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TEXTILE TREATING COMPOUNDS AND METHOD OF APPLYING THEM TO TEXTILES

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7 Claims. (Cl. 8—115.5)

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This invention relates to textile finishing compounds, to a process of treating cellulosic, proteinaceous and other textile materials in order to improve their properties, and to the improved cellulosic, proteinaceous and other textile materials thereby produced.

Cellulosic and like textile materials have heretofore been rendered water repellent by treating them with alkyl silicon halides. These compounds are said to react with hydroxyl groups at the surface of the textile, forming a chemical bond therewith and splitting out hydrogen halide. Because of the presence of hydrogen halide, however, considerable care must be exercised in carrying out the process to avoid weakening the cellulosic fabric or otherwise damaging it. It is necessary, for example, to apply the silicon halide at a low temperature under a vacuum or other conditions adapted to carry off hydrogen halide as it is formed. Because of the inconvenience which such precautions entail, such silicon halides have been limited in their application to the treatment of woolen goods and like materials which are unaffected by inorganic acids.

Moreover, silicon halides are quite difficult to handle. They hydrolyze readily even in the presence of atmospheric moisture to form silica polymers and hydrogen halides, and thus must be applied in the absence of moisture. Aqueous solutions cannot of course be used. The lower members of the series are corrosive, highly volatile, low boiling liquids, not pleasant to work with in a textile mill.

Now, in accordance with this invention, cellulosic proteinaceous and other textile materials are treated with quaternary ammonium salt derivatives of alkyl alkoxy silicon compounds. These compounds improve the water repellency and/or softness, dimensional stabilization, flame resistance and crease resistance of the textiles treated therewith. These improved properties may result from reaction of the compounds of the invention with the textile material, either at the silicon-oxygen linkage or at the quaternary ammonium group or both, possibly forming cross linkages between adjacent textile molecules, or giving rise to polymerization of the compound or its decomposition products in situ to form a resin. Whatever the explanation for their occurrence, the improved properties are permanent, and withstand ordinary laundering and dry cleaning procedures.

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THE COMPOUNDS OF THE INVENTION

They are characterized by the formula:

$$R_nSi[-O-Y-N\ (tert)\ X]_{4-n} \qquad (1)$$

where: n is an integer from 1 to 3.

R is a saturated or unsaturated, substituted or unsubstituted, aliphatic, aromatic or cycloaliphatic group, or an

$$-(O-\overset{R_n}{\underset{|}{Si}})_y-[O-Y-N\ (tert)\ X]_{3-n}$$

linkage, where y is an integer from 1 to about 20. The R radicals, if more than one, may be the same or different.

Y is bivalent or trivalent organic radical which may be an aliphatic, aromatic or cycloaliphatic hydrocarbon radical of 1 to about 30 carbon atoms or a radical containing a linkage selected from the group consisting of ester, ether, amide, carbamate, and urea linkages, such as COO, —O—, CONR', OCONR', NR'CONR', CONR'CONR', $OCH_2NR'CONR'$, OCONR'CONR', where R' is hydrogen or alkyl. Y may, for example, be methylene, ethylene, propylene, phenylene, decylene, octadecylene, montanylene, butylene, cyclohexylene, or naphthylene, with or without the linkages mentioned.

N(tert) is the residue of a tertiary amine. Typical tertiary amine residues include those in which three nitrogen valences are taken up in one ring, as in pyridine, pyrazine, pyrimidine, quinoline, isoquinoline, acridine, and phenanthridene, those in which two nitrogen valences are taken up in one ring, as in piperidine, or tetrahydroquinoline or tetrahydroisoquinoline, and a third taken up with an alkyl group, and those in which three valences are taken up with alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, and hexy, whether n-, secondary or tertiary. R may, for example, be methyl, ethyl, propyl, hexyl, decyl, octadecyl, phenyl, tolyl, chlorophenyl, dichlorophenyl, trichlorophenyl, pentachlorophenyl, naphthyl, cyclohexyl, cyclopentyl, chloromethyl, chloropropyl, fluorophenyl, octenyl, or oleyl. X is an anion.

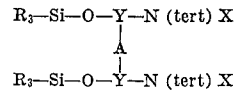
When R represents an

$$O-Si[O-Y-N\ (tert)\ X]_{3-n}$$

group the formula assumes this aspect:

$$[X\ (tert)\ N-Y-O]_{3-n}-\overset{R_n}{\underset{|}{Si}}-[O-\overset{R_n}{\underset{|}{Si}}-]_y[O\,Y\,N\ (tert)\ X]_{3-n} \qquad (2)$$

When Y is trivalent, the formula assumes this aspect:

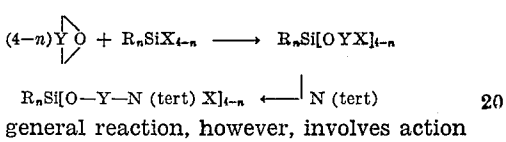


(3)

where A is an alkylene radical and the other radicals are as described above. A may also be an aromatic or cycloaliphatic radical.

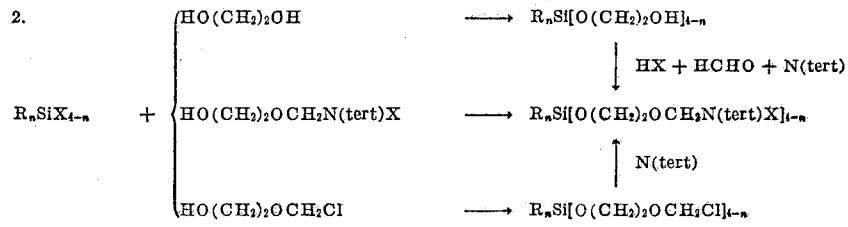
When Y is a bivalent hydrocarbon residue, these compounds may be prepared from the corresponding halogenosilane and epoxide, according to the procedure set forth in J. Am. Chem. Soc. 67 1548 (1945):

1.



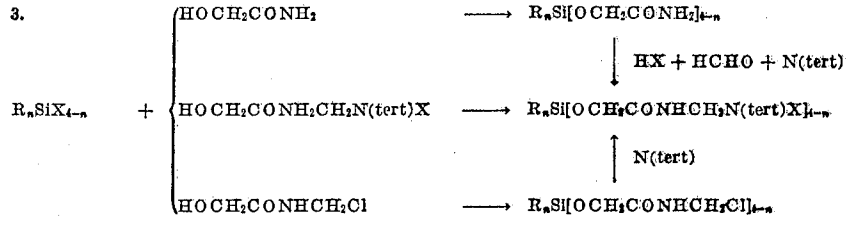
The general reaction, however, involves action of the corresponding alcohol, its chloromethyl ether, or quaternary ammonium salt on the halogeno silane (Ann. Chim. Phys. (4) 9, 5 (1866); Ann. 488, 56 (1931); and J. Am. Chem. Soc. 68, 70 (1946):

2.

