United States Patent Office 3,305,391 Patented Feb. 21, 1967

3,305,391

TREATMENT OF FIBROUS MATERIALS WITH CERTAIN AMINO COMPOUNDS AND CERTAIN POLYACID POLYHALIDES

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No Drawing. Filed Dec. 12, 1963, Ser. No. 329,965
19 Claims. (Cl. 117—141)

This invention relates to a process for the treatment of fibrous materials and particularly to a process for the treatment of wool. More specifically the invention is concerned with improvements in the properties of fibrous materials such as wool by an interfacial polymerization reaction utilizing a particular type of an amino compound as one of the reactants whereby an improved material is obtained having anti-bacterial, anti-fungal and insecticidal properties and in addition is stabilized against dimensional changes.

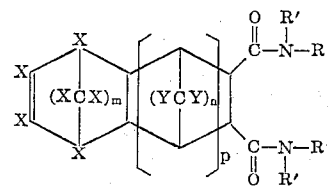
In regard to the present improvement in the dimensional stability of fibrous material the problem of shrinkage in certain fibers or fabrics, and particularly wool, was heretofore present when such fibers or fabrics underwent cleaning operations and particularly washing. One theory which accounts for 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, none of which, however, also simultaneously imparts other desirable properties such as anti-fungal, anti-bacterial and insecticidal properties. All of these prior art methods in addition to being devoid of the aforesaid property inducting characteristics also 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. One method of treating these fabrics and, as hereinbefore set forth, particularly wool, is passing said fabric through an aqueous solution of a diamino compound, removing the excess solution by padding, centrifuging, vacuum extraction, etc. and thereafter passing the material through a polyacid polyhalide and particularly a polyacid polychloride containing at least two acid chloride groups per molecule 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 fibrous

materials, and particularly wool, may be treated in a similar manner with a specific type of an amino compound which is hereinafter set forth in greater detail whereby the treated material will not only possess the desirable physical characteristics hereinbefore set forth but will also possess anti-fungal, anti-bacterial and insecticidal properties, the latter properties being due to the particular structure of the amino compound which is utilized for the interfacial polymerization process. This combination of desirable characteristics will allow the use of the treated materials in certain instances and places which heretofore have required the material to undergo more than one treating to effect the desired results or will not allow the material to be used in certain instances which required that the material be both shrink-proof and insecticidal.

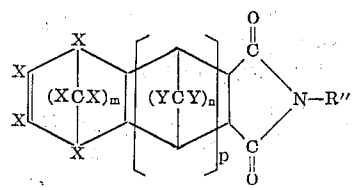
It is therefore an object of this invention to provide a process for treating fibrous materials to impart desirable physical characteristics thereto.

Another object of this invention is to provide a process for the treatment of fabrics, and particularly wool, by utilizing a particular type of a compound whereby the treated fabric will be less susceptible to shrinkage and will possess other desirable physical characteristics.

Taken in its broadest aspect, one embodiment of this invention resides 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 an amino compound selected from the group consisting of



and



in which R is selected from the group consisting of alkylamine, alkylenepolyamine, polyalkylenepolyamine, arylamine, arylenepolyamine, polyarylenepolyamine, cycloalkylamine, cycloalkylenepolyamine and polycycloalkylenepolyamine radicals, R′ is selected from the group consisting of hydrogen, alkyl, aryl and cycloalkyl radicals, R″ is selected from the group consisting of alkylenepolyamine, polyalkylenepolyamine, arylenepolyamine, polyarylenepolyamine, cycloalkylenepolyamine and polycycloalkylenepolyamine radicals, X and Y are selected from the group consisting of hydrogen and halogen radicals, at least two X's being halogen, *m* is an integer of from one to two, *n* ranges from zero to two and *p* ranges from zero to one, 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.

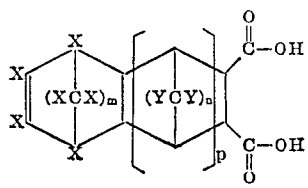
A further embodiment of this invention is found in a process for the treatment of wool which comprises contacting said wool with an aqueous solution containing an amino compound comprising the diethylenediamino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro - 5,8-methano-2,3-naphthalenedicarboxylic acid, 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 an amino compound comprising the tetraethylenetetramino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano - 2,3 - naphthalenedicarboxylic acid, and thereafter contacting said wool with a hydrocarbon solution of a polyacid polychloride containing at least two acid chloride groups per molecule.

