

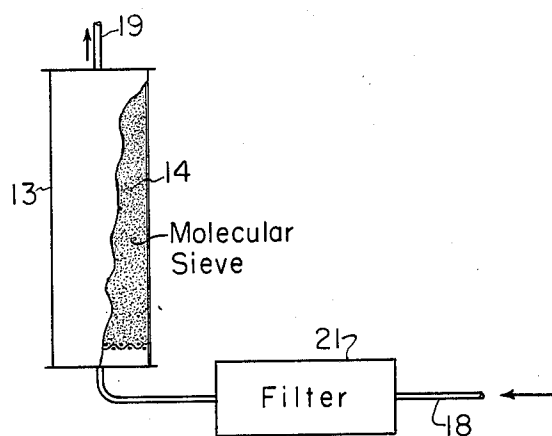
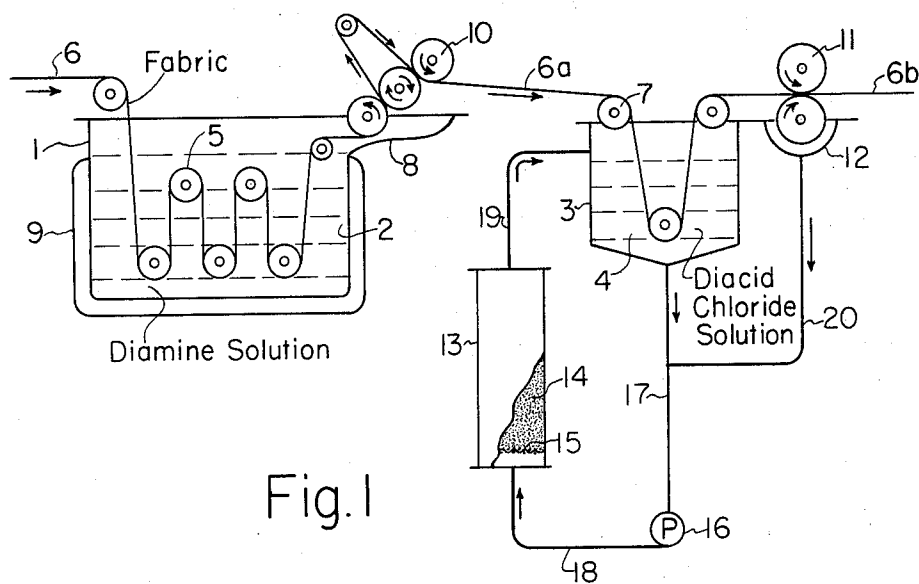
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CONTINUOUS SHRINKPROOFING OF WOOL TEXTILES

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3,243,253

CONTINUOUS SHRINKPROOFING OF WOOL TEXTILES

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This invention relates to and has among its objects the provision of novel methods for treating fibrous materials, particularly wool, in continuous manner. A particular object of the invention is the provision of methods for effectively shrinkproofing wool textiles in continuous operation. Further objects and advantages of the invention will be obvious from the following description wherein parts and percentages are by weight unless otherwise specified. The abbreviation "y.p.m." used herein means yards per minute.

FIGURE 1 in the annexed drawing is a schematic diagram of a form of apparatus for carrying out the process of the invention.

FIGURE 2 is an enlarged view, partly in cross-section, of an alternative form of the purification unit.

In the patent of Miller, Whitfield and Wasley (3,078,138, issued Feb. 19, 1963) there are disclosed processes for shrinkproofing wool wherein a condensation polymer—typically a polyamide—is formed in situ on the wool fibers and grafted to the wool, that is, chemically combined therewith. In a typical embodiment of their process, a wool fabric is serially impregnated with two solutions—the first being a solution of a diamine in water, the second being a solution of a diacid chloride in a water-immiscible, volatile, inert solvent. By such treatment the fibers are coated with superposed layers of the mutually-insoluble solutions, for example, an inner layer of diamine in water and an outer layer of diacid chloride in water-immiscible solvent. Under these conditions the diamine and diacid chloride react almost instantaneously at the interface between the phases, producing in situ on the fibers a high-molecular weight, resinous polyamide which coats the fibers and renders the fabric shrinkproof without detriment to the hand, porosity, and other valuable properties of the fabric. Moreover, the polyamide is chemically bonded to the wool so that the shrinkproofing effect is highly durable, i.e., the polyamide deposit is not removed by repeated washing of the treated fabric in conventional soap and water or detergent and water laundering formulations, or in conventional dry cleaning formulations. From a procedural standpoint, the process has the advantage of simplicity and rapidity in that the basic operation is simply a serial impregnation of the fabric in the two solutions. Another point is that the process does not require any heat-curing of the treated fabric as is commonly necessary in most resin shrinkproofing procedures.

For reasons of economy and efficiency it is desired in many industrial operations to conduct processes in a continuous manner, as opposed to batch treatment. It can readily be visualized that it would be advantageous to conduct the above-described shrinkproofing treatment in a continuous manner, particularly in application of the treatment to long lengths of wool textiles such as fabrics, yarns, roving, top, etc. In contemplating adaptation to continuous operation, consideration must be given to matters of operation—such as consumption of reagents—as

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well as quality of the product since the operation will be successful only if it yields a good product coupled with efficiency of operation. It has been found that when the treatment in question is applied continuously, various problems are encountered and these problems become more severe as the treatment goes on. Typical among these are the following:

Formation of hydrogen chloride fumes at the second solution—the one containing the diacid chloride. These fumes are not only corrosive to the equipment in the area but present a health hazard to operating personnel.