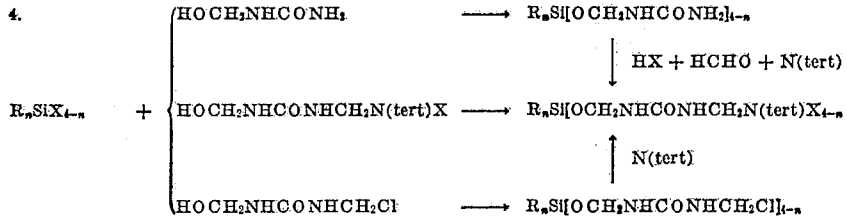


Similarly, a hydroxy amide, urea, ester, carbamate or hydroxy hydrocarbon halide may be used, or their chloromethyl ethers or quaternary ammonium salts:

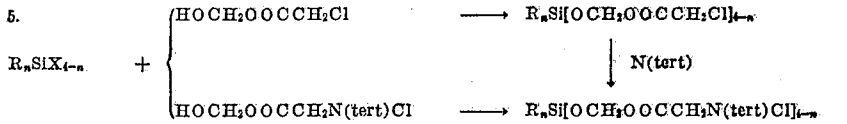
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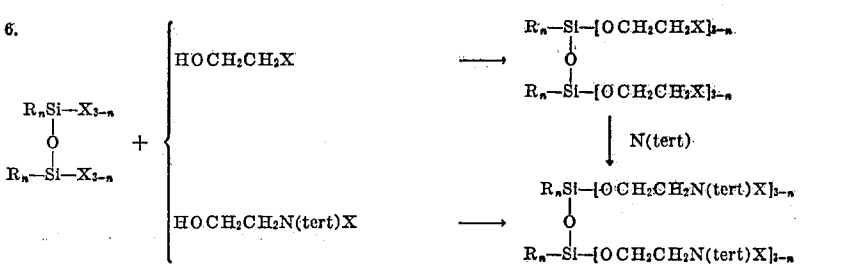
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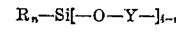


6.



These compounds are white or pale-colored solids, or viscous liquids, soluble or dispersible in water, pyridine, dioxane, xylene, mesityl oxide, benzene, chloroform, ethyl alcohol, carbon, tetrachloride, ethylene dichloride, ether and acetone.

The quaternary ammonium group of these compounds is decomposed by heating the dry compound above about 90° C., liberating the tertiary amine and a radical of the form



It may also be hydrolyzed by water at temperatures as low as 60 to 80° C., forming these products.

In considering the possible reactions that may follow decomposition of this group, it must be borne in mind that the radical Y also influences the reactions which may occur. Y groups which include urea, amide or carbamate groups, and thus are of the form —$CONHCH_2$— are readily polymerized; whether or not the silicon-oxygen linkage is hydrolyzed affect only the type of polymers formed. For example, if the compound contains two quaternary ammonium groups, linear polymers may form even though the silicon-oxygen linkage remain unhydrolyzed.

The silicon-oxygen linkage is hydrolysable, but its ease of hydrolysis depends upon the number of carbon atoms of the R group attached to the silicon atom. Hydrolysis may be inhibited in the

presence of a tertiary amine, such as pyridine, trimethylamine, triethylamine, or quinoline. When all of the R groups are less than about 6 carbon atoms, the linkage is hydrolized more or less rapidly by moisture at room temperature, and the hydrolysis is exothermic. If an R group of 6 to about 10 carbons present, the linkage is hydrolyzed at room temperature only by dilute acid or base, the required conditions for hydrolysis thereafter growing more severe as the number of carbons increases, i. e., as the R groups impart to the compound more of the character of a hydrocarbon. Hydrolysis when an R group $C_{17}H_{35}$ is present may, for example, be accomplished only by warming in dilute acid or base at 40 to 80° C., or by subjecting it to a steam treatment.

Thus, during treatment, apparently two unrelated reactions may occur, and these may proceed concurrently or successively, depending upon the treatment conditions. The free radical liberated by decomposition of the quaternary ammonium group, may polymerize to form a resin, may react with another free radical to form a dimer, or react with water to form a fatty alcohol. If the reaction is brought about in the presence of cellulose, it may react with a hydroxyl group of the cellulose molecule to form an ether of the general structure

cellulose-O—Y—O—Si—R_n

This ether may also hydrolyze to give the radical O—Si—R_n and the ether cellulose-O—Y—. The former may react as described below, while the latter may cross-link with another cellulose molecule.

The radicals liberated by hydrolysis of the Si—O linkages are of the form R_n—Si— or R_n—Si[—O—] and Y—N(tert)X. The latter may react as set forth above.

The former may polymerize to form a silicone resin, a siloxane, R_n—Si—O—Si—R_n, or a silanol R_n—Si—OH. If n=2, the resin will probably be a typical linear silicone fluid, while if n=1, cross-linking between silicone chains may occur, and a silicone solid will result. Interesting polymers are formed when mixtures of compounds are employed in which n is 1, 2 and 3 (i. e., mixtures where n=1 and 2, or 1 and 3, or 2 and 3). The preparation of silicone resins is now well understood, and beyond the scope of this invention. The discussion by Hardy and Megson, Quarterly Reviews, 2, 25 (1948), is of assistance in determining proper ratios of the resin components.

Moreover, the former may also react with a hydroxyl group of the cellulose molecule, yielding an ether of the form cellulose-O—Si—R_n, or possibly, in addition, cross-linkages between cellulose molecules, where n=1 or 2. Also, when n=1 or 2, reaction may occur with two or more hydroxyls of the same cellulose molecule. This cellulose-oxygen linkage is not stable to moisture, where R is an alkyl group of less than 3 carbons; in this case, upon hydrolysis a silicone polymer may be formed as set forth. However, the greater the number of carbon atoms in the R group, the more stable this ether bond is; when an R group of ten or more carbon atoms is present, it is quite resistant to hydrolysis, even by acid or base, and even appears to be more resistant to hydrolysis than the silicon-oxygen bond of the compounds of the invention.