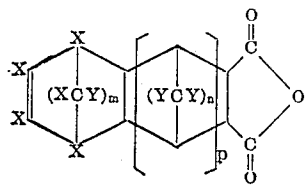
A more specific embodiment of this invention resides in a process for the treatment of wool which comprises contacting said wool with an aqueous solution containing an amino compound comprising the diethylenediamino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro - 5,8-methano-2,3-naphthalenedicarboxylic acid and thereafter contacting said wool with a hydrocarbon solution 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 fibrous material, and particularly wool may be treated with an amino compound and specifically a compound selected from the group consisting of the amino-amides and amino-imides of a polyhalopolyhydropolycyclicdicarboxylic acid, both of which contain at least two reactive amino groups per molecule, and thereafter further contacting the fibrous material with a polyacid polyhalide containing at least two acid halide groups per molecule whereby an interfacial polymerization process is effected with the result that the treated fibrous material possesses an excellent resistance to shrinking as well as possessing anti-bacterial, anti-fungal and insecticidal properties. The particular amino-amide or polyamino-imide is prepared by condensing a polyhalopolyhydropolycyclicdicarboxylic acid or anhydride thereof with an amino compound. Any suitable polyhalopolyhydropolycyclicdicarboxylic acid or anhydride thereof may be used in the preparation of the desired compound, said acid or anhydride thereof being illustrated by the following general formulas:

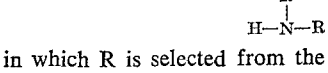


and



in which X is selected from the group consisting of halogen and particularly chlorine and/or bromine, and hydrogen radicals, at least two of the X's being halogen, Y is also selected from the group consisting of halogen and hydrogen radicals, *m* is an integer of from one to two, *n* ranges from zero to two and *p* ranges from zero to one. Representative examples of the polyhalopolyhydropolycyclicdicarboxylic acids or anhydrides thereof which may be utilized include 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid or the anhydride thereof which may be prepared by condensing maleic acid or maleic anhydride with hexachlorocyclopentadiene. Another example of the acid or anhydride which may be used comprises 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3 - naphthalenedicarboxylic acid which is prepared by condensing a conjugated aliphatic diene such as 1,3-butadiene with maleic acid and thereafter further condensing the resultant cyclohexenedicarboxylic acid, which is 1,2,3,6-tetrahydrophthalic acid, with a halocycloalkadiene such as hexachlorocyclopentadiene to form the desired product. It is to be understood that the corresponding anhydride may be prepared by utilizing maleic anhydride as one of the starting materials in place of maleic acid. Yet another example of a polyhalopolyhydropolycyclicdicarboxylic acid or anhydride which may be used is one which is prepared by condensing cyclopentadiene with maleic acid or maleic anhydride to form norborn-5-ene-2,3-dicarboxylic acid or anhydride and thereafter condensing this product with hexachlorocyclopentadiene to form 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethano-2,3-naphthalenedicarboxylic acid or anhydride. It is to be understood that other starting materials may also be utilized to form similar acids or anhydrides. Illustrative examples of these starting materials include other acids such as fumaric acid, itaconic acid, citraconic acid, glutaconic acid, etc.; conjugated aliphatic dienes include 2-methyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 2,4-hexadiene, 2,3-dimethyl-1,3-butadiene, 1,3-heptadiene, 2,4-heptadiene; conjugated octadienes, nonadienes, etc.; other suitable halo substituted cycloalkadienes which may be used include 1,2-dichlorocyclopentadiene, 1,2,3-trichlorocyclopentadiene, 1,2,3,4-tetrachlorocyclopentadiene, 1,2,3,4,5 - pentachlorocyclopentadiene and similar compounds in which all or part of the chlorine is replaced by other halogen atoms and particularly bromine.

The particular amino compounds which may be condensed with the aforementioned polyhalopolyhydropolycyclicdicarboxylic acid or anhydride thereof will possess the generic formula:



in which R is selected from the group consisting of hydrogen, alkylamine, alkylenepolyamine, polyalkylenepolyamine, arylamine, arylenepolyamine, polyarylenepolyamine, cycloalkylamine, cycloalkylenepolyamine, and polycycloalkylenepolyamine radicals.

