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INTERFACIAL POLYMERIZATION ON WOOL USING A POLYACID POLYHALIDE AND A COMBINATION OF POLYAMINES

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ABSTRACT OF THE DISCLOSURE

Process for shrinkproofing wool by contacting the wool with an amine solution containing a diamine and a small amount of polyamine having more than two amino groups per molecule, and, either before or after said amine treating step, contacting the wool with a polyacid polyhalide solution. The amine solution is exemplified by a 2% aqueous solution of mixed amines containing 95% hexamethylenediamine and 5% N^1,N^3 -diisopropyl-diethylenetriamine, and the polyacid solution by a 2% benzene solution of sebacyl chloride.

This invention relates to a process for the treatment of fibrous materials and particularly to a treatment of wool. More specifically the invention is concerned with a dimensional stabilization of fibrous materials by an interfacial polymerization reaction utilizing a novel combination of compounds.

Heretofore the problem of shrinkage in certain fibers or fabrics, and particularly to wool, was present when such fibers or fabrics underwent cleaning operations and particularly washing. One theory which accounts for the shrinkage of the fabric, and particularly wool, is that the wool fibers contain many so-called hooks or barbs which, when the fabric is washed, come in contact with each other in an interlocking fashion and thus tend to hold the individual strands or fibers together, said action resulting in a matting or shrinking of the fabric and preventing the fabric from resuming its normal dimensions or configuration. This is of particular disadvantage especially when the article being cleaned or washed is used as clothing. This disadvantage may be overcome by treating the fabric with certain compounds to form a polymer whereby the fabric is rendered relatively shrink-proof or shrink-resistant. The prior art teaches certain methods for imparting dimensional stability to wool all of which have the disadvantage of either altering some of the desirable characteristics of the fiber, such as fiber strength and handle, or requiring a post cure. The fabrics treated according to the process hereinafter set forth in greater detail will possess many desirable physical characteristics including an excellent resistance to shrinkage, smoothness after drying, excellent hand, increased break strength and tear strength as well as improved resistance to abrasion, chemicals and pilling and, in addition, does not require a post cure. A method of treating these fabrics and, as hereinbefore set forth, particularly wool, is passing said fabric through an aqueous solution of a diamine, removing the excess solution by padding, centrifuging, vacuum extraction, etc., and thereafter passing the material through a diacid halide and particularly a diacid chloride in a water-immiscible solution whereby the polymer is formed almost instantaneously at the interface, removing the excess solution by similar means hereinbefore set forth and washing the treated fabric. However, it has now been unexpectedly discovered that an improved shrinkproofing and an improved handle may be achieved by utilizing a combination of a diamine and at least one other

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amine containing more than two amino groups per molecule. For example, a wool fabric was treated in a manner hereinafter set forth in greater detail with an aqueous solution of hexamethylenediamine and N^1,N^3 -diisopropyl-diethylenetriamine, followed by treatment with a water-immiscible hydrocarbon solution of sebacyl chloride. The resulting fabric, upon repeated washings, shrunk less than half as much as a sample of the same wool fabric which was treated with an aqueous solution containing only hexamethylenediamine followed by treatment with a hydrocarbon solution of sebacyl chloride. Other combinations of diamines and polyamines also showed the synergistic effect of the combination over the individual components. Furthermore, the handle of the fabrics which were treated using the combination of a diamine and an amine containing more than two amino groups per molecule was judged to be superior in all respects by an impartial panel over those fabrics which were treated by a diamine alone.

The use of an amine compound containing more than two amino groups per molecule alone was shown by the prior art to be inferior in all respects to the results obtained when using a diamine alone. We have likewise observed this phenomena, and therefore the superior results obtained when combining a diamine with one or more amine compounds containing more than two amino groups per molecule was totally unexpected.

It is therefore an object of this invention to provide an improved process for treating fibrous materials.

Another object of this invention is to provide a process for the treatment of fabrics, and particularly wool, utilizing a novel combination of compounds whereby the treated fabric will be less susceptible to shrinkage and with a much better hand than heretofore obtained by other methods.