Formation of gummy or resinous materials in the diacid chloride solution which tend to deposit as lumps or streaks on the fabric and to gum up the fabric guide and press rolls.

Reduction in the degree of shrink resistance imparted to the fabric. When the operation is initiated the product has an excellent shrink resistance. However, as the operation continues, product quality is not maintained, i.e., its shrink resistance becomes inadequate. In typical runs, for example, initial felting shrinkage is 1% or less (on area basis) whereas after continued operation of several thousand yards of fabric the product will exhibit a felting shrinkage (on area basis) of 10% or more.

Excessive consumption of reagents, particularly diacid chloride, by formation of resinous material and hydrolysis products, such as dicarboxylic acid and/or dicarboxylic acid monochloride, in the second solution.

In accordance with the present invention the basic principles of the aforesaid processes are utilized in conjunction with a novel system of purification whereby to obviate the above problems and to yield a combination of desirable results from both the standpoint of the effectiveness of the treatment and efficiency of operation. More particularly, by applying the teachings of the present invention one is enabled to operate continuously at a useful and economical production rate for long periods of time while producing a finished product which has a high degree of shrinkage resistance and in which the polymer is uniformly formed on the fibers. Moreover, in operating in accordance with the invention, little if any hydrogen chloride or other hydrolytic products or polymers are formed in the second treating bath and there is no gumming of the various mechanisms associated with this bath. Another advantage of the invention is that the products exhibit a high degree of shrink resistance even though the amount of polymer formed on the wool is very small. For example, as little as 1/2 to 1% of polymer formed on the wool in accordance with the process of the invention produces products which are essentially shrinkproof on washing in conventional aqueous laundering media. This advantage not only contributes to economy of operation but also to preservation of the desirable properties of the wool, including the hand thereof.

Our investigations on this subject have shown that the problems described above are caused by entry of materials from the first solution into the second solution. Thus, as the fabric leaves the first solution it carries with it water, diamine, and usually also adjuvants such as sodium carbonate (added as an HCl-acceptor for the diamine-diacid chloride polymerization), and a wetting agent. Obviously, if all these named agents would remain in the fabric, no substantial problems would arise. However, in practical operation it is inevitable that as the fabric enters the second solution, some proportion of these agents (water, diamine, and adjuvants) becomes detached from the fabric, enters the second solution, and mixes therewith. The groundwork, as it were, is then laid for various undesirable effects. It is believed that detachment of water from the entering fabric is particularly responsible for these effects, because of its hydrolytic

activity. Thus, a primary reaction is the formation of hydrogen chloride by hydrolysis of the diacid chloride present in the solution. Also produced in such hydrolysis are compounds such as dicarboxylic acid and/or dicarboxylic acid monochloride. Formation of these may be visualized as involving complete or partial hydrolysis of diacid chloride—the active reagent in the second solution. Such hydrolysis of the diacid chloride not only involves a waste of this reagent but interferes with successful shrinkproofing. Thus it is theorized that the hydrolytic products, such as dicarboxylic acid monochloride, act as polymerization terminators and decrease the chain length of the polymer formed on the fibers. As a result, the shrinkproofing effect is diminished. Another untoward effect is that resinous material is formed in the second solution, presumably by reaction of the detached diamine with such agents as diacid chloride or its hydrolytic products (dicarboxylic acid or dicarboxylic acid monochloride). This resinous material tends to gum up the mechanism—for example, the guide and press rolls—and may deposit as blobs, spots, or streaks on the fabric.

In accordance with the invention, the undesirable effects noted above are largely eliminated by continuously subjecting the second (diacid chloride) solution to a purification treatment to remove water, hydrolysis products, and suspended matter. This treatment may take various alternative forms. A practical and effective way of accomplishing the purification involves continuously withdrawing the diacid chloride solution from the tank which contains it, continuously passing the withdrawn liquid through a dehydrating agent, such as a conventional molecular sieve, and continuously flowing the so-purified liquid back into the tank. By such treatment, the particles of water which become detached from the entering fabric and which commingle with the diacid chloride solution are continuously removed, whereby hydrolysis of diacid chloride is curtailed. Also, any hydrogen chloride which may have been formed by hydrolysis is adsorbed by the molecular sieve. Thereby, fuming and corrosive action are eliminated. Moreover, since hydrogen chloride is believed to promote the hydrolysis of diacid chlorides, its removal from the solution minimizes such undesired reaction. A further point is that any resinous materials, sludge, suspended particles, etc. which form in the diacid chloride solution are also removed by filtering action of the bed of particles which make up the dehydrating agent or molecular sieve. As a net result of the use of the purification treatment, the diacid chloride solution is kept essentially free from water, hydrogen chloride, resinous materials, organic hydrolytic products, sludge, etc. and, moreover, the shrinkproofing effect attained remains at a desired level even with long-continued operation of the process. Moreover, by such treatment the waste of diacid chloride is essentially eliminated—this reagent is consumed for its intended purpose (reaction with the diamine on the fabric) rather than being consumed in valueless hydrolysis reactions.