Specific examples of amino compounds which may be condensed with the aforementioned polyhalopolyhydropolycyclicdicarboxylic acids or anhydrides thereof include alkylenepolyamines such as ethylenediamine, propylenediamine, butylenediamine, pentylenediamine, hexylenediamine, etc., N-alkyl substituted diamino alkanes such as N-methyldiaminoethane, N-ethyldiaminoethane, N-methyl-1,3-diaminopropane, N-ethyl-1,3-diaminopropane, other N-alkyl-1,3-diaminopropanes in which the alkyl group may contain carbon atoms ranging from 3 up to about 20 carbon atoms and thus the alkyl group is selected from propyl hexyl, heptyl, octyl, decyl, tridecyl, pentadecyl, eicosyl radicals, etc. In addition, other N-alkyl diaminoalkanes such as the N-alkyl-1,4-diaminobutanes, N-alkyl - 1,2 - diaminopentanes, N-alkyl-1,5-diaminopentanes, N-alkyl-1,6-diaminohexanes, etc. may also be used.

Other amine compounds which may be used include polyalkylenepolyamines and N substituted derivatives thereof including

diethylenetriamine,
dipropylenetriamine,
dibutylenetriamine,
dipentylenetriamine,
dihexylenetriamine,
diheptylenetriamine,
dioctylenetriamine, etc.,

triethylenetetramine,
tripropylenetetramine,
tributylenetetramine,
tripentylenetetramine,
trihexylenetetramine,
triheptylenetetramine,
trioctylenetetramine, etc.,
tetraethylenepentamine,
tetrapropylenepentamine,
tetrapentylenepentamine,
tetrahexylenepentamine,
tetraheptylenepentamine, etc.,
pentaethylenehexamine,
pentapropylenehexamine,
pentabutylenehexamine,
pentapentahexamine, etc.,
N^1,N^3-dimethyldiethylenetriamine,
N^1,N^3-diethyldiethylenetriamine,
N^1,N^3-dipropyldiethylenetriamine,
N^1,N^3-di-sec-butyldiethylenetriamine,
N^1,N^3-dimethyldipropylenetriamine,
N^1,N^3-diethyldibutylenetriamine,
N^1,N^3-di-sec-butyldibutylenetriamine, etc.

Aromatic amines which may be used include polyarylenepolyamines such as diaminodiphenylamine, aminodinaphthylamine, diaminodinaphthylamine. It is to be understood that in the polyamino aromatic compounds the nitrogen atoms may be in a position ortho-, meta- or para- to each other. It may, if so desired, also contain an alkyl group attached to one or both nitrogen atoms, the alkyl groups containing from 1 to 20 or more carbon atoms each. Illustrative compounds include

p,p'-di-methylaminodiphenylamine,
p,p'-di-ethylaminodiphenylamine,
p,p'-di-propylaminodiphenylamine,
p,p'-dibutylaminodiphenylamine,
p,p'-di-amylaminodiphenylamine,
p,p'-di-hexylaminodiphenylamine,
p,p'-di-heptylaminodiphenylamine,
p,p'-di-octylaminodiphenylamine, etc.;
o,p'-di-methyldiphenylamine,
o,p'-di-ethyldiphenylamine,
o,p'-di-propyldiphenylamine,
o,p'-di-butyldiphenylamine, etc.

It is also contemplated within the scope of this invention that cycloalkylpolyamines and polycycloalkylenepolyamines such as 1,2-diaminocyclohexane, 1,3-diaminocyclohexane, 1,4 - diaminocyclohexane, 1,2,4 - triaminocyclohexane, 1,2,5-triaminocyclohexane, N,N'-dimethyl-1,2 - diaminocyclohexane, N,N' - dimethyl-1,4-diaminocyclohexane, etc.; dicyclopentylenetriamine, dicyclohexylenetriamine, tricyclopentylenetetramine, tricyclohexylenetetramine, etc., as well as the N-alkylated derivatives thereof may also be used. It is to be understood that the aforementioned amine compounds are only representatives of the class of compounds falling within the generic formula hereinbefore set forth, and that the present invention is not necessarily limited thereto.

It is also contemplated within the scope of this invention that N-alkyl-1,3-diaminopropanes in which the alkyl group contains from about 8 to about 25 carbon atoms of which a number of the class are commercially available may also be utilized although not necessarily with equivalent results. For example, certain amine compounds known as "Duomeen T" "Diam 26" in which the alkyl group is derived from tallow and contains from about 12 to about 20 carbon atoms per group and mostly 16 to 18 carbon atoms per group may be utilized as the amine starting material in the present invention.