Taken in its broadest aspect, one embodiment of this invention is found in a process for the treatment of a fibrous material which comprises contacting said fibrous material with one solution selected from the group consisting of a solution containing at least one diamine and at least one polyamine containing more than two amino groups per molecule and a solution containing a polyacid polyhalide containing at least two acid halide groups per molecule, said solutions being mutually immiscible, and thereafter contacting said fibrous material with the other of said solutions.

Another embodiment of this invention resides in a process for the treatment of a fibrous material which comprises contacting said fibrous material with a first solution containing at least one diamine and at least one polyamine containing more than two amino groups per molecule, and thereafter contacting said fibrous material with a second solution containing a polyacid polyhalide containing at least two acid halide groups per molecule, said second solution being immiscible with said first solution.

A further embodiment of this invention resides in a process for the treatment of a wool which comprises contacting said wool with a first solution containing at least one diamine and at least one polyamine containing more than two amino groups per molecule, and thereafter contacting said wool with a second solution containing a polyacid polyhalide containing at least two acid halide groups per molecule, said second solution being immiscible with said first solution.

Yet another embodiment of this invention is found in a process for the treatment of wool which comprises contacting said wool with an aqueous solution containing ethylenediamine and tetraethylenepentamine, and thereafter contacting said wool with a water-immiscible organic solution containing a polyacid polyhalide containing at least two acid halide groups per molecule.

A specific embodiment of this invention is found in a process for the treatment of wool which comprises contacting said wool with an aqueous solution containing ethylenediamine, tetraethylenepentamine and triethylenetetramine, and thereafter contacting said wool with a water-immiscible organic solution containing a polyacid polyhalide containing at least two acid halide groups per molecule.

A more specific embodiment of this invention is found in a process for the treatment of wool which comprises contacting said wool with an aqueous solution containing ethylenediamine, tetraethylenepentamine and triethylenetetramine, and thereafter contacting said wool with a hydrocarbon solvent containing sebacoyl chloride.

Other objects and embodiments will be found in the following further detailed description of this invention.

As hereinbefore set forth, it has now been discovered that the treatment of fibrous material, and particularly the treatment of wool for retarding shrinkage thereof, may be effected with improved results by treating the fabric with a solution containing a mixture of a diamine and a polyamine which contains more than two amino groups per molecule and thereafter treating the fabric with a solution of a polyacid polyhalide containing at least two acid halide groups per molecule, said solutions being mutually immiscible.

The diamines which are employed in this invention are aliphatic diamines such as ethylenediamine, diaminopropanes, diaminobutanes, diaminopentanes, diaminohexanes, etc., N-methylethylenediamine, N-ethylethylenediamine, N-propylethylenediamine, N,N'-dimethylethylenediamine and N,N'-diethylethylenediamine, similarly substituted N,N' - diaminopropanes, N,N' - diaminobutanes, N,N'-diaminopentanes, N,N'-diaminohexanes, diaminodiethyl ether, polyethylene glycol diaminoethyl ethers, etc., aromatic diamines such as o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, bis-methyleneaminobenzenes, naphthalene diamines and ring substituted phenylene and naphthalene diamines, etc., cycloaliphatic diamines such as 1,2-, 1,3-, 1,4-diaminocyclohexanes, isomeric diaminotetralins and decalins, etc., heterocyclic diamines such as piperazine, diaminothiophene, etc. The polyamines which are utilized in conjunction with the aforementioned diamines will contain either primary or secondary terminal amine groups. Examples of these polyamines, which may also be defined as amines containing more than two amino groups per molecule, include aliphatic polyamines such as diethylenetriamine, dipropylenetriamine, dibutylenetriamine, dipentylenetriamine, dihexylenetriamine, triethylenetetramine, tripropylenetetramine, tributylenetetramine, tripentylenetetramine, tetraethylenepentamine, tetrapropylenepentamine, tetraheptylenepentamine, tetrabutylene-pentamine, tetrapentylenepentamine, N-methyldiethylenetriamine, N-ethyldiethylenetriamine, N-methyltriethylenetetramine, N-ethyltriethylenetetramine, N¹,N³ - dimethyldiethylenetriamine, N¹,N³ - diisopropyldiethylenetriamine, N¹,N³ - di-sec-butyl-diethylenetriamine, N¹,N⁴ - dimethyltriethylenetetramine, N¹,N⁴ - diisopropyltriethylenetetramine, N¹,N²,N⁴ - trimethyltriethylenetetramine, N¹,N²,N⁴ - triisopropyltriethylenetetramine, N¹,N²,N⁴ - trimethyltetraethylenepentamine, N¹,N⁵ - diisopropyltetraethylenepentamine, etc., aromatic polyamines as 1,2,4-triaminobenzene, 1,3,5-triaminobenzene, diaminobenzidine, triaminonaphthalenes, diaminodiphenylamines, diaminodibenzylamines, etc., cycloaliphatic polyamines such as the isomeric triaminocyclohexanes, triaminocyclohexanes, etc., heterocyclic polyamines such as aminopiperazine, triaminofuran, triaminothiophene, etc. It is to be understood that the aforementioned diamines and amines containing more than two amino groups per molecule are only representatives of the class of compounds which may be used and that the present invention is not necessarily limited thereto.