A typical embodiment of the invention is explained below, having reference to FIG. 1 of the annexed drawing which schematically illustrates a form of apparatus suitable for continuously treating fabrics in accordance with the invention. This apparatus includes tank 1 for holding an aqueous diamine solution 2 and tank 3 for holding the diacid chloride solution 4, the solvent in this case being one which is inert, volatile, and essentially water-immiscible. A series of guide rolls 5 are provided for leading fabric 6 through the diamine solution 2 and guide rolls 7 are provided for leading the fabric through the diacid chloride solution 4. A conventional heating jacket 9 is provided about tank 1 to maintain the temperature of the diamine solution at the desired level. A set of three pad rolls 10, arranged to provide two nips (squeezes) is provided to press the fabric after its exit from the diamine tank 1. Excess diamine solution expressed from the fabric flows via trough 8 back to tank 1. A pair of pad rolls 11 are provided for pressing the fabric

after its exit from diacid chloride tank 3. A semi-circular trough 12 about the bottom roll 11 is provided to catch liquid pressed out of the fabric after it leaves the diacid chloride solution 4. The subsequent treatment of this liquid will be explained below. Pad rolls 10 and 11 have a surface of neoprene or other resilient elastomer resistant to the reagents used.

Tank 3 may be provided with a conventional enclosure (equipped with openings for the passage of the fabric) to minimize evaporation of the solvent. A similar arrangement may be provided to enclose tank 1 and the mechanisms associated therewith to minimize contact of carbon dioxide (in the atmosphere) with the diamine solution, still in tank 1 or deposited on the fabric.

The heart of the novel purification system is column 13, packed, for example, with beads 14 of a water-absorbing zeolite or other molecular sieve, supported on screen 15. Diacid chloride solution is continuously withdrawn from the base of tank 3 by pump 16 through pipe 17. This liquid is then forced through pipe 18, into column 13, and thence via pipe 19 back to tank 3. The liquid collecting in trough 12 is very likely to contain undesired materials (e.g., water) because of the pressing action of rolls 11 and in the preferred modification of the invention, this liquid is led via pipe 20 directly into the purification system. It is possible, however, to lead the expressed liquid into tank 3 since the impurities it carries will be removed as the liquid from tank 3 is constantly recirculated through the purification system.

In operation of the system, the fabric to be treated, 6, is entered into solution 2, passed therethrough in an extended sinuous path defined by guide rolls 5, then passed through squeeze rolls 10 whereby excess solution is expressed from the fabric. The diamine-impregnated fabric, designated 6a, is entered into diacid chloride solution 4 and is then passed through squeeze rolls 11 to remove excess liquid. Since solution 4 is constantly being purified as above described, the desired polymerization reactions take place on the fibers which make up the fabric, without occurrence of the undesired side-reactions noted hereinabove. The fabric 6b, now having a polyamide formed in situ on its fibrous elements, is then usually subjected to washing with a conventional washing medium—warm water containing a small proportion of soap or a synthetic detergent—and rinsed in order to remove unreacted materials and particles of resinous reaction product which are not firmly attached to the textile fibers. Following this washing, the fabric, if undyed, is dyed and finished in the usual manner. If the fabric has already been dyed, it is dried and finished in the usual manner, for example, sheared and semi-decated.

When the molecular sieve material 14 in column 13 becomes saturated with water, etc., it is regenerated in known manner. Prior to regeneration, it is preferred to back-wash the bed with a warm alkaline solution containing a surface-active agent (for example, water at 120° F. containing about 0.5% sodium carbonate and 0.05 to 0.1% of a non-ionic surfactant) to flush out sludge, occluded material, solvent, etc. This may be followed by a rinse with water. The molecular sieve is then regenerated by heating. This can be done, for example, by forcing hot gas (such as air or nitrogen) through the column. Generally, the gas is heated to a temperature of about 300–500° F. and the flow of purge gas is directed in a direction reverse to that used in regular operation of the column. For uninterrupted operation of the fabric-treating system, one may provide two separate columns of the molecular sieve material. By a suitable arrangement of pipes and valves, one column can be in use while the other is being regenerated.

Referring to FIG. 2 in the annexed drawing, there is shown an alternative form of the purification system. In this system, a conventional filter 21 is interposed between pump 16 and column 13. The filter prevents any solid contaminants such as suspended material, sludge, etc., which may be in the liquid, from clogging the bed of

molecular sieve material 14. Filter 21 may take the form, for example, of a conventional plate-type filter pre-coated with a diatomaceous earth filter-aid.

As noted hereinabove, a basic modification of the present improvement involves continuous recirculation of the diacid chloride solution through a dehydrating system. Many different types of dehydrating agents may be used for this purpose and the type of dehydrating agent may be varied as desired without departing from the ambit of the invention. In the preferred modification of the invention, we use a dehydrating agent which has the ability to absorb HCl, as well as water. An obvious point in the selection of a dehydrating agent is that it should be inert; that is, it should not react with the diacid chloride or with the solvent used for this compound. Various anhydrous salts may be used such as calcium chloride or calcium sulphate. Generally, however, such salts are not preferred as when they take up water they tend to get sticky and the bed becomes clogged. Better results are obtained with water-insoluble materials such as silica gel, alumina, charcoal, activated carbon, bentonites, attapulgite, porous glasses, etc. Particularly preferred are the materials conventionally known as molecular sieves. These are alumino-silicates or zeolites, the crystals of which contain minute pores. In fact, the cross-sections of these pores are of molecular dimensions. As a result, they can be used to separate mixtures by making use of the differences in the size and shape of the molecules in the mixture. For example, when the diacid chloride solution is contacted with the crystals, the low-molecular weight components such as water and hydrogen chloride enter the pores and are absorbed by the crystals; the components of larger molecular weight—the diacid chloride and solvent—cannot enter the pores and simply pass by the particles. A particularly useful aspect of the molecular sieves is their high capacity for water. Thus in general, a molecule sieve will adsorb five times as much water as will such materials as silica gel or activated alumina. As the molecular sieve, one may employ natural zeolites or synthetic zeolites. The preparation of the synthetic zeolites is known and forms no part of the present invention; indeed, they are commercial products available on the open market.

