

(11) 1 487 374

(21) Application No. 38794/74 (22) Filed 5 Sept. 1974

(31) Convention Application No. 12813/73

(32) Filed 6 Sept. 1973 in

(33) Switzerland (CH)

(44) Complete Specification published 28 Sept. 1977

(51) INT CL² C07C 91/10 D06M 13/34 15/12

(52) Index at acceptance

C2C 20Y 313 31Y 323 32Y 339 360 361 362 364 36Y 456 45Y
502 50Y 620 643 644 796 79Y LJ

C3R 27K8E 27K8F 27K9E 27K9F

21Y 235 23Y 240 242 24Y 262 26Y 270 272 274 27Y 364
36Y 370 385 390 39Y 581 588 59X 59Y 610 612 636 65Y
662 66Y 70Y 744 74Y 795 L2

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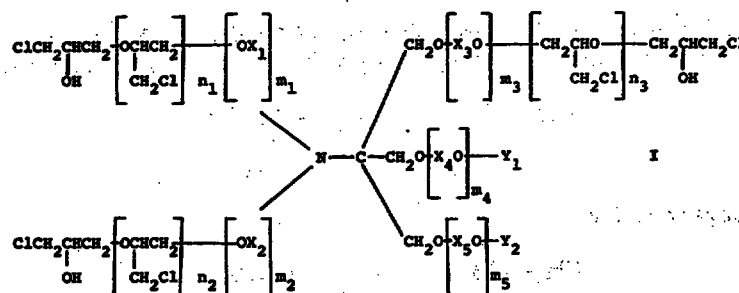


(54) IMPROVEMENTS IN OR RELATING TO ORGANIC COMPOUNDS AND THEIR USE IN THE ANTISTATIC TREATMENT OF FIBROUS MATERIALS

(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

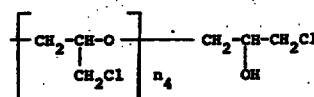
The present invention is concerned with improvements in or relating to organic compounds and their use in the treatment of synthetic, semi-synthetic or natural fibrous material to reduce the tendency thereof to accumulate static electricity.

Accordingly, the present invention provides a method of antistatically treating synthetic, semi-synthetic or natural fibrous material having a tendency to accumulate static electricity, which comprises applying thereto one or more compounds of formula I.

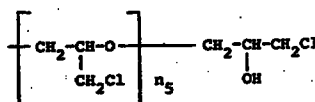


wherein each X_1 , X_2 , X_3 , X_4 and X_{52} independently, is 1,2-ethylene, 1,2-propylene or 1,2-butylene,

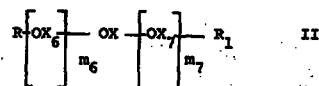
each of m_1 and m_2 , independently, is an integer 1 to 30,
each of m_3 , m_4 and m_5 , independently, is 0 or an integer 1 to 30,
each of n_1 , n_2 and n_3 , independently, is 0 or an integer 1 or 2,
 Y_1 is hydrogen or a radical of the formula



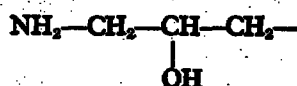
wherein n_4 is 0 or an integer 1 or 2, and Y_2 is hydrogen or a radical of the formula



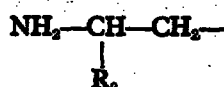
wherein n_5 is 0 or an integer 1 or 2, and wherein the sum of m_1, m_2, m_3, m_4 and m_5 is an integer 2 to 100 and the sum of n_1, n_2, n_3, n_4 and n_5 is 0 or an integer 1 to 7, in association with one or more compounds of formula II,



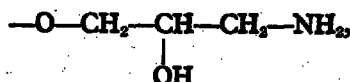
wherein R is a radical of the formula



or



wherein R_2 is hydrogen, methyl or ethyl, R_1 is NH_2 — or a radical of the formula

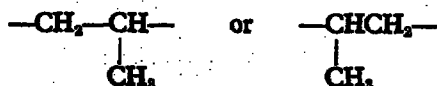


X is alkylene (C_2 — C_{12}), phenylene, phenyleneoxyphenylene or phenylenesulphonylphenylene,

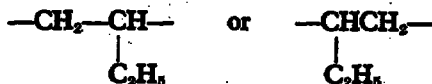
each X_6 and X_7 , independently, is 1,2-ethylene, 1,2-propylene or 1,2-butylene, and

each of m_6 and m_7 , independently, is an integer 1 to 38, the sum of m_6 and m_7 being an integer 2 to 39, and/or one or more precondensates of the compounds of formulae I and II, and curing the applied compounds, precondensate(s) or mixture of compounds and precondensate(s) on the material.

In the formulae I and II above, when any of $\text{X}_1, \text{X}_2, \text{X}_3, \text{X}_4, \text{X}_5, \text{X}_6$ and X_7 is a 1,2-propylene or 1,2-butylene group, such group may be arranged either way round, i.e. as

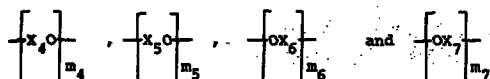
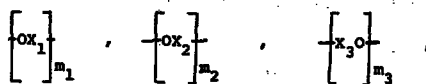


for 1,2-propylene and as



for 1,2-butylene.

Furthermore, when any one of m_1, m_2, m_3, m_4, m_5 and m_7 is greater than 1, the appropriate repeating units may be the same or different so that each chain



independently, may consist of a plurality of the same or different alkyleneoxy units. Moreover, when the repeating chain units are different, they may repeat in an ordered or random pattern.

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As will be apparent from the description below, the compounds of formulae I and II and likewise the precondensates thereof are generally produced in the form of mixtures of compounds. While separation of such mixtures may in some cases be possible, in general it is found that such mixtures perform satisfactorily in the method of the invention and therefore separation is not necessary. Accordingly the method of the present invention embraces the use of one or more compounds of formula I and of formula II, and/or their precondensates.