The reaction of the acid or anhydride with the amino compound is effected in any suitable manner depending upon the particular acid or anhydride and the particular amine which are to be condensed. For example, when an amino-imide is the desired product the amino compound which is used will have to contain at least one primary amino group and at least two other amino groups while if an amino-amide is the desired product the particular amino compound may contain two or more secondary amino groups. The reaction conditions for the condensation of the acid or anhydride and the amine will again depend upon the particular reactants which are undergoing condensation and whether or not the reaction is effected in the presence of a substantially inert organic solvent such as benzene, toluene, the xylenes, n-pentane, n-hexane, n-heptane, etc.; the reaction temperature usually being in a range of from about 50° up to about 250° C. or more and the reaction pressure ranging from atmospheric up to about 50 atmospheres or more, said pressure being sufficient to maintain a major portion of the reactants in the liquid phase. For example, if the condensation is effected in the presence of a benzene solvent, the reaction will usually be effected at the reflux temperature, i.e. about 85° C. while the use of a toluene as a solvent will enable the reaction to be effected at temperatures of about 115° C. It is also contemplated within the scope of this invention that if an amino-amide of the particular acid is desired, the acid or anhydride thereof may be first esterified by treating said acid or anhydride with a lower alkyl alcohol such as methyl alcohol, ethyl alcohol, propyl alcohol, etc. until esterification has occurred. The ester is then condensed with the particular amino compound to form the desired amino-amide of the acid. In addition, the reactants are usually present in a mole ratio of from about 2 to about 10 moles of amine compound per mole of acid or anhydride. The reaction time will be sufficient to effect substantially complete reaction and may vary from about 0.5 up to about 12 hours or more, the reaction being substantially complete when the theoretical amount of water or alcohol which is formed has been removed.

Following the completion of the reaction, the solvent, if any has been used, is removed in any suitable manner including distillation under atmospheric or subatmospheric pressure following which the excess amine compound is removed by any suitable means including distillation under reduced pressure and the desired reaction product is recovered. If desired, the amino-amide or amino-imide containing excess amine may be used without further purification.

Examples of amino-amides or amino-imides of polyhalopolyhydropolycyclicdicarboxylic acids which may be used in the process of the present invention to treat fibrous materials include the diethylenediamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8 - methano-2,3-naphthalenedicarboxylic acid, the diethylenediamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethano-2,3-naphthalenedicarboxylic acid, the diethylenediamino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3 - naphthalenedicarboxylic acid, the diethylenediamino imide of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a - octahydro - 1,4,5,8-dimethano-2,3-naphthalenedicarboxylic acid, the tetraethylenetetramino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano - 2,3 - naphthalenedicarboxylic acid, the tetraethylenetetramino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a - octahydro - 1,4,5,8-dimethano-2,3-naphthalenedicarboxylic acid, the tetraethylenetetramino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano - 2,3 - naphthalenedicarboxylic acid, the tetraethylenetetramino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a - octahydro - 1,4,5,8-dimethano-2,3-naphthalenedicarboxylic acid, the di-sec-butyldiethylenediamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3 - naphthalenedicarboxylic acid, the di-sec-butyldiethyllenediamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethano-2,3 - naphthalenedicarboxylic acid,

the hexaethylenehexamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a - octahydro - 5,8 - methano - 2,3-naphthalenedicarboxylic acid, the hexaethylenehexamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethano-2,3-naphthalenedicarboxylic acid, the propyleneamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3 - naphthalenedicarboxylic acid, the propyleneamino amide of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a - octahydro - 1,4,5,8, - dimethano-2,3-naphthalenedicarboxylic acid, the diphenyldiamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid, the diphenyldiamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethano-2,3 - naphthalenedicarboxylic acid, the cyclohexyleneamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a - octahydro - 5,8-methano-2,3-naphthalenedicarboxylic acid, the cyclohexyleneamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethano-2,3 - naphthalenedicarboxylic acid, the pentaethylenepentamino amide of 1,4,5,6,7,7-hexachlorobicyclo[2.2.1] - 5 - heptene - 2,3 - dicarboxylic acid, the pentaethylenepentamine imide of 1,4,5,6,7,7-hexachlorobicyclo - [2.2.1]-5-heptene - 2,3 - dicarboxylic acid, the hexaethylenehexamino amide of 1,4,5,6,7,7-hexachlorobicyclo[2.2.1] - 5 - heptene - 2,3 - dicarboxylic acid, the hexaethylenehexamino imide of 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-2,3 - dicarboxylic acid, etc. It is to be understood that the aforementioned amino-amides and amino-imides of the various polyhalopolyhydropolycyclicidicarboxylic acids are only representatives of the class of compounds which may be used and that the present invention is not necessarily limited thereto.

