydroxyphenyl) propane per 100 ml. water, with addition of sufficient sodium hydroxide to dissolve the bisphenol, and 0.1% of a commercial wetting agent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, then immersed for 60 second in a solution containing 1.5 ml. sebacyl chloride and 1.5 ml. hexane-1,6-diol bischloroformate per 100 ml. benzene. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air.

The following results were obtained:

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
3.1	32.1

**Embodiment III.—Component A: Mixture of diamine and diol.**—In this modification of the invention, a mixture of a diamine and a diol is used as Component A. Various interpolymers may then be deposited on wool fibers by appropriate selection of the ingredients of Component B. Typical examples of some of the alternatives which may be employed are given below:

EMBODIMENT III—COMPONENT A: DIAMINE AND DIOL

Component B	Interpolymer formed
Diacid chloride.....	Copoly (amide-ester).
Bischloroformate.....	Copoly (urethane-carbonate).
Diisocyanate.....	Copoly (urea-urethane).
Diacid chloride and bischloroformate.....	Tetrapoly (amide-urethane-ester-carbonate).
Diacid chloride and diisocyanate.....	Tetrapoly (amide-urethane-urea-ester).

In formulating Component A for practice of Embodiment III of the invention, one may use any of the diamines and diols set forth above. The relative amounts of diamine and diol which comprise Component A may be varied depending on the character of the interpolymer to be produced. For example, in a system using a diacid chloride as Component B, the proportion of amide to ester units in the interpolymer may be increased by increasing the ratio of diamine to diol in Component A.

In many cases it is preferred to employ the diamine and diol in equimolar proportions, thus to provide an interpolymer having any equal proportion of different units. For example, by using an equimolar mixture of diamine and diol as Component A and a bischloroformate as Component B, the resulting interpolymer will contain substantially an equal ratio of carbonate and urethane units. However, the use of equimolar proportions is by no means critical and one can use as Component A any mixture containing 10 to 90% (molar basis) of diamine and the remainder (90 to 10%) of diol.

With regard to Component B, one may use a diacid chloride, bischloroformate, diisocyanate, or mixtures of these. The types of interpolymer resulting from different values chosen for Component B are exemplified in the initial paragraph of the description of this embodiment of the invention.

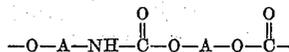
Numerous variations in procedure will suggest themselves to those skilled in the art in the application of Embodiment III of this invention, without departing from the fundamentals of the invention as taught herein. Some of these variations are explained below.

If desired, one may use as Component A, a single compound containing terminal hydroxy and amino groups, for example, 2-aminoethanol, 3-aminopropanol, 4-aminobutanol, 6-aminohexanol, 8-aminooctanol, o-aminophenol, m-aminophenol, p-aminophenol, para (4-aminophenyl) phenol, etc. Then, by suitable selection of Component B, various interpolymers may be formed on the wool. Some of the possible alternatives in this system are given below:

COMPONENT A—COMPOUND CONTAINING TERMINAL AMINO AND TERMINAL HYDROXY GROUPS

Component B	Interpolymer formed
Diacid chloride.....	Copoly (ester-amide).
Bischloroformate.....	Copoly (carbonate-urethane).
Diisocyanate.....	Copoly (urethane-urea).

A typical example of procedure in this area would be to use as Component A a compound of the type HO-A-NH<sub>2</sub> (wherein A is the hexamethylene radical) and to use as Component B hexane-1,6-diol bischloroformate whereby to produce a copoly (urethane-carbonate) having units of the structure:



This embodiment (III) of the invention is further demonstrated by the following illustrative examples.

The shrinkage tests referred to in the examples were carried out as described above in the paragraph entitled "Standard shrinkage test." The control (untreated) wool used in these experiments had an area shrinkage of 47%.

The commercial wetting agent referred to in the examples was Triton X-100, isoctylphenyl ether of polyethylene glycol.

The petroleum solvent referred to in the examples was a commercial hydrocarbon mixture having the following characteristics: 96% aromatics, 3% naphthenes, 1% paraffins; specific gravity 0.87; boiling range 314–362° F.

**Examples 11 and 12.—Copoly (Amide-Ester)**

Component A: Diamine and diol.

Component B: Diacid chloride.

(11) A solution was prepared containing 2 g. hexamethylene diamine, 5 g. 2,2-bis (3-methyl-4-hydroxyphenyl) propane, 1.5 g. NaOH and 4.0 g. Na<sub>2</sub>CO<sub>3</sub> per 100 ml. water and 0.1% of a commercial wetting agent. A sample of wool cloth was immersed for 60 seconds in the solution, then removed, run through squeeze rolls to remove excess liquid and immersed for 60 seconds in a second solution containing 3 ml. sebacyl chloride per 100 ml. benzene. The cloth was removed from the second solution, run through squeeze rolls to remove excess liquid, rinsed in water and dried in air.

(12) Wool cloth was treated as in Example 11 above except that the second solution contained 3 g. terephthalyl chloride per 100 ml. benzene.

The results are tabulated below:

Example	Interpolymer resin deposited on wool, percent	Area shrinkage, percent
11.....	4.75	2.0
12.....	3.7	9.1

**Example 13.—Copoly (Carbonate-Urethane)**

Component A: Diamine and diol.

Component B: Bischloroformate.