In general it is preferable that at least some precondensate of the compounds of formulae I and II is employed in the method of the invention.

By the term "precondensate" in relation to the compounds of formulae I and II, as employed herein, is meant a partially condensed mutual product thereof having capacity for further condensation by way of crosslinking, e.g. under curing conditions. Such precondensates are characterised by their water solubility and the relatively higher viscosities of their aqueous solutions compared with those of the compounds of formulae I and II from which the precondensates are derived. Such precondensates are novel and are also provided by the present invention.

The precondensates of the invention may be produced by dissolving the compounds of formulae I and II in water or in an aqueous water-miscible organic solvent, such as an aqueous alcohol solution, e.g. aqueous isopropanol, under non-acidic conditions, and allowing the reaction to proceed, preferably with stirring. The reaction temperature generally lies in the range 0 to 100°C, preferably above 15°C, more preferably from 20 to 90°C, e.g. 20 to 30°C. The reaction is allowed to proceed until the desired degree of condensation has been effected. The degree of condensation can be followed by observing the increase in viscosity. In general a reaction period of between 1 and 4 hours is required in order to obtain some increase in viscosity and yet maintain the reaction mixture in homogeneous and stirrable condition. The reaction may be terminated either by diluting the reaction mixture with water or, more preferably, by acidifying the slightly basic reaction mixture with either organic acids or inorganic acids, preferably the latter, e.g. concentrated hydrochloric acid, to a pH of below 7.0, e.g. between 2.0 and 6.0, more preferably between 5.0 and 6.0. As will be appreciated, acidification of the reaction mixture will cause protonation of the basic amino centres, thus discouraging reaction at these centres. Protonated forms of the precondensates are also provided by the present invention, the basic amino centres of the non-protonated form being partially or fully protonated in the corresponding protonated form.

The ratio by weight of the compounds of formula I to the compounds of formula II, in the production of the precondensate and also for use as a mixture in the method of the invention, will vary depending on the nature of the compounds, e.g. the relative number of chlorohydrin groups and free hydrogen atoms available for reaction, and the nature of the antistatic treatment desired. However, in general, satisfactory results may be obtained when the weight ratio of the compound of formula I to the compound of formula II is 1:0.4 to 3, more preferably 1:1 to 2, e.g. 1:1.5. In general, the weights are preferably arranged to ensure that between 0.1 to 3, more preferably 0.3 to 1.3 chlorohydrin groups of the compound of formula I are available for reaction with each reactive hydrogen atom of the amine of formula II.

The present invention further provides a vendable twin pack containing as separate components a compound of formula I or a mixture of compounds of formula I and a compound of formula II or a mixture of compounds of formula II in a weight ratio of 1:0.4 to 3, respectively, for use in the method of the invention. Preferably the vendable twin pack has in physical relationship therewith direction specifying the use of the compounds in accordance with the method of the invention.

The compounds of formulae I and II and/or their precondensates are generally applied to the fibrous materials in the method of the present invention in the form of aqueous liquors, and for trade and also for storage purposes, the compounds of formulae I and II and/or their precondensates are preferably in the form of a concentrated aqueous stock solution. Preferably such concentrated aqueous solutions contain between 10 and 50%, more preferably 20 to 30%, e.g. 25% by weight of the compounds and/or their precondensates. In order to ensure that condensation or further condensation does not ensue on prolonged storage, any basic amino group is preferably converted to protonated form by adjusting the pH to below 7.0, e.g. between 2.0 to 6.0, more preferably 5.0 to 6.0, e.g. 5.5. Thus the present invention further provides a stable, concentrated stock solution which comprises one or more compounds of formula I and of formula II and/or one or more precondensates of the compounds of formulae I and II, in protonated form, in aqueous solution at a concentration of between 10 and 50% by weight and at a pH of below 7.0.

The application liquors themselves, for use in the method of and also provided by the present invention, may be prepared from the concentrated aqueous solutions by diluting them with water to between 1 and 10%, preferably between 2 and 7%, e.g. 5%, by weight concentration and, if necessary, adjusting the pH of the solution to above 5.5, preferably from 5.5 to 7.0, or more preferably from 6.0 to 7.0, to enable condensation or further condensation to ensue. Such pH adjustment may be effected by the addition of a water-soluble base, either inorganic, e.g. sodium hydroxide or sodium carbonate, or organic, e.g. triethanolamine or sodium acetate.

The application liquor provided by the present invention comprises one or more compounds of formula I and of formula II and/or one or more precondensates of the compounds of formulae I and II, in aqueous solution at a concentration of compounds and/or precondensate(s) in solution of between 1 and 10% by weight and at a pH of between 5.5 and 7.0.

As will be appreciated from the foregoing description, the tendency of the compounds of formulae I and II and/or precondensates thereof, to condense or, as the case may be, further condense, will depend on three basic parameters, namely pH, temperature and concentration. Accordingly, the preparation of stable concentrated solutions or suitable application liquors will therefore necessitate consideration of the relationship between the above mentioned parameters.

The application liquors are preferably applied by a process which comprises padding or spraying the liquor onto the fibrous material to be antistatically treated, expressing a proportion of the liquid carrier, preferably to obtain between 60 and 80%, e.g. 70% by weight take-up, based on the dry weight of the material, and then curing the liquor by heating. Suitable curing temperatures are between 60°C and 150°C, preferably between 100° and 150°C, e.g. 140°C. The curing period will depend *inter alia* on the curing temperature, but in general will lie in the range of 30 seconds to 10 minutes. Conveniently, the curing step is simultaneously effected when drying the treated material.