The treatment of the fibrous material and particularly wool for retarding shrinkage thereof as well as endowing the material with anti-bacterial, anti-fungal and insecticidal properties may be effected with improved results by treating the fabric with a solution of an amino compound of the type hereinbefore set forth in greater detail and thereafter treating the fabric with a solution of polyacid polyhalide containing at least two acid halide groups per molecule, the solutions being mutually immiscible. Examples of polyacid polyhalides and preferably polyacid polychlorides 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 isocinchomeronic 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-tetracarboxybutanetetrachloride, 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 pentachloride, 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 cyclohexypolycarbonyl 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 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 an amide or imide of a polyhalopolyhydropolycyclicdicarboxylic acid is placed in an appropriate apparatus such as a dipping vat, pan, tray or trough. The aforementioned amide or imide of a polyhalopolyhydropolycyclicdicarboxylic acid 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. It is further contemplated that the solution containing the aforementioned amide or imide of a polyhalopolyhydropolycyclicdicarboxylic acid may also contain other polyamino compounds as reactive diluents or reactive solvents. The amide or imide of a polyhalopolyhydropolycyclicdicarboxylic acid 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 a quantity of an amide or imide of a polyhalopolyhydropolycyclicdicarboxylic acid. 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 amide or imide

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 necessariry 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 the aforementioned amide or imide of a polyhalopolyhydropolycyclicdicarboxylic acid.

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

In this example an imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4*a*,5,8,8*a* - octahydro - 5,8-methano - 2,3 - naphthalenedicarboxylic acid was prepared by charging 206 grams (2.0 mole) of diethylenetriamine to a reaction flask provided with a Dean-Stark adapter and stirring means. The flask was immersed in an ice bath and the temperature of the diethylenetriamine was lowered to about 3° C. While maintaining the flask and contents thereof at this temperature there was added 85 grams (0.2 mole) of 5,6,7,8,9,9 - hexachloro - 1,2,3,4,4a,5,8,8a - octahydro-5,8-methano-2,3-naphthalenedicarboxylic anhydride during a period of 15 minutes. During the addition of the anhydride the immediate reaction was exothermic in nature, the well temperature reaching 15° C. Upon completion of the addition, the reaction mixture was allowed to reach room temperature at which time the mixture was an amber-colored viscous slurry containing undissolved anhydride. The slurry was heated for a period of about three hours to a temperature of 178° C. during which time all of the anhydride dissolved forming a dark solution. The reaction was considered complete when 4 cc. of water was collected in the Dean-Stark adapter. At the end of this time the solution was allowed to cool to room temperature, the solution at room temperature being a very viscous oil.

The diethylenediamino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a - octahydro - 5,8 - methano - 2,3 - naphthalenedicarboxylic acid was used without isolation to treat a wool fabric which weighed 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. The woolen fabric was immersed for 30 seconds at room temperature (about 25° C.) in an aqueous solution containing 2% of the solution containing diethylenediamino imide of 5,6,7,8,9,9 - hexachloro - 1,2,3,4,4a,5,8,8a - octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid plus 4% of sodium carbonate and 0.1% of a wetting agent comprising Triton X–100. At the end of this time the excess solution was expressed by padding the fabric, following which the fabric was next immersed for 30 seconds at room temperature in a benzene solution containing 2% sebacoyl chloride. The excess solution was again expressed by padding and washed six times in a standard household automatic washing machine, said washing being for a period of one 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, spun dried and finally air dried over night. The percent of area shrinkage was calculated to be 4.7% and the weight uptake of polymer was found to be 1.8%. In addition, the treated fabric was found to contain organic bound chlorine. The treated fabric, when exposed to various species of bacteria and fungi, did not support their growth nor did carpet beetles or moths deposit their larvae.