Although we have obtained excellent results with the use of a purification system containing solely a dehydrating agent, preferably one of the molecular sieve type, it is within the ambit of the invention to employ a dehydrating agent in conjunction with other agents or devices. Among these auxiliaries may be mentioned filtering devices (such as screens or beds of divided material such as sand, diatomaceous earth, or the like) and ion exchange resins. The ion exchange resins may be in separate beds of cation exchangers and anion exchangers or may be in mixed cation-anion exchange beds. Ion exchange materials would assist the desired purification by removing such cations or cationic materials as sodium ions and diamine and by removing such anions or anionic materials as chloride ion, free carboxylic acid, carbonate ions, etc.

In utilizing the present invention in the continuous shrinkproofing of wool, it is preferred to include in the total system the features disclosed in the copending application of Fong, Brown, Wasley, Whitfield and Miller, Ser. No. 174,315, filed Feb. 19, 1962. Although these features form no part of the present invention, they are explained herein to provide a complete description of the preferred environment in which to utilize the present invention. The features in question are described in the following paragraphs, numbered 1 to 5:

(1) *Condition of fabric.*—The fabric prior to entering the first (diamine) solution should be in a neutral or alkaline state, that is, its pH should be at least 7. If the fabric is in an acid state (as may be encountered with carbonized wool or wool dyed in acid dye baths) the diamine solution does not properly impregnate and exhaust onto the fabric, with the end result that the degree of shrinkproofing or the uniformity thereof is adversely

affected. However, where the fabric is in a neutral condition as it enters the diamine solution, a complete and uniform penetration of the solution and exhaustion of the diamine into the fabric is obtained with the result that the product exhibits a high degree of shrink resistance uniformly over the area of the treated fabric. It is not essential that the fabric prior to treatment be in a neutral state; it can also be in an alkaline state to attain like results of high level and uniformity of shrinkproofing. Usually, however, it is preferred that the pH of the fabric not exceed about 9 to avoid any possibility of yellowing or other degradation of the wool. Taking into consideration the above matters, if the fabric to be treated is in an acid state, it must be neutralized prior to entry into the diamine bath. Such neutralization can be accomplished by soaking it in an aqueous solution of an alkaline substance, preferably one which has inherent buffering capacity. Thus, for example, the fabric may be soaked in a dilute (about 0.1 to 5%) solution of an alkaline agent such as sodium carbonate, sodium bicarbonate, borax, trisodium phosphate, tetrasodium pyrophosphate, sodium metaphosphate, ammonia, sodium acetate, soap, or the like. Ordinarily, the treatment is conducted by washing the textile in a conventional alkaline scouring medium whereby the wool is put in proper pH condition and any extraneous materials such as spinning oils etc. are removed from the goods. After such treatment, the fabric is rinsed in water and is then dried or directly entered into the diamine solution. It is obvious that the concentration of alkaline agent, the time of soaking or washing, etc. will vary depending on the condition of the fabric as received at the plant and these may be adjusted as necessary to yield a fabric having a pH of at least 7 and preferably not over about 9.

(2) *Temperature of diamine solution.*—Another item is that the temperature of the diamine solution should be maintained at a temperature of about 90 to 150° F. Thus it has been observed that at temperatures substantially below the stated level, the penetration and rate of exhaustion of the diamine solution into the fabric is too slow for continuous operation. On the other hand, at temperatures much above 150° F. the quality of the wool may be adversely affected by yellowing or other degradation changes. By operating within the stated temperature range, penetration of the diamine solution into the fabric and exhaustion of the diamine onto the fabric occur at a high rate and uniformly, without adverse effect on the quality of the wool. In general, the temperature which provides optimum results will vary with the nature of the diamine used and openness of the fabric construction. In the case of hexamethylene diamine and when treating a woolen type fabric, optimum results are obtained where the solution is held at about 110–120° F.

(3) *Time of contact between fabric and diamine solution.*—As noted above, successful operation of the continuous operation requires a thorough and uniform impregnation of the diamine solution into the fabric and time for adsorption of diamine by the wool (i.e., exhaustion of the diamine onto the wool). These processes are not instantaneous even with an efficient wetting agent incorporated into the diamine bath and therefore the fabric must be held in contact with the solution for a substantial period of time long enough to attain the desired results. In continuous operation the time of contact can be extended without slowing the production rate by threading the fabric back and forth in a tank filled with the diamine solution. In any particular case the time of such holding or delay will vary depending upon a series of factors including the geometry of the fabric, the temperature of the diamine solution, the initial pH of the fabric, the particular diamine used and its concentration, the type and concentration of wetting agent added to the diamine solution, etc. For example, a fine, tightly-woven, worsted material would require a longer delay time than a coarse, woolen fabric. A higher temperature of the diamine solu-