When the compounds of the invention are applied to cellulosic or proteinaceous materials and then decomposed, it will be understood that any or all of the above chemical reactions may occur consecutively or simultaneously. Thus, any or all of these cellulose ethers may be formed:

$$[\text{Cellulose-O}]_{4-n}\text{—Si—}R_n$$

$$[\text{Cellulose-O—Y—O—}]_{4-n}\text{Si—}R_n$$

$$\text{Cellulose-O—Y—OH}$$

$$\text{Cellulose-O—Y—O-Cellulose}$$

$$[\text{Cellulose-O—}]_{3-n}\text{Si—O-Cellulose}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad R_n$$

$$[\text{Cellulose-O—Y—O}]_{3-n}\text{—Si—O—Si—O—Y—O-Cellulose}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad |\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad R_n\qquad R_n$$

One reaction may occur to the exclusion of the others. Also, additional reactions not yet understood and not set forth may be responsible in whole or in part for the improvement in properties obtained when the compounds of the invention are applied to textiles.

This reaction takes place with cellulosic materials as a class regardless of their physical form, whether fibers, roving, yarns, fabrics or films; typical natural cellulosic materials including cotton, flax, jute, hemp, ramie, linen, sisal, bast and wood pulp. Reaction also occurs with artificial cellulosic films and fibers such as regenerated cellulose, cellulose acetate, cellulose acetate butyrate, cellulose propionate, cellulose acetate propionate and ethyl cellulose. Apparently a similar reaction occurs with the protein molecule; the compounds give similar results with wool, silk, casein, albumen, alginate and like proteinaceous films or fibers, regardless of their stage of manufacture. They are also useful with synthetic fibers, such as nylon (i. e., polyamides) and vinyon (i. e., polyvinyl resins).

When the compounds of the invention are applied to cellulosic or proteinaceous textiles, the properties of the textile are modified depending upon the particular compound employed and the quantity of the compound deposited in or on the material. In general, the more compound employed, the more intense is the degree of improvement observed. Amounts between about 0.025% and about 20% by the dry weight of the treated textile are usually sufficient. Factors, other than quantity, influencing the modification of properties obtained are listed in the following table. It will be understood that any one or all of the factors listed for a given property may be utilized to introduce such property into the textile.

Property	Influencing Factor
Water repellency	Y=10 to 30 carbons. n=1 or 2. R=1 to 20 carbon alkyl group or an aromatic or cycloaliphatic group bearing such an alkyl group.
Dimensional stabilization	Y=6 to 12 carbons. n=1, 2, or 3. R=1 to 3 carbon alkyl.
Flame resistance	Y=halogen containing [1] group of 1 to 6 carbons. n=1 to 3. R=aromatic or cycloaliphatic halogen containing [1] group.
Crease resistance	Y=1 to 5 carbons. n=1, 2 or 3, or a mixture of 1 and 2, 1 and 3 or 2 and 3. R=1 to 3 carbon alkyl.
Softness	Y=1 to 30 carbons. n=2 or 3. R=1 to 3 carbon alkyl.

[1] The higher the proportion of halogen, the better the flame resistance.

Other finishing agents may be applied to the textile, as is described below.

THE PROCESS OF THE INVENTION

In brief, the textile material is treated with a solution or dispersion of a compound or mixture of compounds of the invention, and then subjected to a treatment adapted to bring about chemical reaction between the compound and itself and/or the textile molecule, i. e., the protein or the cellulose. Towards this end, the material may be subjected to an acid or alkali treatment, and/or heated or baked for a time and at a temperature sufficient to cure it. The solvent is wholly or partially removed by heat and/or in a vacuum. If desired, curing may be carried out simultaneously with solvent removal or drying. The cured material may be washed with acid or alkali to remove unreacted material and undesirable by-products of the reaction.

The conditions for carrying out the impregnation depend upon the nature of the material being treated, the compound and the concentration of the treating solution, and the type of finish desired. The compounds are ordinarily employed in the form of an aqueous solution or dispersion. If, however, the silicon-oxygen linkage is susceptible to hydrolysis at the treating conditions, substantial amounts of a tertiary amine may be added. For this purpose pyridine, quinoline, quinaldine, triethanolamine, and triethylamine are suitable. If tightly woven fabrics are to be treated, it is frequently advantageous to add to the treating solution a small quantity of alcohol, acetone or a wetting agent of the cationic or nonionic type, to assist penetration. Solutions of the compounds in organic liquids such as toluene, benzene, ethyl alcohol, pyridine, and ethylene dichloride, which may be anhydrous if desired, may also be employed.

The concentration of the treating solution depends upon the material being treated and the result desired. Soft finishes which impart only a small degree of water-repellency and flame resistance are obtained when the treating solution contains between about 0.1 and about 0.5% of the compound, while highly flame retardant, water repellent, soft finishes are obtained when the concentration is between about 0.5 and about 20% compound, depending upon the structure of the compound employed. The material may also be rendered crease resistant and dimensionally stable by use of treating solutions of these concentrations. These figures are based on a 100% pick-up of treating solution by weight of the material being treated. If a lower pick-up is obtained, the concentration of the treating solution should be increased proportionately. This is particularly true, for example, when tightly woven fabrics are being treated.

In order to prevent or minimize loss in tensile strength and tendering when cellulosic materials are treated with the compounds of the invention, the pH of the treating solution should be adjusted so that the cured treated material has a pH between 5 and 7.5, preferably 6 and 7. The pH of the cured material is considered as equivalent to that of the water extract obtained by immersing 20 grams of the cured material in 500 cc. of water for one-half hour. In most cases it will be found if the pH of the treating solution is between 5 and 10, good results will be had. Buffers, which preferably are non-volatile at the curing temperature used, and inert both to the compounds of the invention and to the textile material, are employed to maintain the pH of the treating solution at the desired value. Bases such as triethanolamine, diethanolamine, sodium acetate, ammonium acetate, pyridine, hexamethylene tetramine, and sodium formate, or acids such as lactic, glycolic or alpha hydroxybutanoic acids may be added to adjust the pH of the solution.

Other textile finishing agents may be added to the treating solution to give a fuller or stiffer handle to the material. Substances such as ammonium acetate, carragheen moss, gum tragacanth, natural resins and waxes, ammonium stearate or water-soluble cellulose derivatives, such as methyl, hydroxyethyl and sodium carboxymethyl cellulose, may be added. Other water repellent compounds may be added if desired, provided they do not diminish the effect of the compounds of the invention. Cationic quaternary ammonium compounds may be employed, for example, octadecyloxymethylpyridinium chloride, N,N'-di(chloropyridiniummethyl) paraphenylene di-carbamate, stearamidomethylpyridinium chloride and hexamethylene or decamethylene di(oxymethylpyridinium chloride). Where these additional agents are insoluble in water, they are frequently dispersed in the treating solution by the quaternary ammonium compounds of the invention, which also have detergent properties.