Preferably, the treatment results in an increase of the dry weight of the material of from 0.1 to 6%, more preferably 1 to 4%.

Apart from the compounds of formulae I and II and/or their precondensates, the application liquors and stable concentrated aqueous solutions may also contain other chemical treating agents, for example, softening agents, water repellants, dyes or pigments.

Synthetic, semi-synthetic or natural materials, suitable for treatment by the method of the invention, are of fibrous form. The method is particularly suited to the treatment of paper, cotton or wool, or fibrous cellulose acetate, synthetic polyamides, polyester or polyacrylonitrile or blends of such materials, e.g. polyester/cotton blend fabrics.

Apart from their reduced tendency to accumulate static electricity, materials treated in accordance with the present invention do not exhibit any undue tendency to soil and the soft handle of the material is not unduly affected. The antistatic treatment in accordance with the invention is, moreover, notably durable, possessing notable wash fastness under both domestic washing and dry cleaning conditions. The method of the invention may also advantageously be effected in conjunction with other material treatments, for example, pigmentation or anionic dyeing. Thus, pigments, e.g. as prints, may be fixed by a simultaneous antistatic treatment, e.g. by incorporating the compounds of formulae I and II and/or a precondensate thereof in the printing paste. In addition, the affinity of anionic dyes for the material and the steam resistant properties of the anionic dyeings may be improved by an antistatic treatment of the material prior to or during dyeing.

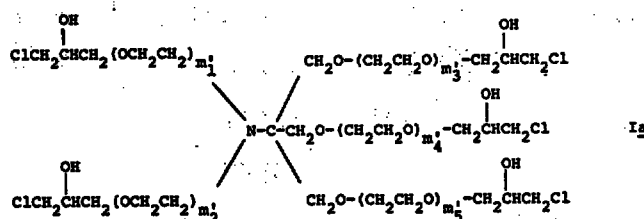
Preferred compounds of formula I, either for use in the method of the invention or in the production of the precondensates of the invention, are the compounds wherein in formula I;

(i) the sum of m_1 , m_2 , m_3 , m_4 and m_5 is an integer 2 to 20, particularly when each of m_1 and m_2 , independently, is an integer 1 to 4 and each of m_3 , m_4 and m_5 , independently, is 0 or an integer 1 to 4;

(ii) each X_1 , X_2 , X_3 , X_4 and X_5 , independently, is 1,2-ethylene or 1,2-propylene, more preferably 1,2-ethylene; and/or

(iii) each of n_1 , n_2 , n_3 , n_4 and n_5 is 0.

Thus, particularly preferred compounds are the compounds of formula Ia,



wherein each of m_1' and m_2' , independently, is an integer 1 to 19, and each of m_3' , m_4' and m_5' , independently, is 0 or an integer 1 to 18, the sum of m_1' , m_2' , m_3' , m_4' and m_5' being 2 to 20, especially the compounds wherein the sum of m_1' , m_2' , m_3' , m_4' and m_5' is 15.

Preferred compounds of formula II, either for use in the method of the invention or in the production of the precondensates of the invention are the compounds wherein

(i) X is 1,2-ethylene, 1,2-propylene or 1,2-butylene, and, more preferably, each of X, the X₆'s and the X₇'s, independently, is 1,2-ethylene or 1,2-propylene, especially when X, the X₆'s and the X₇'s are the same 1,2-ethylene or -propylene group, preferably 1,2-ethylene;

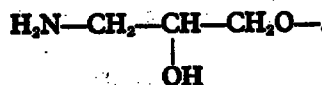
(ii) the sum of m_1 and m_2 is an integer 4 to 22, especially 12 or 13;

and/or

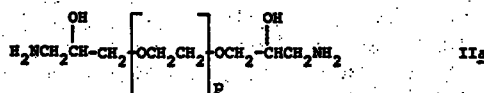
(iii) R is a radical



and/or R_1 is a radical

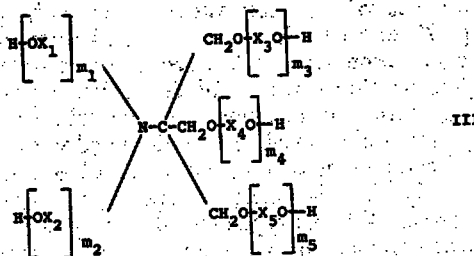


Thus, particularly preferred compounds of formula II are the compounds of formula IIa.



wherein p is an integer 5 to 23, especially an integer 13 or 14.

The compounds of formula I are novel and also form part of the present invention. They may be produced, in accordance with a further aspect of the invention, by a process which comprises condensing a compound of formula III,

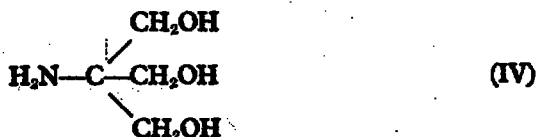


wherein $X_1, X_2, X_3, X_4, X_5, m_1, m_2, m_3, m_4$ and m_5 are as defined above, with epichlorohydrin, in a molar ratio of 1:3 to 12 respectively.

The process may be effected by the addition of epichlorohydrin to the compound of formula III at a temperature between 90 and 110°C. Preferably a small amount, e.g. 1 to 3 percent by weight, based on the weight of the compound of formula III, of a condensation catalyst, especially a strong Lewis acid, in particular tin tetrachloride or boron trifluoride etherate, is added to assist the condensation. The reaction is allowed to proceed until no further epichlorohydrin distills off.

The compounds of formula III, employed as starting material in the produc-

tion of the compounds of formula I, may be produced by alkoxylation of a compound of formula IV,



with one or more 1,2-alkylene oxides selected from 1,2-ethylene oxide, 1,2-propylene oxide and 1,2-butylene oxide in a molar ratio of compound of formula IV: total alkylene oxide of 1:2 to 100, respectively.