After treating the fabric, and particularly wool, with the combination of diamine and amine containing more than two amino groups per molecule in a manner herein-

after set forth in greater detail, and removal of the excess solution, the fabric is then passed through a water-immiscible solution of a polyacid polyhalide containing at least two acid halide groups per molecule and preferably a diacid dichloride. Examples of diacid dichlorides which may be used include aliphatic diacid dichlorides such as oxalyl chloride, malonoyl chloride, succinoyl chloride, glutaroyl chloride, adipoyl chloride, pimeloyl chloride, suberoyl chloride, azelaoyl chloride, sebacoyl chloride, etc., aromatic diacid dichlorides such as phthalyl dichloride, isophthalyl dichloride, terephthalyl dichloride, etc., cycloaliphatic diacid dichlorides such as the isomeric cyclohexyldicarbonyl dichlorides, etc., heterocyclic diacid dichlorides such as isocinchomeric acid dichloride, lutidinic acid dichloride, thiophenedicarboxylic acid dichlorides, etc. Examples of polyacid polyhalide containing more than two acid halide groups per molecule include aliphatic acid halides such as 1,2,3-tricarboxypropane trichloride, 1,2,4-tricarboxybutane trichloride, 1,1,4-tricarboxybutane trichloride, 1,2,3,4-tetracarboxybutane tetrachloride, 1,1,4,4-tetracarboxybutane tetrachloride, 1,2,5-tricarboxypentane trichloride, 1,1,5-tricarboxypentane trichloride, 1,2,4,5 - tetracarboxypentane tetrachloride, 1,1,2,5,5 - pentacarboxypentane penta-chloride, etc.; aromatic polyacid polyhalides such as mesitoic acid trichloride, trimellitic acid trichloride, hemimellitic acid trichloride, prehnitoic acid tetrachloride, isodurenoic acid tetrachloride, pyromellitic acid tetrachloride, etc.; cycloaliphatic polyacid polychlorides such as the isomeric cyclohexylpolycarbonyl polychlorides, etc. It is also contemplated within the scope of this invention that the corresponding polybromides may also be used, although not necessarily with equivalent results. The aforementioned polyacid polychlorides are contained in a water-immiscible organic solvent, the hydrocarbon solvents which are preferred comprise those having a medium boiling range including aliphatic hydrocarbons such as hexane, heptane, octane, mixed solvents known in the trade as Stoddard's solvent, V.M. and P. naphtha, etc., aromatic hydrocarbons such as benzene, toluene, m-xylene, o-xylene, p-xylene, ethyl benzene, etc., cyclic paraffins such as cyclopentane, methylcyclopentane, etc., or halogenated solvents such as carbon tetrachloride, perchloroethylene, dichlorobenzene, etc.

The mixture of the diamine and polyamine containing more than two amino groups per molecule will preferably contain a predominant proportion of the diamine. This proportion can be varied, although not necessarily with equivalent results as will be hereinafter illustrated in greater detail, although it appears that the polyamine containing more than two amino groups per molecule should be present in an amount of from about 5 to about 25% by weight of the total amine content.