The treating operation is preferably carried out at temperatures below 40° C. if the compounds of the invention are readily decomposed in aqueous or organic solvent solutions or dispersions. More stable compounds may be applied at more elevated temperatures, in some cases even at the boiling point, but even the most stable compounds tend to hydrolyze when kept at such temperatures for any extended period of time, and give a less satisfactory finish not as resistant to organic solvents. In general, therefore, the treating operation is carried out at between 10° and 40° C.

The treatment is carried out by padding or soaking the material in the treating solution or dispersion. Conventional 2 or 3 roll padders may be used. The material is preferably subjected to pressure during or after treatment in order to insure thorough impregnation. Surplus liquor is removed by squeezing or hydroextracting. When the textile material is being dimensionally stabilized and/or crease-proofed, an effect obtained with certain of the compounds of the invention, it is then stretched while still wet to its original dimensions so that drying and baking may be carried out while the material is under tension. This stretching step is unnecessary when the material is merely to be rendered flame retardant and/or water-repellent.

In this connection, it should be noted that the effects of the treatment are not always entirely fast to severe laundering. For this reason it is important that the treatment be applied to the fabric in its normal, relaxed state, i. e., its normal dimensions. If treatment and curing are carried out with an over-stretched fabric, the latter will be stabilized at its extended size. When the stabilization effect is worn off on laundering, the fabric will then shrink to its normal, relaxed size. On the other hand, if the process is carried out on a fabric in its normal dimensions, the gradual loss of finish during laundering will not cause shrinkage.

From this point on, the process followed must take into consideration the particular compound employed and the finish desired, that is, whether

it is desired to decompose the compound at the quaternary ammonium group only, or both it and the silicon-oxygen linkage.

It is not necessary to hydrolyze the silicon-oxygen linkage. When it is stable to hydrolysis, permanent water-repellency, softness and flame retardance may be imparted by merely decomposing the quaternary ammonium group in situ on the textile. In this event the impregnated textile is dried at a temperature low enough to inhibit decomposition of the quaternary ammonium group (see later) and then cured. This procedure gives good results with compounds such as octadecyldimethyl(ethoxypyridinium chloride) silane and trimethyl(octadecyloxypryridinium chloride) silane.

When it is desired to hydrolyze the silicon-oxygen linkage as well, it is possible by suitable steps first to bring about decomposition of the quaternary ammonium halide group, and then to hydrolyze the silicon-oxygen linkage. In this procedure, the impregnated textile is dried, cured at a temperature between about 80 and about 200° C., impregnated with a solution adapted to hydrolyze the silicon-oxygen linkage, and then warmed at 40° to 150° C. and cured a second time at temperatures from about 80 to about 250° C. This procedure gives consistently good results with most of the compounds of the invention. It does require two impregnation, drying and two baking steps, however.

Alternatively, both decompositions may be caused to occur simultaneously, or hydrolysis of the silicon-oxygen linkage may be made to occur first.

These procedures are quicker and more economical, since in the latter case the hydrolysis of the silicon-oxygen linkage may be made to occur in the first textile treating bath or directly thereafter, and the subsequent chemical reactions carried nearly to completion before the textile is dried, and then completed during the baking step, at which time decomposition of the quaternary ammonium salt also occurs, while in the former case both decompositions are made to occur during the first curing step. These procedures have the advantage of requiring only one impregnation, drying and curing.

If the impregnated textile material is heated at temperatures above about 100° C. while still wet, premature decomposition of the quaternary ammonium group may occur. It is usually important that this be prevented, since in many instances no permanent effect may thereafter be obtained. In such cases, it is best to first dry the fabric thoroughly so that baking and curing may be carried out in the absence of moisture. Thick or tightly woven fabrics especially must be dried with care, for they tend to retain moisture for a long period of time, even at elevated temperatures. The drying temperature is preferably between 30 and 80° C., but the temperature of drying is less important than the speed and other conditions. If the fabric is dried in more or less stagnant air, as in an oven without artificial circulation, it should not be submitted to a drying temperature of more than 30° C. When, on the other hand, it is dried in a blast of hot air so that the water may be removed rapidly, say in about 3 minutes, then the drying temperature may rise to 80° C. Again, when the treated material is dried on a steam-heated cylinder at 120° C., no permanent effect may be obtained.

The curing or baking temperatures should be between 80° and 260° C. For decomposition of the quaternary ammonium salt, temperatures between 80° and 150° C. are preferred, while curing of the silicone-containing reaction products may require temperatures up to 50° C. to 100° C. higher; that is, the preferred range in this case lies between 100 and 250° C. The time of baking is inversely proportional to the temperature used, and both depend to some extent on the nature of the compound and of the textile material. A longer baking time and a relatively low temperature should be used with thick or tightly woven fabrics in order that the heating may be uniform throughout, while open weave fabrics or fabrics of synthetic fibers, such as nylon, may safely be heated at higher temperatures. If tendering of the material is to be avoided, the time of baking is preferably kept as short as possible and the baking temperature as low as possible.

In the case of open weave fabrics, if a brisk circulation of air is provided around and through the material, the preliminary drying step may be omitted and the treated material heated at once at the baking or curing temperature.

The drying operation may be carried out in a covered tenter frame, while curing or baking is best carried out on a loom, mat, roll or air lay dryer.

Hydrolysis of the silicon-oxygen linkage, which is usually accompanied by polymerization and other chemical interaction of the hydrolysis products if $n=2$ or 1, may be carried out in aqueous neutral, alkaline or acidic media at room or elevated temperatures. It may therefore occur spontaneously in the, initial treating solution. Addition of a substantial amount of a tertiary amine, from 0.5 to 1.5 moles of the amine per mole of the compound, seems to inhibit either the hydrolysis or the subsequent chemical reactions; upon volatilization of the amine in a later heating step, both reactions proceed as though it had never been present. It may also be carried out after impregnation and/or curing while the textile is traveling through a bath of the hydrolysing media, or while the textile is wet with such a medium or its vapors.

Hydrolysis in neutral or alkaline solution favors formation of linear or cage type polymers, while hydrolysis in acidic media favors formation of cyclic silicon compounds. Acid hydrolysis may also be objectionable with cellulosic fabrics because tendering may result. It is desirable that only the stoichiometric amount of water to form the expected polymer be present, but this is not essential, and in fact is a condition almost impossible to attain after the compound has been applied to the textile.