Example II

A reaction flask which is provided with stirring means is immersed in an ice bath and 103 grams (1.0 mole) of diethylenetriamine is added thereto. Following this 47 grams (0.1 mole) of the dimethyl ester of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a - octahydro - 5,8 - methano-2,3-naphthalenedicarboxylic acid which has been prepared by reacting methyl alcohol with 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a - octahydro - 5,8 - methano - 2,3-naphthalenedicarboxylic anhydride in the presence of an acid catalyst is slowly added thereto during a period of about 15 minutes. The flask containing the reaction mixture is removed from the ice bath and allowed to warm to room temperature. The mixture is then heated to a temperature of about 175° C. and maintained thereat for a period of about three hours. At the end of this time the flask and contents thereof are allowed to cool to room temperature, the excess diethylenetriamine is removed by distillation and the desired product comprising the diethylenediamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3-napthalenedicarboxylic acid is recovered. A piece of wool fabric which is marked in a manner similar to that hereinbefore set forth, that is, by marking three 25.5 cm. distances in both the warp and filling direction, is passed through an aqueous solution containing 2% of a solution comprising a mixture of the diethylenediaminoamide of 5,6,7,8,9,9-hexacholoro-1,2,3,4,4a,5,8,8a - octahydro - 5,8-methano - 2,3 - naphthalenedicarboxylic acid dissolved in hexamethylenediamine as well as 0.1% of Triton X–100 and 4% soda ash. The excess solution is expressed by padding and the wool is passed through a benzene solution containing 2% sebacoyl chloride for a period of about 30 seconds. The fabric is then padded to remove excess solution, washed six times in a standard household automatic washing machine for a period of one hour using a common household detergent, a wash water temperature of about 50° C. and a rinse with cool water containing a water softener. The wool is dried in a manner similar to that hereinabove set forth, that is, at atmospheric conditions over night. The percent of area shrinkage is found to be approximately the same as that set forth in Example I above with a corresponding percentage of polymer uptake and chlorine percentage. The treated fabric is found to exhibit similar anti-bacterial, anti-fungal and insecticidal properties as set forth in Example I.

Example III

In this example the dimethyl ester of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a - octahydro - 5,8 - methano - 2,3-naphthalenedicarboxylic acid is prepared in a manner similar to that set forth in Example II, that is, by treating the corresponding anhydride with methyl alcohol in the presence of an acid catalyst. The reaction vessel is charged with 189 grams (1.0 mole) of tetraethylenepentamine along with 150 cc. of benzene. The system is refluxed at a temperature of about 85° C. to remove any water which may be present, following which 47 grams (0.1 mole) of the dimethyl ester of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a - octahydro - 5,8 - methano - 2,3-naphthalenedicarboxylic acid is slowly added during a period of about one hour. The mixture is again heated to reflux and maintained thereat for a period of about three hours. At the end of this time the reaction mixture is allowed to cool to room temperature and the desired product comprising the tetraethylenetetramino amide of

5,6,7,8,9,9 - hexachloro - 1,2,3,4,4a,5,8,8a - octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid is recovered.

A piece of wool fabric which is marked in a manner similar to that set forth in Example I above is treated by contacting said wool for a period of about 30 seconds at room temperature with an aqueous solution containing 2% by weight of a solution comprising tetraethylenetetraamino amide of 5,6,7,8,9,9 - hexachloro - 1,2,3,4,4a,5,8,8a-octahydro - 5,8-methano-2,3-naphthalenedicarboxylic acid dissolved in propylenediamine along with 0.1% Triton X–100 and 4% soda ash. The excess solution is expressed by paddling and the wool is thereafter contacted for a similar period of time at a similar temperature with a benzene solution containing 2% sebacoyl chloride. The excess solution is again expressed by padding and the fabric washed for a period of one hour in an automatic washing machine using a common household detergent, the temperature of the wash water being about 50° C. The fabric is rinsed with cold water containing a water softener and allowed to dry overnight at atmospheric conditions. The percentage of area shrinkage will be determined to be approximately the same as that found in the wool sample of Example I, with a similar weight uptake of polymer and chlorine content. The treated fabric will exhibit similar anti-bacterial, anti-fungal and insecticidal properties as set forth in Example I.

Example IV

To a reaction flask fitted with a Dean-Stark adapter and stirring means is charged 189 grams (1.0 mole) of tetraethylenepentamine and 150 cc. of benzene. The system is refluxed to remove any water which may be present following which 47 grams (0.1 mole) of 5,6,7,8,9,9 - hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3-naphthalenedicarboxylic anhydride is slowly added during a period of about one hour. The mixture is maintained at reflux for a period of about four hours during which time the theoretical amount of water is collected. The reaction mixture is then allowed to cool to room temperature, the benzene is removed as well as the excess tetraethylenepentamine and the desired product comprising the tetraethylenetetramino imide of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a - octahydro - 5,8 - methano-2.3-naphthalenedicarboxylic acid is recovered.