The process of this invention may be effected in any suitable manner and may comprise either a batch or continuous type operation, said process being effected at any suitable temperature from about 0° C. to about 80° C., the preferred range being from about 25° C. to 35° C. When a batch type operation is used, a quantity of the mixture of diamine and at least one polyamine containing more than two amino groups per molecule is placed in an appropriate apparatus such as a dipping vat, pan, tray or trough. The aforementioned mixture of diamine and at least one polyamine of the type hereinbefore set forth in greater detail may be present in an aqueous solution; however, it is also contemplated that other solvents which are immiscible with the second solution may be used, although not necessarily with equivalent results. The mixture of diamine and polyamine is present in an amount ranging from about 0.5% up to about 5% by weight of the total solution, the preferred range being from about 1.5 to about 2.5%. In the preferred embodiment of this invention the solution will also contain a sufficient amount of a basic material such as sodium carbonate, calcium carbonate, potassium carbonate, etc. to neutralize the

acidic constituents which are formed during the interfacial polymerization reaction. In addition, it is preferred that the solution also contain a wetting agent such as a polyoxyalkylated alkyl phenol, one such wetting agent being known in the trade as Triton X-100. The fibrous material is immersed in the aforementioned solution for a sufficient length of time to be thoroughly wetted, said time ranging from about 15 seconds up to about 5 minutes, the preferred time being from about 30 to about 60 seconds. The material is then removed from the bath and excess solution is removed by any conventional means such as by padding, centrifuging, extracting, etc. Following this, the fibrous material is immersed in a second vat, trough, etc. containing a polyacid polychloride in a solvent of the type hereinbefore set forth which is immiscible with the first solution. The polyacid polychloride is present in the solvent in an amount in the range of from about 0.5 to about 5% by weight of the total solution, the preferred range being from about 1.5 to about 2.5%. During this second immersion the polymer thus formed at the interface is grafted to the fibrous material. The contact time for the second immersion is also from about 15 seconds up to about 5 minutes, the preferred time being from about 30 to about 60 seconds. Following the desired immersion time the fabric is removed and treated in a manner similar to that hereinbefore set forth to remove excess solution therefrom. The recovered fabric is then usually washed, dried or subjected to any further treatment which may be desired such as dyeing, etc.

In the preferred embodiment of this invention the treatment of the fibrous material is effected in a continuous manner. One method of effecting this continuous process is to pass the fibrous material through a solution of the diamine and at least one polyamine containing more than two amino groups per molecule. This passage of the fibrous material through the solution may be effected by a continuous immersion through a bath of the solution or by passage of the material through a spraying zone, the immersion or passage through the spraying zone being of a sufficient duration to insure a complete wetting of the fibrous material. The solution of the amines will, as in the batch type process, also contain a sufficient amount of a basic material and a wetting agent. The wetted material is then treated in a manner similar to that hereinbefore set forth to remove excess solution and passed through a second solution or through a spraying zone of the type hereinbefore set forth; that is, a polyacid polychloride in a solvent immiscible with the first solution. Following completion of the contact treatment of the fibrous material with the polyacid polychloride solution, the excess is again removed by conventional means of the type hereinbefore set forth and the material is then recovered.

It is also contemplated within the scope of this invention that the sequence of steps hereinbefore described may be reversed, although not necessarily with equivalent results. For example, the wool may be first contacted with a polyacid polyhalide hydrocarbon solution and thereafter contacted with an aqueous solution of a diamine and a polyamine containing more than two amino groups per molecule.

The following examples are given to illustrate the process of the present invention which, however, are not intended to limit the generally broad scope of the present invention in strict accordance therewith.

Example I

The fabric which was used in this and all subsequent examples was all wool weighing 6.5 ounces per square yard and contained 35 ends and 32 picks. The yarn size was 4.6 run and had 13 twists per square inch. The shrinkage was determined by marking three 25.5 cm. distances in both the warp and filling directions.