Hydrolysis may be carried out at from 10° to 100° C., depending upon the ease of hydrolysis, as set forth previously. The reaction may be exothermic. Usually it is complete in 15 minutes to an hour, but it may require up to five hours. Solution pH values between about 5 and about 10 are preferred, but stronger solutions may be used where no fabric damage is caused. Bases such as sodium and ammonium hydroxide and acids such as hydrochloric or sulfuric are suitable.

The chemical reactions subsequent to hydrolysis are expedited by higher temperatures, and should also be conducted in the presence of moisture, and/or an acid or base. Following hydrolysis, and without rinsing, therefore, the treated textile may be warmed while keeping it

wet, as in a moist atmosphere, at from 40° to 150° C., for from 15 minutes to several hours, and then cured at 80° to 250° C. for a period of a few minutes to several hours. Again, possible damage to the fabric governs the temperature and time employed. The cured fabrics may be washed and/or rinsed, prior to or after final curing, to remove acid or base, by products and unreacted material.

Example 1

Dry ethylene oxide gas is bubbled slowly through one mole of trimethylchlorosilane contained in a three-neck flask fitted with calcium chloride tube, water cooled reflux condenser and gas inlet tube. Pressure inside the vessel is maintained a few millimeters above atmospheric and the chlorosilane is heated to boiling at the start of the reaction. The reaction is exothermic, so that no heating is required after reaction has begun. The reaction is permitted to continue for about two to three hours. The 2-chloroethoxy trimethyl silane is recovered and purified by fractional distillation.

The procedure is repeated using trichloromethyl silane, and the trichloroethoxymethyl silane likewise is recovered and purified by fractional distillation.

Pyridinium hydrochloride is prepared by bubbling dry hydrogen chloride gas into a solution of pyridine in dry benzene. The pyridinium salt of each of the ethoxy silanes is prepared by pouring the silane slowly, with constant stirring, into the pyridinium hydrochloride solution and then warming it at 40° to 80° C. until the quaternary pyridinium salt precipitates. The precipitated salt is filtered off and dried in vacuo. The salts have the formulae:

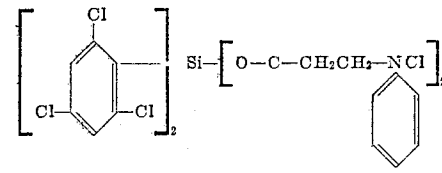
$$(CH_3)_3SiOCH_2CH_2NC_5H_5Cl$$
$$CH_3Si[OCH_2CH_2NC_5H_5Cl]_3$$

Equal parts of each salt, together with an equal weight of pyridine, are dissolved in water to form a ten per cent solution. The pH of the solution is adjusted to 8.0 by addition of a small amount of triethanolamine. A cotton twill fabric is padded with the solution at room temperature to a 100% pick-up by weight. The treated fabric is warmed at 60° C. until dry and baked at 120° C. for three minutes. The fabric is then padded with a 0.3 per cent solution of sodium hydroxide, heated at 40° C. During passage, the temperature of the wet cloth rises spontaneously to 60–65° C. Next, the fabric is removed from the padder and allowed to stand at room temperature in a moist atmosphere for two hours. It is then dried and cured by heating at 150° for 15 minutes. Finally, the fabric is washed with a soap solution, rinsed and dried. The material is water repellent, and also has good crease-resistance, dimensional stability and shrinkage resistance.

Example 2

One mole of di-(1,3,5-trichlorophenyl) dichloro silane is heated to 60° C. in a three-neck, round bottom flask fitted with calcium chloride tube, reflux condenser and gas inlet. Ethylene oxide gas is bubbled through the mixture until reaction is complete, which requires about three to six hours. The mixture is distilled and the di-(2-chloroethoxy) di(1,3,5-trichlorophenyl) silane recovered.

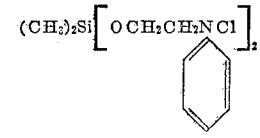
One mole of the silane is dissolved in 350 cc. of dry benzene together with one mole of pyridine. Dry hydrogen chloride gas is bubbled through this solution while warming it at 50° C. until formation of the corresponding pyridinium chloride of the formula:



The compound is dissolved in a mixture of equal parts of pyridine and anhydrous ethanol to form an eight per cent solution. A viscose rayon fabric is padded with this solution to a hundred per cent pick-up by weight. The fabric is then passed through a bath containing 1% sodium hydroxide solution and held at a temperature of 50° C., at a rate such that each section of the cloth remains in the solution for one-half hour. The wet cloth is warmed at 60° C. for another hour in a moist atmosphere to prevent evaporation. The fabric is dried at 60° C., baked at 150° C. for 15 minutes, and rinsed. The resulting fabric is flame resistant and shows improved water repellency, both of which are permanent to washing.

Example 3

200 parts of ethylene chlorohydrin and 220 parts of dry pyridine are heated together for 24 hours at 100° C., care being taken to exclude moisture. One mole of dimethyl dichloro silane is placed in a 3-liter, 3-necked flask fitted with a dropping funnel, calcium chloride tube and reflux condenser. To this is added, with cooling and over a period of two and one-half hours, the hydroxyethyl pyridinium chloride solution. The mixture is warmed at 60° until evolution of hydrogen chloride ceases, and then subjected to a vacuum to remove hydrogen chloride and excess pyridine, together with unreacted silane, and the pyridinium salt recovered. This salt has the formula:



This procedure is repeated using trimethylchlorosilane.

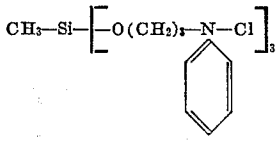
One part of trimethyl (ethoxy pyridinium chloride) silane and two parts of dimethyl (diethoxy pyridinium chloride) silane are dissolved in a solution containing equal parts of pyridine and water, to form a five per cent solution. This solution is padded on a wool fabric to a 100% pick-up by weight. The fabric is dried at 50° C. and then baked at 130° C. for 5 minutes. The cured fabric is immersed in a 0.5% sodium hydroxide solution and traveled slowly through the solution so that each portion of the fabric remains in the solution for one hour. The temperature of the bath is held at 40° to 50° C. during the treatment. The fabric is then removed from the bath and allowed to remain in a humid oven at a temperature of 60° C. for two hours. The fabric is dried and cured at 175° C. for twenty minutes. The treated fabric has improved dimensional stability and is water repellent.

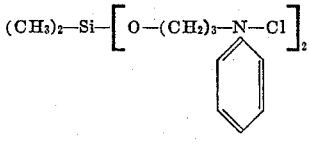
A nylon fabric treated in the same way and baked at 205° C. for five minutes in the final step likewise has increased water repellency.