A wool sample similar in nature to that set forth in Example I above and marked in a similar manner is treated by contacting the wool with an aqueous solution containing a 2% solution of tetraethylenetetramino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid dissolved in hexamethylenediamine along with 0.1% Triton X–100 and 4% soda ash, said contact time being for a period of about 30 seconds at room temperature. The excess solution is expressed by padding and the fabric contacted for a period of 30 seconds at room temperature with a benzene solution containing 2% sebacoyl chloride. The excess solution is again expressed by padding and the wool sample is washed for a period of about one hour in an automatic washing machine using a wash water of about 50° C. The sample is then rinsed with cool water, dried and examined for area shrinkage. The percent of area shrinkage will be approximately the same as that set forth in Example I above with a corresponding weight uptake of polymer and a corresponding chlorine weight content. The treated fabric will exhibit similar antibacterial, anti-fungal and insecticidal properties as set forth in Example I.

Example V

To a reaction flask fitted with stirring means and a nitrogen well was charged 201 grams (0.1 mole) of di-sec-butyldiethylenetriamine. The flask was then immersed in an ice bath to lower the temperature of the amine to about 3° C. Following this 42 grams (0.1 mole) of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro - 5,8-methano-2,3-naphthalenedicarboxylic anhydride was slowly added during a period of about 15 minutes. The reaction was exothermic in nature, the well temperature reaching approximately 15° C. The reaction mixture was allowed to reach room temperature and thereafter was heated to a temperature of about 210° C. for a period of one-half hour. The mixture was allowed to cool to room temperature and the excess amine removed by distillation. The reaction product which comprised the di-sec-butyldiethylenediamino amide of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a - octahydro - 5,8-methano-2,3-naphthalenedicarboxylic acid was recovered and an aqueous solution prepared which contained 2% of a solution comprising this amide dissolved in hexamethylenediamine along with 0.1% Triton X–100 and 4% soda ash.

A wool sample of a similar nature and similar markings to that used in Example I above is contacted with 30 seconds at room temperature with the above aqueous amide solution. The excess solution is expressed by padding and the wool fabric is then contacted with a benzene solution containing 2% sebacoyl chloride. The excess solution is again removed by padding and the fabric treated in a manner similar to that hereinbefore set forth, that is, by washing, rinsing and drying. The percentage of area shrinkage will compare to that set forth in Example I above as will the weight uptake of polymer and the chlorine content of the fabric. The treated fabric will exhibit similar antibacterial, anti-fungal and insecticidal properties as set forth in Example I.

Example VI

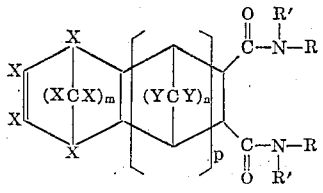
In this example the dimethyl ester of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a - octahydro-1,4,5,8-dimethano-2,3-naphthalenedicarboxylic acid is prepared in a manner similar to that set forth in Example II. The reaction vessel was charged with 41.2 grams of diethylenetriamine along with 200 cc. of benzene. The system was refluxed at a temperature of 83° C. while 48.3 grams of the aforementioned dimethyl ester was added during a period of 5 minutes. The solid ester readily dissolved in the solution. Upon cooling to room temperature a small amount of solids formed and were removed by filtration. Following this the benzene solvent and excess diethylenetriamine were removed by distillation. The taffy-like residue slowly crystallized and was identified as the diethylenediamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a - octahydro-1,4,5,8-dimethano-2,3-naphthalenedicarboxylic acid.

A piece of wool fabric which is marked in a manner similar to that set forth in Example I above is treated by contacting said wool for a period of about 30 seconds at room temperature with an aqueous solution containing 2% by weight of a solution comprising diethylenediamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro - 1,4,5,8 - dimethano-2,3-naphthalenedicarboxylic acid dissolved in propylenediamine along with 0.1% Triton X–100 and 4% soda ash. The excess solution is expressed by padding and the wool is thereafter contacted for a similar period of time at a similar temperature with a benzene solution containing 2% sebacoyl chloride. The excess solution is again expressed by padding and the fabric is washed for a period of 1 hour in an automatic washing machine using a common household detergent, the temperature of the wash water being about 50° C. The fabric is rinsed with cold water containing a water softener and allowed to dry overnight at atmospheric conditions. The percentage of area shrinkage will be determined to be approximately the same as that found in the wool sample of Example I, with a similar weight uptake of polymer and chlorine content. The treated fabric will exhibit similar anti-bacterial, anti-fungal and insecticidal properties as set forth in Example I.