In this example a wool fabric which had been marked was passed through a 2% aqueous solution of hexameth-

ylenediamine containing 0.1% Triton X-100 and 4% soda ash during a contact time of 30 seconds at room temperature (25° C.). Following this the wool was padded to remove excess solution and passed into a benzene solution containing 2% sebacoyl chloride. The treated wool was again padded to remove excess solution, washed six times in a standard household automatic washing machine, said washing being for a period of 1 hour using a common household detergent, a wash water temperature of about 50° C. and a rinse with cool water (room temperature) containing a water softener. Following this the wool was ironed to remove wrinkles without stretching, and allowed to dry at atmospheric conditions overnight. The heretofore measured distances were predetermined and the percentage of the area shrinkage was calculated. In this example it was determined that the area shrinkage amounted to 2.8%.

Example II

In this example a piece of wool fabric was treated in the manner similar to that hereinbefore set forth in Example I above. The wool was marked by three 25.5 cm. distances in both the warp and filling direction and thereafter passed through an aqueous solution containing 2% diethylenetriamine as well as 0.1% Triton X-100 and 4% soda ash. After a treatment similar to that set forth in Example I above of the wool including passage through a 2% solution of sebacoyl chloride in benzene, the fabric was washed, ironed and air dried in a similar manner. The shrinkage, as determined by a recalculation of the distances between the marks placed in the wool before treatment, amounted to, in this particular instance, a 4.8% shrinkage or 1.72 times the area shrinkage obtained in Example I above.

Example III

In this example a wool sample measured in the same manner as hereinbefore set forth, was subjected to treatment with a 2% solution of triethylenetetramine containing a wetting agent and a basic material. After completion of the experiment which conformed in all instances to the procedure utilized in Examples I and III above, the percent area shrinkage was again determined. It was determined that the area shrinkage of the wool utilizing this polyamine was 6.3%, or 2.25 times that obtained in Example I.

Example IV

In this example a wool sample was treated in a manner similar to that set forth in the above examples, the amine utilized in this example comprising a 2% solution of tetraethylenepentamine also containing a wetting agent and a basic material. Upon completion of the two-step treatment, the second step utilizing a 2% sebacoyl chloride in benzene, the sample was washed, ironed and dried in a manner similar to that hereinbefore set forth above. The area shrinkage as determined in a similar manner was 6.2% or 2.21 times that found in Example I above.

Example V

In this example a wool sample was treated in a similar manner by passing through an aqueous solution containing 2% of N¹,N³-diisopropyl-diethylenetriamine along with Triton X-100 and soda ash. Upon completion of the identical steps hereinbefore set forth it was determined that the area shrinkage of this sample was 5.5% or 1.97 times that obtained in Example I.

Example VI

A wool sample was treated by passage through an aqueous solution of 2% N¹,N³-di-sec-butyl-diethylenetriamine and also containing a wetting agent and soda ash, following which the sample was treated with a sebacoyl chloride in benzene solution in a manner similar to that hereinbefore set forth. Upon completion of the various

steps hereinbefore set forth in greater detail, it was determined that the area shrinkage of this sample amounted to 7.0% or 2.5 times the shrinkage found in Example I above.

Example VII

In this example a wool sample was treated in a manner similar to that hereinbefore set forth by passage through an aqueous solution containing 2% of ethylenediamine along with 0.1% Triton X-100 and 4% soda ash followed by a treatment with a benzene-sebacoyl chloride solution. Upon completion of the various steps hereinbefore described, the area shrinkage of the same was determined to be 3.7% or 1.32 times the area shrinkage found in Example I.

Example VIII

A wool swatch was marked in a manner similar to that set forth in Example I above and passed through an aqueous solution containing 2% of 1,3-diaminopropane along with the wetting agent and basic compound. Upon completion of the various steps hereinbefore set forth, the area shrinkage of the wool swatch was found to be 3.4% or 1.22 times that found in Example I above.