Example 4

Propylene oxide is bubbled into a mixture of

methyl trichlorosilane and dimethyl dichlorosilane held at 60° C., according to the procedure set forth in Example 1, until reaction is complete. The solution is then distilled to recover the mixture of propoxy silanes. The silanes are then added to a solution of pyridinium hydrochloride in benzene and the mixture warmed at 50° C. for one hour to form the corresponding pyridinium chlorides of the formulae:

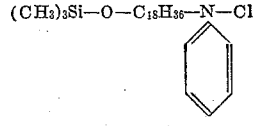




These are dissolved in a mixture of equal weights of water and pyridine to form a ten per cent solution. An acetate rayon gabardine fabric is padded with the solution to 100% pick-up weight. The treated fabric is dried at 70° C. and then cured at 140° C. for 5 minutes. The cured fabric is immersed in a bath containing 1.5% aqueous sodium hydroxide, warmed at 50° C., for one hour. It is then warmed in a humid atmosphere in an oven at 60° C. for three additional hours and finally dried and cured at 160° C. for 20 minutes. The resulting fabric is water repellent, crease resistant and dimensionally stable.

Example 5

One mole of ω-chloroctadecanol and 250 parts of pyridine are heated together for 24 hours at 100° C., care being taken to exclude moisture. The solution is added dropwise to two moles of trimethylchlorosilane contained in a three-necked, 2-liter flask fitted with reflux condenser, dropping funnel and calcium chloride tube. The flask is kept at a temperature of 50° C. during the reaction and addition of the pyridinium halide continued over a period of three hours. Reaction is continued until evolution of hydrogen chloride ceases. The mixture is then subjected to a vacuum to remove unreacted pyridine and trimethylchlorosilane. The quaternary pyridinium halide is recovered. This compound has the formula:

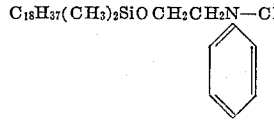


This compound is dissolved in water to form an eight per cent solution whose pH is adjusted to 8 by addition of triethanolamine. A cotton poplin fabric is padded with this solution to a 100% pick-up by weight. The fabric is dried at 60° C. and then baked at 130° C. for 3 minutes. The cured fabric is immersed in a 5% sodium hydroxide solution which is warmed to 60° C. Passage through the solution is regulated so that the fabric remains therein for one-half hour. The fabric, while still wet, is then warmed at 80° C. for an additional 30 minutes in a moist atmosphere and then heated rapidly to 150° C. and held at that temperature for 10 minutes. The resulting product is water repellent and shows improved dimensional stability.

Example 6

One mole of octadecyldimethylchlorosilane is placed in a three-neck, two-liter flask fitted with reflux condenser, calcium chloride tube and gas inlet tube. The silane is heated to 50–60° C. and ethylene oxide then bubbled through the mixture until reaction is complete. This may be evidenced by failure of the mixture to gain additional weight. The mixture is then subjected to a vacuum to remove unreacted silane. The octadecyldimethylchloroethoxysilane may be purified by fractional distillation at 2 millimeters pressure.

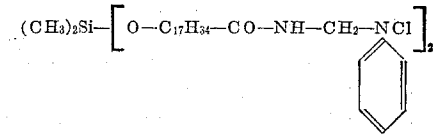
Pyridinium hydrochloride is prepared by bubbling dry hydrogen chloride into a solution of pyridine in dry benzene. The chloroethoxysilane is added slowly to this solution while warming the latter to 60° and with rapid stirring. The pyridinium halide which forms has the formula:



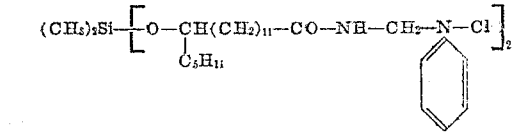
This compound is dissolved in water to form a 10% solution. A rayon fabric is padded with this solution to a 100% pick-up by weight, dried at 70° C. for one hour and then baked at 140° C. for 5 minutes. After rinsing, a sample of the fabric shows good water repellency. The remainder of the cured fabric is immersed in a bath containing an aqueous 1% solution of sodium hydroxide held at 65° C. and travelled through it at such a rate that a given portion remains in the bath for one-half hour. The fabric is then dried slowly at 80° C. and finally cured at 150° C. for 15 minutes, rinsed and dried. The treated fabric shows a somewhat better water repellency than the other sample, but both portions are satisfactory.

Example 7

One mole of dimethyldichlorosilane is placed in a three-necked two-liter flask fitted with stirrer, reflux condenser, dropping funnel and calcium chloride tube. To this is added dropwise a solution of ω- or λ-hydroxystearamide dissolved in petroleum ether. The reaction mixture is kept at a temperature of 60° C. and heating continued until evolution of hydrogen chloride ceases. To the solution is added one mole of paraformaldehyde. The mixture is heated to 40° C. and dry hydrogen chloride bubbled through the solution until the chloromethyl compound is formed. Water from the reaction is removed as it is formed by a trap affixed below the reflux condenser. Reaction is complete when no further water is liberated. The solvent and excess hydrogen chloride are removed by subjecting the solution to a vacuum and the chloromethyl compound so obtained is added dropwise to an excess of pyridine at 40° C. The precipitate which forms is separated and dried in vacuo. The ω-hydroxy derivative has the formula:



while the λ-hydroxy derivative has the formula:

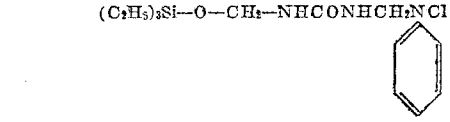


The compound is dissolved in water to form a 6% solution by weight. A cotton fabric is padded with this solution to 100% pick-up by weight, dried at 50° C. and then baked at 110° C. for one-half hour. The cured fabric is immersed in a bath containing 1% ammonium hydroxide solution for one and one-half hours. During this period the temperature of the bath rises to 35–40° C. The treated fabric is then warmed to 60° C. in a moist atmosphere, to prevent loss of water, for an additional hour, and is then dried, and cured at 125° C. for one hour. The product obtained using either compound is permanently water repellent and also shows a high degree of dimensional stabilization.

Example 8

One mole of triethylchlorosilane is placed in a three-necked round bottom flask fitted with mercury-sealed stirrer, calcium chloride tube and dropping funnel. The silane is warmed to 60° C. and to it is added, dropwise, with constant stirring, a solution of monomethylolurea in benzene. The mixture is heated at this temperature until evolution of hydrogen chloride ceases.