The reaction may be effected by the addition of the alkylene oxide to the compound of formula IV at a temperature of between 155 and 180°C, in the presence of a small amount, e.g. 1 to 2% by weight based on the weight of the compound of formula IV, of an alkali, for example sodium hydroxide, and the reaction allowed to proceed at the above temperature for a sufficient period to allow complete alkoxylation.

In practice, it is not necessary to isolate the resulting compounds of formula III, the reaction mixture being employed directly in the production of compounds of formula I by reducing the temperature thereof to 90 to 110°C and addition thereto of epichlorohydrin together with, if required, a condensation catalyst.

The compounds of formula II, employed in the method or in the production of the precondensate of the invention, may be produced by alkoxylation of a compound of formula V,



wherein X is as defined above, with one or more 1,2-alkylene oxides selected from ethylene oxide, propylene oxide and 1,2-butylene oxide, in a molar ratio of compound of formula V: total alkylene oxide of 1:2 to 39 (or 1:2 to 40 when R is a radical



respectively, to produce an alkoxide adduct, e.g. polyglycol 600, and

a) converting at least one terminal —OH group of the resulting alkoxide adduct to a more reactive group, e.g. chlorine, and condensing with ammonia and/or

b) condensing the resulting alkoxide adduct or a monoaminated product from a) above with epichlorohydrin and converting the terminal chlorine atom(s) of the resulting product to amino group(s) by reaction with ammonia.

The alkoxylation of the compound of formula V to produce the alkoxide adduct may be effected in manner known *per se*, e.g. by adding the alkylene oxide to the diol of formula V, at an elevated temperature, e.g. 220–240°C. The resulting alkylene oxide adduct is then reacted with, for example, a chlorinating agent, such as thionyl chloride in accordance with process variant a) or with epichlorohydrin at an elevated temperature, e.g. 70 to 80°C, in the presence of a strong Lewis acid as catalyst, e.g. tin tetrachloride or boron trifluoride etherate in accordance with process variant b). The terminal chlorine atoms in each of the resulting products are converted to amino groups by adding thereto an aqueous ammonia solution at a temperature of from 15 to 25°C in the presence of an alkali, e.g. sodium hydroxide.

Examples of compounds of formula V are 1,2-ethylene glycol, 1,3-propylene glycol, 1,4-butylene glycol, 1,5-pentamethylene glycol, 1,6-hexamethylene glycol, 1,10-decamethylene glycol, 4-hydroxyphenol, 4,4'-dihydroxy diphenylether and 4,4'-dihydroxy diphenylsulphone. Of the alkylene oxides mentioned above as alkoxylation agents, ethylene oxide and propylene oxide are preferred.

In the following Examples, which illustrate the invention, parts and percentages are by weight and the temperatures are in degrees Centigrade.

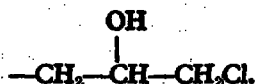
EXAMPLE 1:

a) Compound of formula I

A polychlorohydrin ether of formula I is produced by alkoxylation 121 parts (1 mol) of tris-(hydroxy-methyl)-amino methane with 145 parts (2.5 mols) of propylene oxide at a temperature of between 155 to 175°. When alkoxylation is complete, 462 parts (5 mols) of epichlorohydrin and 2.1 parts of tin tetrachloride are added to

the reaction mixture containing the resulting propylene oxide adduct, the temperature being maintained at 95 to 100°C throughout the reaction.

The structure of the compound produced corresponds to formula I wherein n_1 to n_5 are each 0, the sum of m_1 to m_5 is 3, X_1 and X_2 are each 1,2-propylene and Y_1 and Y_2 are each



b) Compound of formula II

A polyglycol diamine of formula II is produced by condensing 300 parts (0.5 mols) polyglycol 600 in the presence of 3 parts tin tetrachloride at 75° with 92.5 parts (1 mol) epichlorohydrin. The resultant polyglycol bis-epichlorohydrin ether is then added at 20° to 25° to a mixture consisting of 126 parts 30% aqueous sodium hydroxide solution and 136 parts 25% aqueous ammonia solution. The reaction mixture is then heated to 70° and the excess ammonia and water is distilled off completely under vacuum.

The residue containing the polyglycol diamine is dissolved in 334 parts by water to form a fairly viscous approximately 50% aqueous solution.

The structure of the resulting polyglycol diamine corresponds to formula IIa wherein p is 13 or 14.

c) Concentrated aqueous precondensate.

A 25% aqueous precondensate concentrate is produced by dissolving 19 parts (0.03 mols) of the polychlorohydrin ether described in part a) above, in 19 parts of water and adding dropwise 75 parts (0.05 mols) of the polyglycol amine solution described in part b) above, at 25°C (weight ratio of compound of formula I to compound of formula II being 1:2). After stirring the mixture for 2 hours at 25°C, the solution is stabilised by acidification with concentrated hydrochloric acid to a pH of 6.0.

d) Antistatic treatment

The precondensate concentrate described in part c) above is diluted with water to a concentration of 200 gm of the 25% precondensate condensate per litre of solution and the pH is adjusted to 6.2 by the addition of sodium acetate. The resulting application liquor is applied to woven fabrics of polyester, polyacrylonitrile and polyamide in a padding machine, the liquor taken up being adjusted to a level of 70% based on the weight of the fabric. The treated material is then dried at 140°C for 1 minute, curing of the treatment occurring simultaneously. The antistatically treated fabrics exhibit an increase in dry weight of 3.5%.

EXAMPLE 2:

The compound of formula II is produced in the manner described in Example 1 part b) except that instead of adding the polyglycol bis-epichlorohydrin ether to a mixture of sodium hydroxide and ammonia, the sodium hydroxide solution and then the ammonia solution are added to the polyglycol bis-epichlorohydrin ether dropwise at 10 to 15°C.