tion would increase the penetration rate and so shorten the minimum delay required. A fabric initially low in pH would require a longer period of delay than one which was at a higher pH prior to contact with the diamine solution. Generally speaking, a diamine of higher molecular weight or one applied in higher concentration would increase the viscosity of the solution and thus in either of these cases a longer delay would be necessitated. Addition of an effective wetting agent to the diamine solution would shorten the delay period below the levels required, for example, with a solution without a wetting agent. Taking into account these manifold circumstances, it is impossible to set forth the time of delay in numerical limits. However, given any particular set of materials, apparatus, and conditions, the required time of delay can be ascertained by pilot trials employing different periods of delay and selecting the one which attains the desired goal of providing a fabric which is thoroughly and uniformly impregnated with the diamine solution. In a typical situation where the textile is a woolen fabric conditioned to pH 7 to 9, where the diamine is hexamethylene diamine applied in a concentration of about 0.5% and the solution held at 110° F. contains an effective wetting agent, the proper holding time is at least 10 seconds, preferably 20 to 60 seconds.

(4) *Removal of excess liquid after impregnation with the diamine solution.*—After thorough impregnation of the fabric with the diamine solution is assured, the fabric is then subjected to a treatment to eliminate excess liquid (diamine solution and/or water). The aim here is to provide a fabric wherein the diamine solution is, for the most part, distributed on the surfaces of the individual fibrous elements. Expressed another way, the fabric is treated to remove essentially all the solution which is "loosely" associated with the fabric, as in the form of surface deposits or collected in interstices between individual fibrous elements, leaving that portion of the solution which coats the fibers. By such treatment one prevents the formation of resin deposits on the surface of the fabric and in interstitial areas. If such resin deposits were formed, the hand of the fabric would be adversely affected, the product would have a streaked appearance and uniform dyeing could not be attained. Moreover, by removal of excess solution, one decreases the amounts of water, diamine, etc. which are adventitiously dislodged from the fabric as it enters the second solution. This removal of excess solution can be readily accomplished with the usual types of equipment generally used in finishing fabrics, for example, squeeze rolls, vacuum slots, air jets, hot air driers, or combinations of these devices. A preferred technique is the use of a three-roll padder with threading arrangement to give two nips. Regardless of the means used to effectuate the removal of liquid, the treatment is applied to the extent necessary that the fabric exhibits a weight increase (wet pick-up) of 30 to 60%, preferably less than 55%. By so doing, the desired result of substantially limiting the liquid in the fabric to a coating on individual fibers is achieved. At this point the fabric will generally contain about 0.1 to 2% of diamine, based on the dry weight of the fabric.

(5) *Final padding.*—Following passage of the fabric through the second (diacid chloride) bath, the fabric is padded. This treatment not only removes unreacted reagents, solvents, etc. but also enhances the shrinkproofing effect. The theoretical basis of this effect is not understood but experimental trials have demonstrated that padding is markedly beneficial to the shrink resistance of the product. Good results in this regard are attained by pressing the fabric at a pressure of at least 100 lbs. per linear inch (measured across the width of the fabric) and even better results are attained with pressures as high as 300–400 lbs. per linear inch.

In the above description we have stressed application of the invention to a system where the polymer formed in situ in the textile material is produced by the interfacial

reaction of a diamine and a diacid chloride. In its broad aspect, the invention encompasses the utilization of any of the reaction systems—disclosed in Patents 3,078,138, 3,084,018, 3,084,019 and 3,093,441—where one of the reactants is a diamine and the other is a bifunctional compound capable of forming polymers with the diamine. Typical of these bifunctional compounds are diacid chlorides, bischloroformates, diisocyanates, and mixtures thereof. In cases where a diacid chloride is used, the polymer formed is a polyamide; where a bischloroformate is used, the polymer is a polyurethane; where a diisocyanate is used, the polymer is a polyurea. By using mixtures of bifunctional compounds, interpolymers may be produced. Typical of the last is the use of a diamine in conjunction with a mixture of a diacid chloride and a bischloroformate to produce a type of interpolymer which may be termed a copoly amide-urethane. Accordingly, in its broad aspect the invention encompasses application of our novel purification technique described above in connection with any system for shrinkproofing which involves serial impregnation of a wool textile with (1) an aqueous diamine solution and then with (2) a solution of a bifunctional compound capable of forming a polymer with the diamine, said second solution having as its solvent an inert, essentially water-immiscible solvent. It is, of course, obvious that our novel purification technique is applied to the second solution—the one containing the said bifunctional compound. As noted above, typical of the bifunctional compounds which can be employed in the second solution are acid chlorides, bischloroformates, diisocyanates, and mixtures thereof. By applying these types of compounds in serial manner and in essentially mutually-immiscible phases, various types of polymers may be formed in situ on the wool fibers, rendering the textile shrinkproof. Typical examples of compounds which can be employed in a practice of the invention are described below.

As the diamine one may employ any of the aromatic, aliphatic, or heterocyclic compounds containing two primary or secondary amine groups, preferably separated by at least two carbon atoms. The diamines may be substituted if desired with various non-interfering (non-functional) substituents such as ether radicals, thioether radicals, tertiary amino groups, sulphone groups, fluorine atoms, etc. Typical compounds in this category are listed below merely by way of illustration and not by way of limitation: ethylene diamine; trimethylene diamine; tetramethylene diamine; hexamethylene diamine; octamethylene diamine; decamethylene diamine; N,N'-dimethyl-1,3-propanediamine; 1,2 - diamino - 2-methylpropane; 2,7-diamino - 2,6 - dimethyloctane; N,N'-dimethyl - 1,6 - hexane-diamine; 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. Particularly preferred is hexamethylene diamine, i.e., the compound of the above formula where $n=6$.