Example IX

In this example the advantage of utilizing a mixture of a diamine and a polyamine containing more than two groups per molecule was unexpectedly discovered. A wool sample from the same bolt of cloth as used in the above examples was marked in a manner similar to that hereinbefore set forth in Example I above. A mixture of diamines containing 95% hexamethylenediamine and 5% N^1,N^3 -diisopropyl-diethylenetriamine was prepared. This mixture was then used to prepare an aqueous solution containing 2% of the aforesaid mixture as well as 0.1% of Triton X-100 and 4% of soda ash. The aforementioned wool sample was passed through the aqueous solution during a contact time of 30 seconds at room temperature (25° C.). Following this the wool was padded to remove excess solution and passed into a benzene solution containing 2% sebacoyl chloride for a similar contact at similar temperature. The treated wool was again padded to remove excess solution, washed six times in a standard household automatic washing machine, said washing being for a period of 1 hour using a common household detergent, a wash water temperature of about 50° C. and a rinse with cool water (room temperature) containing a water softener. The wool was ironed to remove wrinkles without stretching and allowed to dry at atmospheric conditions over night. The percent of area shrinkage was found to be only 42.8% of the area shrinkage found utilizing hexamethylenediamine without the addition of an amine containing more than two amino groups per molecule and only 30.9% of the area shrinkage was present when utilizing only N^1,N^3 -diisopropyl-diethylenetriamine.

Example X

In this example a mixture of amines was prepared so that the final mixture contained 85% ethylenediamine and 15% tetraethylenepentamine. This mixture was used to make an aqueous solution containing 2% of the amine mixture along with 0.1% of the wetting agent and 4% of the soda ash. A wool sample which was marked in a manner similar to that set forth in Example I above was treated with this aqueous solution for a period of 30 seconds at room temperature, padded to remove excess solution and thereafter treated with a 2% sebacoyl chloride in benzene solution. After removal of the excess solution, washing, ironing and drying, it was determined that the area shrinkage was 35.1% of that obtained when ethylenediamine was used alone and 21% of the area shrinkage found when tetraethylenepentamine was used alone.

Example XI

A mixture of 95% of 1,3-diaminopropane and 5% tetraethylenepentamine was prepared. An aqueous solution containing 2% of this mixture along with a wetting agent and soda ash similar to that hereinbefore set forth was prepared and used to treat a sample of wool which had been heretofore marked in a similar manner. After passage through a second solution containing 2% sebacoyl chloride in benzene, the excess solution was removed, the wool sample was washed, ironed and air dried over night. It was determined that the area shrinkage of this sample was only 41.2% of that utilizing 1,3-diaminopropane alone or 22.6% of that utilizing tetraethylenepentamine alone.

Example XII

In this example a mixture of 85% ethylenediamine, 7.5% tetraethylenepentamine and 7.5% triethylenetetramine was prepared. An aqueous solution containing 2% of said mixture along with 0.1% of a wetting agent and 4% of a basic compound comprising soda ash was utilized to treat a wool sample which had been marked in both the warp and filling directions. The wool was contacted with the aforementioned aqueous solution for a period of 30 seconds at room temperature and thereafter padded to remove excess solution. Following this the wool was passed into a benzene solution containing 2% sebacoyl chloride. The treated wool was again padded to remove excess solution, washed six times in a standard household automatic washing machine. The washing was for a period of 1 hour using a common household detergent, a wash water temperature of about 50° C. and a rinse with cool water (room temperature) which contained a water softener. The wool was then ironed to remove wrinkles without stretching and allowed to dry at atmospheric conditions over night. It was determined that the area shrinkage of this sample amounted to only 37.8% of that found when utilizing ethylenediamine alone, or 22.6% of the area shrinkage when utilizing tetraethylenepentamine alone, and 22.2% of the area shrinkage when using triethylenetetramine alone.

Example XIII

An aqueous solution containing a mixture of 85% ethylenediamine, 7.5% tetraethylenepentamine and 7.5% triethylenetetramine was prepared, said aqueous solution containing 0.1% of a wetting agent and 4% of a basic compound comprising soda ash. A sample of wool which had been marked in both the warp and filling directions at a distance of 25.5 cm. was treated with this mixture by passing the wool through the solution for a period of 30 seconds at room temperature. The wool was padded to remove excess solution and passed through a solution comprising Stoddard's solvent containing 2% by weight of mesitoic acid trichloride. The excess solution was removed by padding and the wool sample subjected to the aforementioned steps of washing, ironing and air drying. When remeasuring the previously marked sample in both the warp and filling directions it was determined that negligible shrinkage had taken place.