The procedures set out in Example 1 are otherwise followed.

EXAMPLE 3:

Compounds of formula II are produced in the manner described in Example 1 part b) except that the 300 parts (0.5 mols) of polyglycol 600 are replaced by 600 parts (0.5 mols) of polyglycol 1200 or 150 parts (0.5 mols) of polyglycol 300 in the reaction with 92.5 parts (1 mol) of epichlorohydrin.

The procedures set out in Example 1 are otherwise followed.

EXAMPLE 4:

a) Compound of formula I

A polychlorohydrin ether of formula I is produced by alkoxyating 121 parts (1 mol) of tris-(hydroxy-methyl)-aminomethane at 160—175° with 660 parts (15 mols) of ethylene oxide. When alkoxylation is complete, 462 parts (5 mols) of epichlorohydrin and 2.1 parts of tin tetrachloride are added to the reaction mixture containing the resulting ethylene oxide adduct, the temperature being maintained at 95 to 100°C throughout the reaction.

The structure of the compound produced corresponds to formula Ia wherein the sum of m_1' , m_2' , m_3' , m_4' and m_5' is 15.

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b) Concentrated aqueous precondensate.

A 25% aqueous precondensate concentrate is produced by dissolving 83 parts of the polychlorohydrin ether described in part a) above, in a solvent mixture consisting of 153 parts of water and 53 parts of isopropanol and adding to the solution so obtained, dropwise at 25°C, 150 parts of the polyglycol amine solution described in Example 1 part b) (weight ratio of compound of formula I to compound of formula II being 1:0.9). After stirring the mixture for 1 hour at 25°, the solution is stabilised by acidification with 8.5 parts of concentrated hydrochloric acid to a pH of 5.5.

c) Antistatic treatment

The precondensate concentrate described in part b) above is diluted with water to a concentration of 200 gm of the 25% precondensate condensate per litre of solution and the pH is adjusted to 7.0 by the addition of 3 gm of sodium bicarbonate. The resulting application liquor is applied to polyester, polyacrylonitrile and polyamide woven fabrics in the manner described in Example 1 part d). Increase in dry weight is 3.5%.

In a slight modification of part a) of this Example, 450 parts of polyglycol amine solution are employed instead of 150 parts (the weight ratio of the compound of formula I to compound of formula II being 1:2.7).

EXAMPLE 5:

A polychlorohydrin of formula I is produced in the manner described in Example 4 part a) by the addition of 132 parts (3 mols) ethylene oxide and 462 parts (5 mols) of epichlorohydrin to 121 parts (1 mol) of tris-(hydroxy methyl)-amine methane. A concentrated aqueous precondensate is produced in the manner described in Example 4 part b) except that 150 parts of the polychlorohydrin ether produced as described above are employed instead of 83 parts.

The procedure set out in Example 4 is otherwise followed.

EXAMPLE 6:

a) Compound of formula I

A polychlorohydrin ether of formula I is produced by alkoxyating 242 parts (2 mols) of tris-(hydroxy methyl)-amine methane with 220 parts (5 mols) of ethylene oxide at a temperature between 160 to 175°. When alkoxylation is complete, 925 parts (10 mols) of epichlorohydrin and a catalytic amount of tin tetrachloride are added to the reaction mixture containing the resulting ethylene oxide adduct, the temperature being maintained at 95° to 100°C throughout the reaction.

The structure of the compound produced corresponds to formula Ia wherein the sum of m_1' , m_2' , m_3' , m_4' and m_5' is 2 or 3.

b) Concentrated aqueous precondensate

A 25% aqueous precondensate concentrate is produced by dissolving 30 parts of the polychlorohydrin ether described in part a) above, in a solvent mixture consisting of 55 parts of water and 20 parts of isopropanol and adding to the resulting solution, dropwise, at 25° to 30°, 150 parts of the polyglycol amine solution described in Example 1 part b) (weight ratio of compound of formula I to compound of formula II being 1:2.5). After stirring the mixture for 2 hours, the solution is stabilised by acidification with 8 parts of concentrated hydrochloric acid to a pH of 5.5.

c) Antistatic treatment

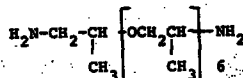
The precondensate concentrate described in part b) above is diluted with water to a concentration of 200 gm of the 25% precondensate concentrate per litre of solution and the pH of the solution is adjusted to 6.9 by addition of 5 gm of sodium bicarbonate. The resulting application liquor is applied to polyester, polyacrylonitrile and polyamide woven fabrics in the manner described in Example 1 part d).

In a slight modification of part b) of this Example, the degree of condensation in the production of the precondensate is increased by heating the mixture to 80° for 4 hours, whereupon a pronounced increase in viscosity of the precondensate solution is observed, the solution still being homogeneous and well-stirrable.

EXAMPLE 7:

a) Concentrated aqueous precondensate

The process of Example 4 part b) is repeated employing 83 parts of the polychlorohydrin ether described in Example 4 part a) and 80 parts of a 50% solution of a polyglycol diamine of the formula



(the weight ratio of the compound of formula I to compound of formula II being 1:0.5) to produce a yellowish concentrated solution (25% concentrate).

b) Antistatic treatment

The precondensate concentrate produced as described in part a) above is diluted with water to a concentration of 200 gm of the 25% precondensate concentrate per litre of solution and the pH is adjusted to 6.0 by the addition of sodium acetate. The resulting application liquor is applied to polyester, polyacrylonitrile and polyamide woven fabrics in the manner described in Example 1 part d).