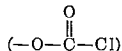
As the diacid chloride one may employ any of the aliphatic, aromatic, or heterocyclic compounds containing two carbonylchloride ($-\text{COCl}$) groups, preferably separated by at least two carbon atoms. The diacid chlorides may be substituted if desired with non-interfering (non-functional) substituents 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,

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maleyl chloride, fumaryl chloride, malonyl chloride, succinyl chloride, glutaryl chloride, adipyl chloride, pimelyl chloride, suberyl chloride, azelalyl chloride, sebacyl chloride, cyclohexane-1,4-biscarbonyl chloride, phthalyl chloride, isophthalyl chloride, terephthalyl chloride, 4,4'-biphenyl-dicarbonyl chloride, β -hydromuconyl chloride, i.e., $\text{ClCO}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{COCl}$, diglycollic acid chloride i.e., $\text{O}(\text{CH}_2-\text{COCl})_2$, higher homologues of this compound as $\text{O}(\text{CH}_2-\text{CH}_2-\text{COCl})_2$ dithiodiglycollic acid chloride, diphenylolpropanediacetic acid chloride, i.e., $(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_4\text{OCH}_2\text{COCl})_2$, 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 $-\text{COCl}$ groups one may use compounds containing one $-\text{CSCl}$ and one $-\text{COCl}$ group or compounds containing two $-\text{CSCl}$ groups. Moreover, although the diacid chlorides are preferred as they are reactive and relatively inexpensive, the corresponding bromides and iodides may be used.

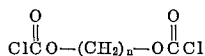
As the diacid chloride, it is generally preferred to use the aliphatic compounds containing two carbonylchloride groups in alpha, omega positions, particularly those of the type $\text{ClCO}-(\text{CH}_2)_n\text{COCl}$ wherein n has a value from 2 to 12. Another preferred category includes the compounds 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

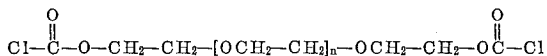


preferably separated by at least two carbon atoms. The bischloroformate may be substituted if desired with non-interfering (non-functional) substituents such as sulphone groups, ether groups, thioether groups, etc. Typical examples of compounds in this category are listed below merely by way of illustration 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



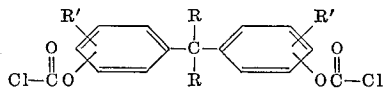
wherein n has a value from 2 to 12. Another preferred category of compounds are the bis-chloroformates derived from polyethylene glycols, e.g.,



wherein n has a value from zero to 10. A useful category

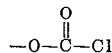
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of aromatic bischloroformates are the bisphenol chloroformates, that is, compounds of the type

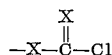


wherein $\text{R}-\text{C}-\text{R}$ represents an aliphatic hydrocarbon group containing 1 to 12 carbon atoms and R' is hydrogen or a low alkyl radical.

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

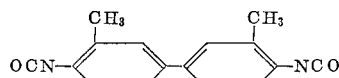


groups one may use any of the compounds containing the sulphur analogues of these groups, for example, the compounds containing two groups of the formula

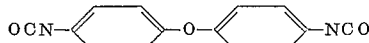


wherein one X is sulphur and the other is oxygen or wherein both X's are sulphur. Moreover, although the bischloroformates are preferred because they are reactive and relatively inexpensive, it is not essential that they contain chlorine and one may use the corresponding bis-bromoformates or bisiodoformates.

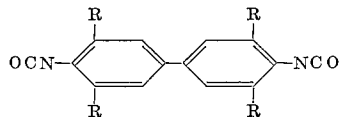
As the diisocyanate one may employ any of the aliphatic, aromatic, or heterocyclic compounds containing two isocyanate ($-\text{NCO}$) groups, preferably separated by at least two carbon atoms. The diisocyanates may be substituted if desired with non-interfering (non-functional) substituents such as 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'-bitolylene-4,4'-diisocyanate, i.e.,



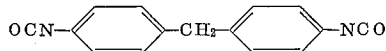
diphenyl ether-4,4'-diisocyanate, i.e.,



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

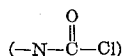


diphenylmethane-4,4'-diisocyanate, i.e.,

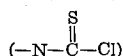


biphenylene diisocyanate, 3,3'-dimethoxy-biphenylene-4,4'-diisocyanate, naphthalene diisocyanates, polymethyl polyphenyl isocyanates, etc. It is also evident that the sulphur analogues of these compounds may be used and such are included within the spirit of the invention. Thus for example, instead of using the compounds containing two $-\text{NCO}$ groups one may use their 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

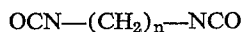


or their sulphur analogues



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, xylylene diisocyanates, and diphenylmethane-4,4'-diisocyanate which may also be termed methylene-bis(p-phenylisocyanate).

Since the process of the invention makes use of an interfacial polymerization (formation of a polymer at the interface between mutually-immiscible phases of the individual reactants), it is evident that the polymer-forming agents need be applied in solutions wherein the solvents are substantially mutually immiscible. Thus the diamine reactant is applied in aqueous solution while the complementary reactant (acid chloride, bischloroformate, or diisocyanate) is applied as a solution in an inert, essentially water-immiscible solvent, preferably one which is volatile, for example, benzene, carbon tetrachloride, toluene, xylene, ethylene dichloride, chloroform, hexane, octane, petroleum ether, or other volatile petroleum hydrocarbon mixture. It is generally preferred that the solutions of both complementary reactants be dilute, that is, they should each contain about $\frac{1}{2}$ to 10%, preferably $\frac{1}{2}$ to 2%, of the reactant. Generally, the conditions of treatment, such as the rate of traversal of the fabric, concentration of the reactants, degree of pressing, etc., are so correlated that the product contains about 0.25 to 3% of polymer.