Example XIV

A wool sample marked in a manner similar to that hereinbefore set forth was treated with an aqueous solution which contained a mixture of 85% ethylenediamine, 7.5% tetraethylenepentamine and 7.5% triethylenetetramine, said mixture of amines being present in an amount of 2% by weight of the total solution. In addition, the aqueous solution also contained 0.1% of a wetting agent comprising Triton X-100 and 4% of soda ash. After contact with the aqueous solution the wool was padded and contacted with a second solution containing 2% trimellitic acid trichloride in Stoddard's solvent. After completion of the washing, ironing and air drying steps the wool sample was remeasured. The remeasurement of the sample of

both the warp and filling directions disclosed that negligible shrinkage had taken place.

Example XV

Additional examples were run utilizing a process similar to that hereinbefore set forth. The results of these examples utilizing various percentages of amines containing more than two amino groups per molecule in combination with a diamine are set forth in Table I below.

TABLE I

Amine Composition	Percent Area Shrinkage Compared to—	
	Diamine	Polyamine
90% hexamethylenediamine plus 10% diethylenetriamine.....	60.7	35.4
90% hexamethylenediamine plus 10% N ¹ , N ³ -diisopropyl-diethylenetetramine.....	71.4	36.3
95% hexamethylenediamine plus 5% N ¹ , N ³ -di-sec-butyl-diethylenetriamine.....	67.9	27.2
90% hexamethylenediamine plus 10% N ¹ , N ³ -di-sec-butyl-diethylenetriamine.....	75	30
95% hexamethylenediamine plus 5% tetraethylenepentamine.....	42.9	19.4
90% hexamethylenediamine plus 10% tetraethylenepentamine.....	53.6	26.2
95% ethylenediamine plus 5% tetraethylenepentamine.....	43.3	25.8
90% ethylenediamine plus 10% tetraethylenepentamine.....	37.8	22.2
95% ethylenediamine plus 5% triethylenetetramine.....	48.6	28.6
90% ethylenediamine plus 10% triethylenetetramine.....	40.6	23.8
90% 1,3-diaminopropane plus 10% tetraethylenepentamine.....	53	29
95% 1,3-diaminopropane plus 5% triethylenetetramine.....	53	28.6

Example XVI

To an impartial panel of five people expert in comparing the various properties of wool by manual manipulation was submitted unidentified samples of the various treated wool swatches for their examination. The panel graded the wools in order of preference, 1 being the higher degree of order, 2 next, etc. A summation of the order will be referred to as preference value. The following table illustrates the results obtained.

TABLE II

Amine system:	Preference value
Ethylenediamine containing 15% tetraethylene pentamine	15
Ethylenediamine containing 10% trimethylene tetramine	16
Hexamethylenediamine containing 5% N ¹ , N ³ -diisopropyl-diethylenetriamine	22
Hexamethylenediamine	29

It is noted that the swatch treated with ethylenediamine containing 15% tetraethylenepentamine received a preference value of 15, the swatch treated with ethylenediamine containing 10% triethylenetetramine received a preference value of 16, the swatch treated with hexamethylenediamine containing 5% N¹, N³-diisopropyl-diethylenetriamine received a preference value of 22 and the swatch treated with hexamethylenediamine alone received a preference value of 29. In all cases examined by the panel similar results were always obtained, the diamine alone always being least preferred while the systems where the fabric was treated with a diamine containing a polyamine having more than two amino groups being always preferred.

We claim as our invention:

1. A process for the treatment of a fibrous material which comprises contacting said fibrous material with one solution selected from the group consisting of a solution containing at least one diamine and at least one polyamine containing more than two amino groups per molecule, said polyamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and a solution containing a polyacid polyhalide containing at least two acid halide

groups per molecule, said solutions being mutually immiscible, and thereafter contacting said fibrous material with the other of said solutions.