EXAMPLE 8:

a) Compound of formula II

A polyglycol diamine of formula II is produced by alkoxyating 125 parts (0.5 mol) of dihydroxy diphenyl sulphone with 330 parts (7.5 mols) of ethylene oxide at 220° to 240°. To the brown viscous liquid so produced, is added 2 parts of tin tetrachloride and 37 parts (0.4 mol) epichlorohydrin and the mixture reacted at 70°. When the reaction is complete, the reaction mixture is cooled to 20° to 25° and 51 parts of a 30% aqueous sodium hydroxide solution and 55 parts of a 25% aqueous ammonia solution added thereto. After the amination, the excess ammonia is removed by heating to 70°. The residue is dissolved in water to produce a 50% aqueous solution of the polyglycol diamine.

b) Concentrated aqueous precondensate

A 25% aqueous precondensate concentrate is produced by dissolving 83.5 parts of the polychlorohydrin ether described in Example 4 part a), in a solvent mixture consisting of 40 parts of water and 55 parts of isopropanol. 223 Parts of the 50% polyglycol diamine solution described in part a) above is added to the resulting solution (the weight ratio of the compound of formula I to the compound II being 1:1.3), dropwise at 20° to 25° and the mixture stirred for 2 hours. The pH of the mixture is then adjusted to 5.6 by the addition of 9.4 ml concentrated hydrochloric acid.

c) Antistatic treatment

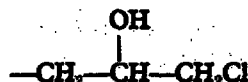
The precondensate concentrate described in part b) above is diluted with water to a concentration of 100 parts of the 25% aqueous precondensate per litre of solution and 15 parts of sodium acetate added per litre of solution giving a pH value of 6.5. The almost neutral application liquor so produced is applied to polyester, polyacrylonitrile and polyamide woven fabrics in accordance with the procedure described in Example 1 part d), the antistatic treatment resulting in an increase in 1.7% in the dry weight of the treated fabrics.

EXAMPLE 9:

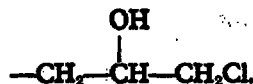
a) Compound of formula I

A polychlorohydrin ether of formula I is produced by alkoxyating 60 parts (0.5 mol) of tris-(hydroxy-methyl)-aminomethane with 110 parts (2.45 mols) of ethylene oxide at a temperature between 160° to 175°. When alkoxylation is complete, 231 parts (2.15 mols) of epichlorohydrin and a catalytic amount of tin tetrachloride are added to the reaction mixture containing the resulting ethylene oxide adduct, the temperature being maintained at 95° to 100°C.

The structure of the compound produced corresponds approximately to formula I wherein n_1 to n_6 are each 0, the sum of m_1 to m_6 is 5, X_1 and X_2 are each ethylene and Y_1 is hydrogen or



and Y_2 is



b) Concentrated aqueous precondensate

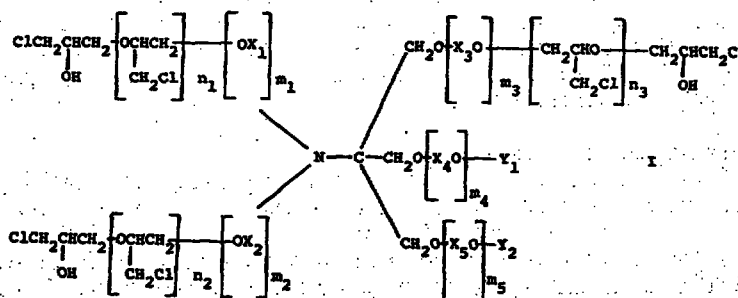
A 25% aqueous precondensate concentrate is produced by dissolving all of the

c) Antistatic treatment

The precondensate condensate described in part b) above is diluted with water to a concentration of 200 parts of the 25% aqueous precondensate per litre of solution and the solution so produced is rendered weakly acidic to neutral (pH 5.2) by the addition of sodium acetate. The resulting application liquor is applied to polyester, polyacrylonitrile and polyamide woven fabrics in accordance with the procedure described in Example 1 part d).

WHAT WE CLAIM IS:—

1. A method of antistatically treating synthetic, semi-synthetic or natural fibrous material having a tendency to accumulate static electricity, which comprises applying thereto one or more compounds of formula I,



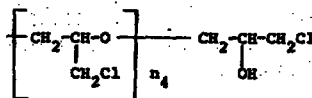
wherein each X_1 , X_2 , X_3 , X_4 and X_5 , independently, is 1,2-ethylene, 1,2-propylene or 1,2-butylene,

each of m_1 and m_2 , independently, is an integer 1 to 30,

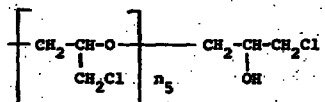
each of m_3 , m_4 , and m_5 , independently, is 0 or an integer 1 to 30,

each of n_1 , n_2 , and n_3 , independently, is 0 or an integer 1 or 2,

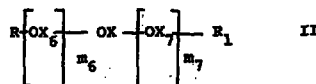
Y₁ is hydrogen or a radical of the formula



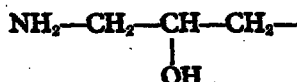
wherein n_4 is 0 or an integer 1 or 2, and Y_2 is hydrogen or a radical of the formula



wherein n_0 is 0 or an integer 1 or 2, and wherein the sum of m_1 , m_2 , m_3 , m_4 and m_5 is an integer 2 to 100 and the sum of n_1 , n_2 , n_3 , n_4 and n_5 is 0 or an integer 1 to 7, in association with one or more compounds of formula II,