It is generally desirable to add reaction promoters or catalysts to either of the reactive solutions, that is, to either the diamine solution or the solution of the complementary reactant (acid chloride, bischloroformate, or diisocyanate) in order to enhance reaction between the active agents. For example, in cases where the system involves reaction between a diamine and a diacid chloride or a bis-chloroformate it is desirable to add to either of the solutions (generally to the diamine solution) a sufficient amount of alkaline material to take up the HCl formed in the reaction. For such purpose one may use a tertiary amine such as pyridine, dimethyl aniline, or quinoline or an alkali-metal hydroxide, or, more preferably, an alkaline material with buffering capacity such as sodium carbonate, sodium bicarbonate, trisodium phosphate, borax, etc. Another plan which may be used involves supplying the diamine in excess so that it will act both as a reagent and as an HCl-acceptor. The reaction 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.

To aid the diamine solution in penetrating into the textile, it is generally preferred to incorporate a minor proportion of a surface-active agent into this solution. For this purpose one may use such agents as sodium alkyl (C_8-C_{18}) sulphates, the sodium alkane (C_8-C_{18}) sulphates, the sodium alkyl (C_8-C_{20}) benzene sulphates, esters of sulphosuccinic acid such as sodium dioctylsulphosuccinate, and soaps, typically sodium salts of fat acids. Surface-active agents of the non-ionic type may

also be used and they have the desirable property of being non-substantive; that is, they are not preferentially absorbed by the wool. Typical examples of non-ionic agents are 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. A useful class of non-ionic agents are the nonylphenoxy polyethyleneoxy ethanolols, containing 9 to 12 moles of ethylene oxide per mole of nonylphenol, as these compounds are readily soluble in the diamine solution even in the presence of relatively high concentrations of sodium carbonate. Generally, only a small proportion of surface-active agent is used, on the order of 0.05 to 0.5%, based on the weight of the solution. In addition to, or in place of the surface-active agent, a supplementary solvent may be added to the primary solvent (water) in quantity sufficient to disperse the active reactant. For such purpose one may employ acetone, or other inert, volatile solvent, particularly one that is at least partially miscible with water.

In the foregoing description we have emphasized the utilization of our invention in connection with the shrink-proofing of wool. However, wool is by no means the only substrate which can be treated. In its broad aspect, the invention can be utilized in the treatment of any fibrous material. Thus in applying the basic processes of Patents 3,078,138, 3,084,018, 3,084,019 and 3,093,441 in a continuous manner to any fibrous material, the same problems such as generation of hydrogen chloride, formation of gummy resinous materials or organic hydrolytic products, wastage of reagents, etc. will be encountered. By application of the improvement described herein, these problems can be obviated. Accordingly, the invention is generically applicable to any fibrous material. Typical examples of such materials are animal hides; leather; animal hair; cotton; hemp; jute; ramie; linen; 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.

EXAMPLE

The invention is further demonstrated by the following illustrative example:

Shrinkage test.—The tests for shrinkage referred to below were conducted in the following manner: The wool samples were washed in a reversing agitator-type household washing machine using a 3-pound load, a water temperature of 105° F., and a low-sudsing detergent in a concentration of 0.1% in the wash liquor. The wash cycle itself was for 75 minutes, followed by the usual rinses and spin drying. After four successive washing operations by this method, the samples were press dried and measured to determine their length and width and the shrinkage calculated from the original dimensions. With a single wash by this method, samples of the control (untreated) fabric gave a shrinkage of 17% in the warp direction and 12% in the fill direction.

The fabric used in this run was a 100% woolen flannel, 60" wide, 12 oz. per lin. yd., plainweave, ends 33, picks 32. Prior to starting the run, the fabric had been treated

as follows: It was carbonized, alkaline-fulled, scoured with aqueous detergent solution, and rinsed, leaving the fabric in a slightly alkaline state. It was then scutched and extracted to remove excess water.

The fabric, without drying, was continuously treated, using an apparatus as shown in FIG. 1.

The bath in tank 1 was an aqueous solution containing 1% of hexamethylene diamine, 2% sodium carbonate, and 0.06% of a non-ionic wetting agent—Igepal CO-710 (nonylphenoxy polyethyleneoxyethanol, containing 10-11 moles ethylene oxide per mole nonylphenol). This solution was maintained at 110° F.-120° F. During the course of the run, water and make-up chemicals (diamine, sodium carbonate, and wetting agent) were added to maintain the concentrations thereof at the stated levels and to maintain the volume of solution in the tank.

The fabric was fed through the system at a rate of 19 y.p.m. The delay time attained by the sinuous arrangement on guide rolls 5 was 20 seconds. Following passage of the fabric through the diamine solution, it was pressed (by pad rolls 10) so that the wet pickup was between 45 and 50%.