A sample of wool cloth was immersed for 60 seconds in a solution containing 2 g. hexamethylene diamine, 5 g. 2,2-bis (3-methyl-4-hydroxyphenyl) propane, 1.5 g. NaOH, and 4 g. Na<sub>2</sub>CO<sub>3</sub> per 100 ml. water and 0.1% of a commercial wetting agent. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, then immersed for 60 seconds in a solution containing 3 ml. hexane-1,6-diol bischloroformate per 100 ml. benzene. The cloth was removed from this solution, run through squeeze rolls to remove excess liquid, rinsed in water, and dried in air.

The following results were obtained:

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
4.9	12.6

*Example 14.—Copoly (Carbonate-Urethane)*

Component A: Diamine and diol.

Component B: Bischloroformate.

A solution was prepared containing 2 g. hexamethylene diamine, 10 g. 2,2-bis (4-hydroxy-dibromophenyl) propane, including sufficient NaOH to dissolve this bisphenol, and 4 g. Na<sub>2</sub>CO<sub>3</sub> per 100 ml. water and 0.1% of a commercial wetting agent. A sample of wool cloth was immersed for 30 seconds in the solution, then removed, run through squeeze rolls to remove excess liquid and immersed for 30 seconds in a solution containing 3 ml. hexane-1,6-diol bischloroformate per 100 ml. petroleum solvent. The cloth was removed from the second solution, run through squeeze rolls to remove excess liquid, rinsed in water and dried in air.

The results are tabulated below:

Interpolymer resin deposited on wool, percent	Area shrinkage, percent
7.7	17.2

This application is a continuation-in-part of our co-pending application, Serial 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 Shrinkproof 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. Interpolymers are the subject of the present application; polyurethanes are the subject of Serial No. 99,319, filed March 29, 1961; 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. 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 struc-

ture. 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; alginic 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 in a first solvent, the other solution containing at least two members of the group consisting of diacid chlorides, bischloroformates, and diisocyanates in a second solvent, said first and second solvents being substantially immiscible with one another.

2. A process for shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diamine in a first solvent, the other solution containing a diacid chloride and a bischloroformate in a second solvent, said first and second solvents being substantially immiscible with one another.

3. A process for shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diamine in a first solvent, the other solution containing a diacid chloride and a diisocyanate in a second solvent, said first and second solvents being substantially immiscible with one another.

4. A process for shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diamine in a first solvent, the other solution containing a bischloroformate and a diisocyanate in a second solvent, said first and second solvents being substantially immiscible with one another.

5. A process for shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diamine in a first solvent, the other solution containing a diacid chloride, a bischloroformate, and a diisocyanate in a second solvent, said first and second solvents being substantially immiscible with one another.

6. A process of shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diol in a first solvent, the other solution containing at least two members of the group consisting of diacid chlorides, bischloroformates, and diisocyanates in a second solvent, said first and second solvents being substantially immiscible with one another.

7. A process of shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diol in a first solvent, the other solution containing a diacid chloride and a bischloroformate in a second solvent, said first and second solvents being substantially immiscible with one another.

8. A process of shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diol in a first solvent, the other solution con-

taining a diacid chloride and a diisocyanate in a second solvent, said first and second solvents being substantially immiscible with one another.

9. A process of shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diol in a first solvent, the other solution containing a bischloroformate and a diisocyanate in a second solvent, said first and second solvents being substantially immiscible with one another.

10. A process of shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diol in a first solvent, the other solution consisting of diacid chlorides, bischloroformates, and diisocyanate in a second solvent, said first and second solvents being substantially immiscible with one another.

11. A process for shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diamine and a diol in a first solvent, the other solution containing at least one member of the group consisting of a diacid chlorides, bischloroformates, and diisocyanates in a second solvent, said first and second solvents being substantially immiscible with one another.

12. A process for shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diamine and a diol in a first solvent, the other solution containing a diacid chloride in a second solvent, said first and second solvents being substantially immiscible with one another.

13. A process for shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diamine and a dial in a first solvent, the other solution containing a bischloroformate in a second solvent, said first and second solvents being substantially immiscible with one another.

14. A process for shrinkproofing wool without significant impairment of its hand which comprises serially impregnating wool with two solutions, one solution containing a diamine and a diol in a first solvent, the other solution containing a diisocyanate in a second solvent, said first and second solvents being substantially immiscible with one another.

15. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a condensation interpolymer formed in situ thereon and chemically bonded to the wool, the recurring units of said interpolymer including at least two members of the group consisting of amide, urethane, urea, ester, and carbonate units.

16. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a copoly (amide-urethane) formed in situ thereon and chemically bonded to the wool.

17. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a copoly (amine-urea) formed in situ thereon and chemically bonded to the wool.

18. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a copoly (urethane-urea) formed in situ thereon and chemically bonded to the wool.

19. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a copoly (ester-carbonate) formed in situ thereon and chemically bonded to the wool.

20. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a copoly (ester-urethane) formed in situ thereon and chemically bonded to the wool.

21. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a copoly (carbonate-urethane) formed in situ thereon and chemically bonded to the wool.

22. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a copoly (amide-ester) formed in situ thereon and chemically bonded to the wool.

23. A modified wool fiber which exhibits improved shrinkage properties as compared with the unmodified wool fiber comprising wool fiber having a copoly (amide-carbonate) formed in situ thereon and chemically bonded to the wool.

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

25. 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 condensation interpolymer-forming intermediates in superposed liquid phases of limited mutual solubility, the said intermediates reacting under such conditions to form an interpolymer in situ on said fibrous elements.

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

27. 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, condensation interpolymer-forming intermediates in a first solvent, the other solution containing the complementary member of said pair of complementary, direct-acting, organic, condensation interpolymer-forming intermediates in a second solvent, said first 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 interpolymer.

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