wherein R is a radical of the formula



or



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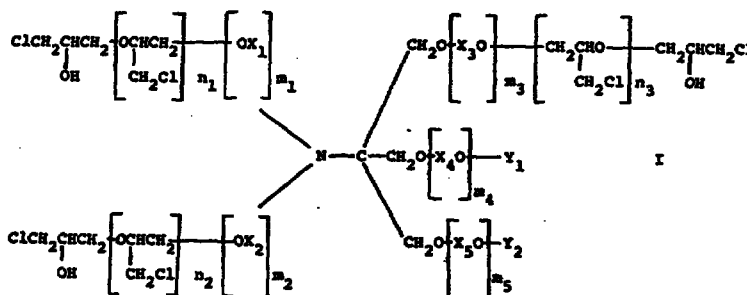
polychlorohydrin ether produced as described in part a) above, in a solvent mixture consisting of 700 parts of water and 240 parts of isopropanol and adding thereto, dropwise, 300 parts of the polyglycol diamine described in Example 1 part b), (the weight ratio of the compound of formula I to the compound of formula II being 1:0.4), the mixture being stirred for 4 hours at 25° to 30°. The 25% concentrate so obtained is stabilised by the addition of concentrated hydrochloric acid to obtain a pH of 5.5.

c) Antistatic treatment

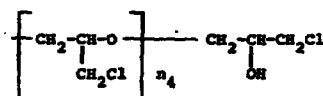
The precondensate condensate described in part b) above is diluted with water to a concentration of 200 parts of the 25% aqueous precondensate per litre of solution and the solution so produced is rendered weakly acidic to neutral (pH 5.2) by the addition of sodium acetate. The resulting application liquor is applied to polyester, polyacrylonitrile and polyamide woven fabrics in accordance with the procedure described in Example 1 part d).

WHAT WE CLAIM IS:—

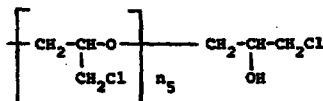
1. A method of antistatically treating synthetic, semi-synthetic or natural fibrous material having a tendency to accumulate static electricity, which comprises applying thereto one or more compounds of formula I,



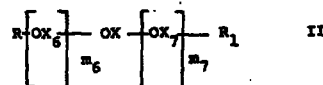
wherein each X_1 , X_2 , X_3 , X_4 and X_5 , independently, is 1,2-ethylene, 1,2-propylene or 1,2-butylene,
each of m_1 and m_2 , independently, is an integer 1 to 30,
each of m_3 , m_4 and m_5 , independently, is 0 or an integer 1 to 30,
each of n_1 , n_2 and n_3 , independently, is 0 or an integer 1 or 2,
 Y_1 is hydrogen or a radical of the formula



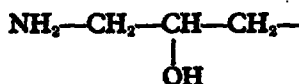
wherein n_4 is 0 or an integer 1 or 2, and
 Y_2 is hydrogen or a radical of the formula



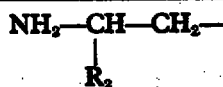
wherein n_5 is 0 or an integer 1 or 2, and wherein the sum of m_1 , m_2 , m_3 , m_4 and m_5 is an integer 2 to 100 and the sum of n_1 , n_2 , n_3 , n_4 and n_5 is 0 or an integer 1 to 7, in association with one or more compounds of formula II,



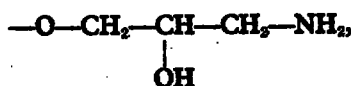
wherein R is a radical of the formula



or

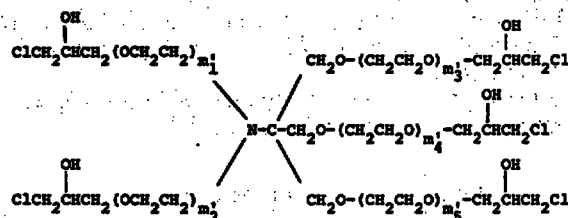


wherein R_2 is hydrogen, methyl or ethyl,
 R_1 is NH_2- or a radical of the formula



- 5 X is alkylene (C_2-C_{12}), phenylene, phenyleneoxyphenylene or phenylenesul-
 phonylphenylene,
 each X_6 and X_7 , independently, is 1,2-ethylene, 1,2-propylene or 1,2-butylene,
 and
 each of m_6 and m_7 , independently, is an integer 1 to 38, the sum of m_6 and m_7 ,
 10 being an integer 2 to 39, and/or one or more precondensates of the com-
 pounds of formulae I and II, and curing the applied compounds, precon-
 densate(s) or mixture of compounds and precondensate(s) on the material.

2. A method according to claim 1, wherein in formula I the sum of m_1 , m_2 , m_3 ,
 m_4 and m_5 is an integer 2 to 20.
 15 3. A method according to claim 2, wherein each of m_1 and m_2 , independently, is
 an integer 1 to 4 and each of m_3 , m_4 and m_5 , independently, is 0 or an integer 1 to 4.
 4. A method according to any one of claims 1 to 3, wherein in formula I, each
 X_1 , X_2 , X_3 , X_4 and X_5 , independently, is 1,2-ethylene or 1,2-propylene.
 5. A method according to claim 4, wherein each X_1 , X_2 , X_3 , X_4 and X_5 is 1,2-
 20 ethylene.
 6. A method according to any one of the preceding claims, wherein in formula
 I, n_1 , n_2 , n_3 , n_4 and n_5 are each 0.
 7. A method according to any one of Claims 1, 2 and 4 to 6, wherein as com-
 pound of formula I is employed a compound of formula Ia,



wherein each of m_1' and m_2' , independently, is an integer 1 to 19, and
 each of m_3' , m_4' , and m_5' , independently, is 0 or an integer 1 to 18, the sum of
 m_1' , m_2' , m_3' , m_4' and m_5' being 2 to 20.