The mercury-sealed stirrer is replaced with a water-cooled reflux condenser. To the reaction mixture is added one mole of paraformaldehyde dispersed in dioxane and dry hydrogen chloride is then bubbled through the mixture. Water which is liberated is separated as it is formed in a trap affixed below the reflux condenser. Reaction is continued by warming the mixture at 60° C. until evolution of water has ceased. Excess hydrogen chloride gas and solvent are removed by subjecting the mixture to a vacuum and warming at 40° C. The compound which separates is added in small amounts to an excess of pyridine with rapid stirring, and the resulting mixture warmed gently at 50° C. for a short period. The pyridinium chloride, of the formula



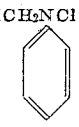
is recovered and dried in vacuo.

This procedure is repeated with dimethyldichlorosilane in place of triethylchlorosilane, and the analogous salt obtained.

Both compounds, in the ratio of one part of the former to two parts of the latter, are then dissolved in a solution containing equal weights of water and pyridine to form a 10% solution by weight. Cotton, wool and rayon fabrics are individually padded with this solution at room temperature to a 100% pick-up by weight and dried at 60° C. The dry fabrics are heated at 125° C. for ten minutes and divided into two portions. One portion is passed slowly through a bath heated to 50° C. and containing aqueous 2% sodium hydroxide solution. The travel time of the cloths through the bath is one hour. The other portion of the cloths is passed through a bath heated to 40° C. containing 2% hydrogen chloride solution. All the cloths are held at 60° C. in a moist atmosphere for one hour, and then baked at 150° C. for 20 minutes, and rinsed. The products show a high degree of permanent water repellency, crease-resistance and dimensional stability.

Example 9

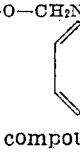
Dimethyldi(oxylaurylcarbamylmethylene pyridinium chloride) silane, of the formula:



is prepared using the procedure of Example 7, ω-hydroxylauryl carbamate being employed instead of ω-hydroxystearamide. This compound is dissolved in water to form an 8% solution by weight. A rayon-cotton gabardine fabric is padded with this solution to a 100% pick-up, dried at 80° C., and then baked at 110° C. for 5 minutes. The cured fabric is padded with a 2% sodium hydroxide solution at 60° C., allowing it to remain in the bath for 20 minutes, and then warmed, while still wet, at 60° C. for two hours and cured at 160° C. for 15 minutes. The resulting fabric is permanently water repellent.

Example 10

To one mole of 1,10-decamethyleneglycol in a three-necked, two-liter, round bottom flask fitted with mercury-sealed stirrer, calcium chloride tube and dropping funnel, is added, dropwise, over a three-hour period, one mole of dimethyloctadecylchlorosilane. Reaction is continued at 60° C. until evolution of hydrogen chloride ceases. Excess hydrogen chloride is then removed in a vacuum, the reaction mixture is dissolved in benzene, and one mole of paraformaldehyde added. The stirrer is replaced with water reflux condenser and the dropping funnel with a gas inlet tube. Dry hydrogen chloride gas is bubbled through the mixture, which is heated to reflux, until the solution becomes clear. Water which forms in the course of the reaction is removed by a trap affixed below the reflux condenser. The mixture is then subjected to a vacuum to remove benzene and excess paraformaldehyde and hydrogen chloride. The product is added in small amounts to an excess of pyridine, and the mixture warmed until the pyridinium chloride separates. This is filtered and dried in vacuo. This compound has the formula:

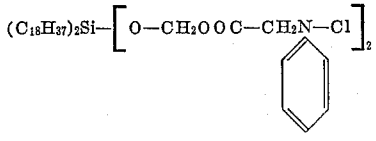


A sufficient quantity of the compound is dissolved in a mixture of equal weights of pyridine and water to form a 5% solution, which is then applied to a rayon fabric. The fabric is dried at 50° C. and cured at 110° C. It is then passed slowly through a bath held at 75° C. and containing an aqueous 2.5% sodium hydroxide solution, so that the travel time is one hour. The cloth is squeezed to a 100% pick-up and then rinsed and finally baked in a humid atmosphere or with steam at 100° C. for one hour and at 150° C. for 15 minutes. The cured cloth is rinsed and dried. The product is permanently water repellent and dimensionally stable.

Example 11

One mole of dioctadecyldichlorosilane is placed in a three-necked flask fitted with mercury-

sealed stirrer, calcium chloride tube and dropping funnel, and heated to 60° C. To this is added, dropwise, over a three-hour period, with constant stirring, one mole of hydroxymethyl α-chloro acetate. Heating is continued until evolution of hydrogen chloride ceases. The reaction product is subjected to a vacuum in order to remove hydrogen chloride gas, and is then added slowly, in small quantities, to an excess of pyridine heated to 40° C. The pyridine solution is then warmed to 60° C. until separation of pyridinium halide, which has the formula:



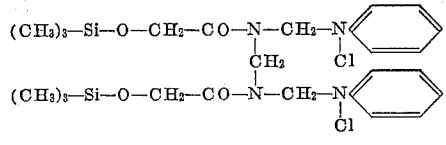
This compound is applied to a cotton fabric using the procedure set forth in Example 10. The treated fabric shows excellent water repellency.

Example 12

Two moles of hydroxy acetamide are added in small portions to 2 moles of trimethylchlorosilane, heated to 60° C. in a three-necked flask fitted with mercury-sealed stirrer, reflux condenser, calcium chloride tube and dropping funnel. Heating is continued until evolution of hydrogen chloride ceases. The product is subjected to a vacuum to remove hydrogen chloride and unreacted chlorosilane.

1.5 moles of the silane is then heated with 0.75 mole of paraformaldehyde in a vacuum until evolution of water ceases. (See French Patent No. 782,330.) The product is recrystallized from carbon tetrachloride.

One mole of the resulting diamidomethane and one mole of paraformaldehyde are mixed with 300 parts of benzene. The mixture is heated at 60° C. and stirred. Dry hydrogen chloride gas is passed in, until when a test portion is cooled no solid is seen to separate. The mixture is allowed to settle and the benzene solution is removed from the lower aqueous layer. Benzene and hydrogen chloride gas are removed under reduced pressure and the chloromethyl compound recovered. This is added in small amounts to an excess of pyridine. The pyridine is warmed at 60° C. until the pyridinium halide separates. This is filtered off and dried. It has the formula:

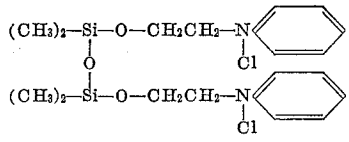


This compound is dissolved in a solution containing equal weights of pyridine and water, to form an 8% solution by weight. This solution is applied to a rayon fabric using the procedure of Example 5. The resulting product is permanently water repellent.