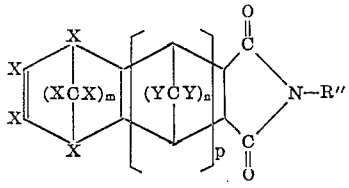
We claim as our invention:

1. A process for the treatment of a fibrous material which comprises successively contacting said fibrous mate-

rial with two mutually immiscible solutions, one of said solutions contains an amino compound selected from the group consisting of



and



in which R is selected from the group consisting of alkylamine, alkylenepolyamine, polyalkylenepolyamine, arylamine, arylenepolyamine, polyarylenepolyamine, cycloalkylamine, cycloalkylenepolyamine and polycycloalkylenepolyamine radicals, R′ is selected from the group consisting of hydrogen, alkyl, aryl and cycloalkyl radicals, R″ is selected from the group consisting of alkylenepolyamine, polyalkylenepolyamine, arylenepolyamine, polyarylenepolyamine, cycloalkylenepolyamine and polycycloalkylenepolyamine radicals, X and Y are selected from the group consisting of hydrogen and halogen radicals, at least two X's being halogen, *m* is an integer of from one to two, *n* ranges from zero to two and *p* ranges from zero to one, and the other of said solutions containing a polyacid polyhalide containing at least two acid halide groups per molecule.

2. A process as set forth in claim 1 wherein said fibrous material is wool.

3. A process as set forth in claim 1 wherein said fibrous material is first contacted with said solution containing said amino compound and is thereafter contacted with said solution containing a polyacid polyhalide containing at least two acid halide groups per molecule.

4. A process as set forth in claim 3 wherein said fibrous material is wool.

5. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing the diethylenediamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4*a*,5,8,8*a*-octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid, and thereafter contacting said wool with a water-immiscible organic solution containing a polyacid polyhalide containing at least two acid halide groups per molecule.

6. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing the diethylenediamino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4*a*,5,8,8*a*-octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid, 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 the tetraethylenetetramino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano - 2,3-naphthalenedicarboxylic acid, 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 the tetraethylenetetramino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid, 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 the diethylenediamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethano-2,3-naphthalenedicarboxylic acid, 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 the diethylenediamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid, and thereafter contacting said wool with a hydrocarbon solution of a polyacid polychloride containing at least two acid chloride groups per molecule.

11. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing the diethyleneamino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a - octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid, 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 the tetraethylenetetramino amide of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid, and thereafter contacting said wool with a hydrocarbon solution of 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 the tetraethylenetetramino imide of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid, and thereafter contacting said wool with a hydrocarbon solution of 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 the diethylenediamino amide of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethano-2,3-naphthalenedicarboxylic acid, and thereafter contacting said wool with a hydrocarbon solution of 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 the diethylenediamino amide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid, and thereafter contacting said wool with a hydrocarbon solution containing sebacoyl chloride.

16. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing the diethylenediamino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid, and thereafter contacting said wool with a hydrocarbon solution containing sebacoyl chloride.

17. A process for the treatment of wool which comcomprises contacting said wool with an aqueous solution containing the tetraethylenetetramino amide of 5,6,7,8,9,9-hexachloro - 1,2,3,4,4a,5,8,8a-octahydro-5,8-methano-2,3-naphthalenedicarboxylic acid, and thereafter contacting said wool with a hydrocarbon solution containing sebacoyl chloride.

18. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing the tetraethylenetetramino imide of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-5,8-methano - 2,3-naphthalenedicarboxylic acid, and thereafter contacting said wool with a hydrocarbon solution containing sebacoyl chloride.

19. A process for the treatment of wool which comprises contacting said wool with an aqueous solution containing the diethylenediamino amide of 5,6,7,8,9,9 - hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethano-2,3-naphthalenedicarboxylic acid, and thereafter contacting said wool with a hydrocarbon solution containing sebacoyl chloride.

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