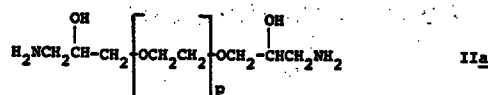
8. A method according to claim 7, wherein in formula Ia the sum of m_1' , m_2' ,
 m_3' , m_4' , and m_5' is 15.
 9. A method according to any one of the preceding claims wherein in formula
 II, X is 1,2-ethylene, 1,2-propylene or 1,2-butylene.
 10. A method according to claim 9, wherein in formula II, each of X, the X_6 's
 and the X_7 's, independently, is 1,2-ethylene or 1,2-propylene.
 11. A method according to claim 10, wherein each of X, the X_6 's and the X_7 's is
 1,2-ethylene.
 12. A method according to any one of the preceding claims wherein in formula
 II the sum of m_6 and m_7 is an integer 4 to 22.
 13. A method according to claim 12, wherein the sum of m_6 and m_7 is 12 or 13.
 14. A method according to any one of the preceding claims wherein in formula
 II, R is a radical



15. A method according to any one of the preceding claims wherein in formula
 II, R_1 is a radical



16. A method according to any one of Claims 1 to 12, 14 and 15 wherein as compound of formula II is employed a compound of formula IIa,



wherein p is an integer 5 to 23.

17. A method according to claim 16, wherein p is 13 or 14.

18. A method according to any one of the preceding claims wherein at least some precondensate of compounds of formulae I and II is employed.

19. A method according to any one of the preceding claims, which comprises padding or spraying an application liquor containing one or more compounds of formula I and of formula II and/or one or more precondensates of the compounds of formulae I and II, as defined in Claim 1, in aqueous solution at a concentration of between 1 and 10% by weight and at a pH of between 5.5 and 7.0 onto the fibrous material to be antistatically treated, expressing a proportion of the liquid carrier to obtain between 60 and 80% by weight take-up, based on the dry weight of the material, and then curing the application liquor by heating.

20. A method according to any one of the preceding claims wherein the treatment results in an increase in the dry weight of the treated material of from 0.1 to 6%.

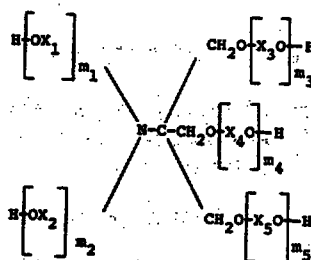
21. A method according to any one of the preceding claims wherein the fibrous material to be antistatically treated is selected from paper, cotton, wool, fibrous cellulose acetate, synthetic polyamides, polyester, polyacrylonitrile and blends of such materials.

22. A method according to Claim 1, substantially as described herein with reference to any one of the Examples.

23. A compound of formula I, as defined in any one of claims 1 to 8.

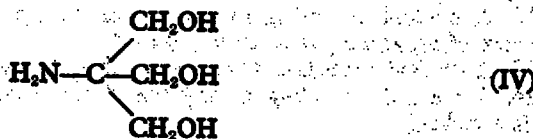
24. A compound according to claim 23 substantially as described herein with reference to any one of the Examples.

25. A process for the production of a compound of formula I, as defined in claim 1, which comprises condensing a compound of formula III,



wherein X_1 , X_2 , X_3 , X_4 , X_5 , m_1 , m_2 , m_3 , m_4 and m_5 are as defined in claim 1, with epichlorohydrin, in a molar ratio of 1:3 to 12 respectively.

26. A process according to Claim 25, wherein the compound of formula III is produced by alkoxyating a compound of formula IV,



with one or more 1,2-alkylene oxides selected from 1,2-ethylene oxide, 1,2-propylene oxide and 1,2-butylene oxide in a molar ratio of compound of formula IV: total alkylene oxide of 1:2 to 100, respectively.

27. A process according to Claim 25 or 26, substantially as described herein with reference to any one of the Examples.

28. An application liquor for use in the method according to any one of Claims



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- 1 to 22, comprising one or more compounds of formula I and of formula II and/or one or more precondensates of the compounds of formulae I and II, as defined in Claim 1, in aqueous solution at a concentration of compounds and/or precondensate(s) in solution of between 1 and 10% by weight and at a pH of between 5.5 and 7.0.
- 5 29. An application liquor according to Claim 28, wherein the concentration is between 2 and 7% by weight.
30. An application liquor according to Claim 28, substantially as described herein with reference to any one of the Examples.
- 10 31. A stable concentrated stock solution comprising one or more compounds of formula I and of formula II and/or one or more precondensates of the compounds of formulae I and II, as defined in Claim 1, in protonated form, in aqueous solution at a concentration of compounds and/or precondensate(s) of between 10 and 50% by weight and at a pH of below 7.0.
- 15 32. A stable concentrated stock solution according to Claim 31, wherein the concentration is between 20 and 30% by weight.
33. A stable concentrated stock solution according to Claim 31, substantially as described herein with reference to any one of the Examples.
- 20 34. A precondensate which comprises a partially condensed mutual product of compounds of formulae I and II, as defined in Claim 1, having capacity for further condensation by way of cross-linking and being water soluble.
35. A precondensate according to Claim 34, substantially as described herein with reference to any one of the Examples.
- 25 36. A protonated form of the precondensate of Claim 34, wherein the basic amino centres of the corresponding non-protonated form are partially or fully protonated.
37. A protonated form of the precondensate according to Claim 36, substantially as described herein with reference to any one of the Examples.
- 30 38. A vendable twin pack containing as separate components, a compound or mixture of compounds of formula I, as defined in Claim 1 and a compound or mixture of compounds of formula II, as defined in Claim 1, in a weight ratio of 1:0.4 to 3 respectively, for use in accordance with the method defined in any one of Claims 1 to 22.
39. A vendable twin pack according to Claim 38, having in physical relationship therewith directions specifying the use of the components in accordance with the method defined in any one of Claims 1 to 22.
- 35 40. A fibrous material whenever antistatically treated by a method according to any one of Claims 1 to 22.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1977
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