The bath in tank 3 was a solution of 3% sebacoyl chloride in an aliphatic petroleum solvent (Stoddard solvent). This solution, having a volume of about 25 gallons, was continuously recirculated at a rate of 5 to 8 gallons per minute through column 13 containing 4 pounds of molecular sieve material. This was a commercial product (Linde molecular sieve, type AW-500)—an acid-stable aluminosilicate in the form of pellets $\frac{1}{16}$ – $\frac{1}{8}$ inch in diameter. The pores in the crystals have an effective diameter of 4 to 5 angstroms. The product absorbs water and HCl but not the sebacoyl chloride nor the solvent. After 3000 yards of fabric had been processed, the molecular sieve material was removed from the column and replaced with 4 pounds of fresh material.

During the run, fresh sebacoyl chloride solution was added as required to maintain the volume of solution in tank 3. Also, sebacoyl chloride was added to maintain the solution in the tank at the proper concentration (3%). During the run wherein 5520 yards of fabric were treated, the total amount of make-up sebacoyl chloride was 47 pounds.

After the fabric had passed through the diacid chloride bath 4, it was pressed (by pad rolls 11) at a pressure of about 300 lbs./lin. inch.

The treated fabric was then washed to remove unreacted reagents, solvents, etc. The washing was conducted with an aqueous liquor (at 120° F.) containing 0.1% Igepal CO-710, and 0.05% formic acid. The acid was added to the wash liquor to neutralize residual sodium carbonate derived from the first (diamine) solution. The fabric was then rinsed and dried. It was estimated that the amount of polymer formed on the wool was 0.5% based on the weight of wool.

During operation of the run, no HCl fumes were formed and the sebacoyl chloride solution remained free from resinous material and suspended material. The treated fabric was completely free from streaks, spots, or lumps of polymer.

At intervals during the run, samples of the fabric were tested for shrinkage by the procedure described above. The results are tabulated below.

Length of fabric treated when sample taken, yards	Area shrinkage (after four 75-min. washes) percent
80	1.2
2080	1.3
3200	2.7
4720	0.5
5520	0.3

Comparative run.—In this run the same procedure as above was followed except that the diacid chloride bath

was not circulated through the purifying system. Hydrogen chloride fumes were formed at the diacid chloride tank 3 and in treating the same length of fabric, 68 pounds of make-up sebacoyl chloride was required (contrasted with 47 pounds when proceeding in accordance with the invention). Also, the shrinkage resistance of the product was not maintained and by the time 2,000 yards of fabric had been processed, the area shrinkage had increased to over 10%.

Having thus described the invention, what is claimed is:

1. In the process wherein a fibrous material is subjected in continuous operation to serial impregnation with (a) a solution of a diamine in water and then with (b) a solution of a bifunctional organic compound capable of forming a polymer with the diamine, said compound being dissolved in an inert, volatile, water-immiscible solvent, the improvement which comprises continuously withdrawing a portion of said solution (b), continuously removing water, hydrolysis products, and suspended matter from said withdrawn portion, and continuously returning said withdrawn portion back to said solution (b).

2. The process of claim 1 wherein bifunctional organic compound is a diacid chloride.

3. The process of claim 1 wherein said fibrous material is wool.

4. In the process wherein a wool textile is subjected in continuous operation to serial impregnation with (a) a solution of a diamine in water and then with (b) a solution of a diacid chloride dissolved in an inert, volatile, essentially water-immiscible solvent, the improvement which comprises continuously withdrawing a portion of said solution (b), continuously removing water, hydrogen chloride, and suspended matter from said withdrawn portion, and continuously returning said withdrawn portion back to said solution (b).

5. In the process wherein a fibrous material is subjected in continuous operation to serial impregnation with (a) a solution of a diamine in water and then with (b) a solution of a bifunctional organic compound capable of forming a polymer with the diamine, said compound being dissolved in an inert, volatile, essentially water-immiscible solvent, the improvement which comprises continuously circulating said solution (b) through a bed of dehydrating agent.

6. The process of claim 5 wherein the dehydrating agent has the ability to absorb HCl as well as water.

7. The process of claim 5 wherein the dehydrating agent is a molecular sieve.

8. In the process of shrinkproofing wool wherein a wool textile is subjected in continuous operation to serial impregnation with (a) a solution of a diamine in water and then with (b) a solution of a bifunctional organic compound capable of forming a polymer with the diamine, said compound being dissolved in an inert, volatile, essentially water-immiscible solvent, the improvement which comprises continuously circulating said solution (b) through a bed of dehydrating agent.

9. The process of claim 8 wherein the dehydrating agent has the ability to absorb HCl as well as water.

10. The process of claim 8 wherein the dehydrating agent is a molecular sieve.

11. In the process of shrinkproofing wool wherein a wool textile is subjected in continuous operation to serial impregnation with (a) a solution of a diamine in water and then with (b) a solution of a diacid chloride, said diacid chloride being dissolved in an inert, volatile, essentially water-immiscible solvent, the improvement which comprises continuously circulating the said solution (b) through a bed of dehydrating agent.

12. The process of claim 11 wherein the dehydrating agent has the ability to absorb HCl as well as water.

13. The process of claim 11 wherein the dehydrating agent is a molecular sieve.

14. The process of claim 11 wherein said dehydrating

agent is an alumino-silicate zeolite having an effective pore diameter of about 4 to 5 angstroms.

References Cited by the Examiner**UNITED STATES PATENTS**

3,078,138 2/1963 Miller et al. ----- 8—128

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Hersh, C. K.: "Molecular Sieves," New York, Reinhold Publishing Corporation, 1961 (see pp. 45, 51, 73, 78, and 83).

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