Example 13

1,1,3,3 - tetramethyl - 1,3,di - 2 - chloroethoxydisiloxane is prepared by adding 200 cc. of cold water to a cold mixture of 2 moles of dimethyl-2-chloroethoxychlorosilane and 1.3 moles of pyridine. The two layers which form are separated, and the upper layer washed several times with 15% sodium hydroxide solution and then dried over calcium chloride. Unreacted silane is removed by fractional distillation in vacuum.

The disilicate is then added in small portions to an excess of pyridine and the resulting mixture warmed at 60° C. until separation of the pyridinium chloride, which has the formula:



This compound is dissolved in a solution containing equal weights of water and pyridine to form a 5% solution. A rayon fabric is padded with this solution to 100% pick-up by weight. It is then dried at 60° C. and cured at 130° C. for 3 minutes. The cured fabric is rinsed and then immersed in 1% aqueous sodium hydroxide solution for one hour at 60° C. It is then warmed in an oven at 60° C. in a humid atmosphere, dried and cured at 150° C. for 15 minutes. The resulting product is water repellent and shows improved shrink resistance.

Example 14

One part of trimethyl(ethoxy pyridinium chloride) silane and two parts of dimethyl di(ethoxy pyridinium chloride) silane are dissolved in water, to form an eight per cent solution. The pH of this solution is adjusted to 9 by addition of triethanolamine. This solution is padded at room temperature on a cotton-rayon fabric to a 100% pick-up by weight. The fabric is heated in an oven at 100° C. in steam of a humid atmosphere for one-half hour, dried and then baked at 150° C. for 15 minutes and rinsed. The treated fabric is dimensionally stable and water repellent.

Example 15

Equal parts of methyltriethoxy pyridinium chloride silane and dimethyldiethoxy pyridinium chloride silane, together with an equal weight of pyridine, are dissolved in water to form a ten per cent solution. The pH of the solution is adjusted to 8.5 by addition of a small amount of triethanolamine. A rayon fabric is padded with the solution at room temperature to a 100% pick-up by weight. The treated fabric is then warmed at 80° C. for one hour in a moist atmosphere, dried, and baked at 120° C. for one hour and at 160° for three minutes, rinsed and dried. It then exhibits good water repellency and crease resistance.

Example 16

A mixture of methyl tri(propoxypyridiniumchloride) silane and trimethyl propoxy pyridinium chloride silane, prepared according to the procedure set forth in Example 1, is dissolved in water in the presence of an equal weight of pyridine to form a six per cent solution. A rayon fabric is padded with the solution to 100% pick-up by weight. The treated fabric is warmed at 70° C. for one hour and then at 85° C. for one hour in a humid atmosphere, and then cured at 140° C. for 35 minutes. The cured fabric is rinsed and dried. It exhibits permanent water repellency, crease resistance, and dimensional stability.

Example 17

Trimethyl(ethoxytributyl quaternary ammonium chloride) silane is dissolved in water to form an eight per cent solution whose pH is adjusted to 9 by addition of triethanolamine. A cotton fabric is padded with this solution to a 100% pick-up by weight. The fabric is warmed in a

humid atmosphere at 60° C. for one and one-half hours, dried, and then baked at 150° C. for 15 minutes, washed with soap solution and rinsed. The resulting product is permanently water repellent.

Example 18

Octadecyldimethyl(ethoxy pyridinium chloride) silane is dissolved in water to form a 10% solution. A rayon fabric is padded with this solution to a 100% pick-up by weight, dried at 70° C. and then baked at 140° C. for 5 minutes, washed with aqueous 10% sodium bicarbonate solution, rinsed and dried. The cured fabric is then permanently water repellent.

Example 19

Trimethyl(oxystearamidomethyl pyridinium chloride) silane is dissolved in water to form an 8% solution by weight. Wool and cotton fabrics are padded with this solution to 100% pick-up, dried at 50° C. and then baked at 110° C. for 15 minutes, washed with soap solution, rinsed and dried. The resulting products are permanently water repellent.

The following is claimed:

1. Compounds having the general formula:

$$R_n\text{—}Si[\text{—}O\text{—}Y\text{—}N(tert)X]_{4-n}$$

where n is an integer from 1 to 3; R is selected from the group consisting of saturated alkyl hydrocarbon radicals, alicyclic hydrocarbon radicals and aryl hydrocarbon radicals having from 1 to about 20 carbon atoms; Y is a bivalent bridging radical selected from the group consisting of alkylene arylene and cycloalkylene hydrocarbon radicals having from 1 to about 30 carbon atoms; N(tert) is a tertiary amine selected from the group consisting of tertiary aliphatic amines and tertiary heterocyclic amines; and X is a chlorine atom.

2. Compounds having the formula

$$R_nSi[O(CH_2)_yNC_5H_5Cl]_{4-n}$$

where n is an integer from 1 to 3, R is an alkyl hydrocarbon radical having less than 20 carbon atoms, and y is an integer from 1 to 30.

3. Trimethyl(ethoxy pyridinium chloride) silane.

4. A process of treating organic textile materials to modify the physical characteristics thereof which comprises impregnating said material with from about 0.1 per cent to 20 per cent by weight of said material of a compound of claim 1 in aqueous solution, drying said material at a temperature of less than about 100° C., and heating said material to a temperature of from 80° to 260° C. to decompose the quaternary ammonium compound while leaving the siloxy linkage intact and to bond the reaction products to the material.

5. A process of treating organic textile material to modify the physical characteristics thereof which comprises impregnating said material with from about 0.1 per cent to 20 per cent by weight of said material of a compound of claim 1 in aqueous solution, drying said material at a temperature of less than about 100° C., heating said material to a temperature of from 80° to 260° C. to decompose the quaternary ammonium compound, then hydrolyzing the silicon-oxygen linkage of said compound, warming said material at a temperature of from about 40° to 150° C. and, finally, heating said material to a temperature of from 80° to 250° C. to bond the reaction products to said material.

6. A process of treating organic textile material to modify the physical characteristics thereof which comprises impregnating said material with from about 0.1 per cent to 20 per cent by weight of said material of a compound of claim 1 in aqueous solution, hydrolyzing the silicon-oxygen linkage of said compound, warming said material at a temperature of from 40° to 80° C., drying said material at a temperature of less than 100° C. and, finally, heating said material at a temperature of from 80° to 250° C. to bond the reaction products thereto.

7. The process as in claim 6 wherein the solution with which said material is impregnated has a pH of from about 5 to 10 whereby said hydrolysis is effected concurrently with said impregnating step.

JOHN ROBERT JANES.

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