2. A process for the treatment of a wool which comprises contacting said wool with one solution selected from the group consisting of a solution containing at least one diamine and at least one polyamine containing more than two amino groups per molecule, said polyamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and a solution containing a polyacid polyhalide containing at least two acid halide groups per molecule, said solutions being mutually immiscible, and thereafter contacting said wool with the other of said solutions.

3. A process for the treatment of a fibrous material which comprises contacting said fibrous material with a first solution containing at least one diamine and at least one polyamine containing more than two amino groups per molecule, said polyamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said fibrous material with a second solution containing a polyacid polyhalide containing at least two acid halide groups per molecule, said second solution being immiscible with said first solution.

4. A process for the treatment of a wool which comprises contacting said wool with a first solution containing at least one diamine and at least one polyamine containing more than two amino groups per molecule, said polyamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a second solution containing a polyacid polyhalide containing at least two acid halide groups per molecule, said second solution being immiscible with said first solution.

5. A process for the treatment of wool which comprises contacting said wool with a first solution containing ethylenediamine and at least one polyamine containing more than two amino groups per molecule, said polyamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a second solution containing a polyacid polyhalide containing at least two acid halide groups per molecule, said second solution being immiscible with said first solution.

6. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing ethylenediamine and tetraethylenepentamine, said pentamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a water-immiscible organic solution containing a polyacid polyhalide containing at least two acid halide groups per molecule.

7. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing 1,3-diaminopropane and triethylenetetramine, said tetramine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a water-immiscible organic solution containing a polyacid polyhalide containing at least two acid halide groups per molecule.

8. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing hexamethylenediamine and tetraethylenepentamine, said pentamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a water-immiscible organic solution containing a polyacid polyhalide containing at least two acid halide groups per molecule.

9. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing hexamethylenediamine and N¹, N³-diisopropyl-di-

ethylenetriamine, said triamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a water-immiscible organic solution containing a polyacid polyhalide containing at least two acid halide groups per molecule.

10. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing ethylenediamine, tetraethylenepentamine and triethylenetetramine, said pentamine and tetramine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a water-immiscible organic solution containing a polyacid polyhalide containing at least two acid halide groups per molecule.

11. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing ethylenediamine and tetraethylenepentamine, said pentamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a hydrocarbon solution of a polyacid polychloride containing at least two acid chloride groups per molecule.

12. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing 1,3-diaminopropane and triethylenetetramine, said tetramine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a hydrocarbon solution containing a polyacid polychloride containing at least two acid chloride groups per molecule.

13. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing hexamethylenediamine and tetraethylenepentamine, said pentamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a hydrocarbon solution containing a polyacid polychloride containing at least two acid chloride groups per molecule.

14. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing hexamethylenediamine and N¹,N³-diisopropyl-diethylenetriamine, said triamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a hydrocarbon solution containing a polyacid polychloride containing at least two acid chloride groups per molecule.

15. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing ethylenediamine, tetraethylenepentamine and triethylenetetramine, said pentamine and tetramine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and

thereafter contacting said wool with a hydrocarbon solution containing a polyacid polychloride containing at least two acid chloride groups per molecule.

16. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing ethylenediamine and tetraethylenepentamine, said pentamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a hydrocarbon solution of sebacyl chloride.

17. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing 1,3-diaminopropane and triethylenetetramine, said tetramine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a hydrocarbon solution containing sebacyl chloride.

18. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing hexamethylenediamine and tetraethylenepentamine, said pentamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a hydrocarbon solution containing sebacyl chloride.

19. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing hexamethylenediamine and N¹,N³-diisopropyl-diethylenetriamine, said triamine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a hydrocarbon solution containing sebacyl chloride.

20. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing ethylenediamine, tetraethylenepentamine and triethylenetetramine, said pentamine and tetramine being present in an amount of from about 5% to about 25% by weight of the total amine content of said solution, and thereafter contacting said wool with a hydrocarbon solution containing sebacyl chloride.

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