United States Patent Office 2,738,290 Patented Mar. 13, 1956

2,738,290

PROCESS OF TREATING TEXTILES AND TEXTILE TREATING COMPOUND

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No Drawing. Application October 1, 1951, Serial No. 249,225

11 Claims. (Cl. 117—65)

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, being a continuation-in-part of my application, Serial Number 74,262, now abandoned.

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 difficclt 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 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 at the quaternary ammonium group, 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.

THE COMPOUNDS OF THE INVENTION

They are characterized by the formula:

$$RnSi[—Y—N(tert)X]_{4-n}$$

where n is an integer from 1 to 3, R is a saturated alkyl or aralkyl group preferably containing about 1 to 10 carbon atoms.

Y is a bivalent aliphatic radical preferably of 1 to about 10 carbon atoms and may, for example, be methylene, propylene, butylene or decylene. Y cannot be ethylene because of the "beta effect" discovered by

Somer et al., J. A. C. S., 68, 1083 (1946), hereinafter more fully described.

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 and isoquinoline; those in which two nitrogen valences are taken up in one ring, as in piperidine and tetrahydroquinoline 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 hexyl, whether n-, secondary or tertiary. R may, for example, be methyl, ethyl, propyl, butyl, hexyl or decyl. X may be either bromine, chlorine or fluorine.

These compounds may be prepared from the corresponding halogenosilane and tertiary amine:

$$RnSi(—Y—X)_{4-n} \xrightarrow{N(tert)} RnSi(Y—N(tert)X)_{4-n}$$

The halogenosilanes may be prepared as follows:

$$SiX_4 + 4-n(YHMgX) \longrightarrow (YH)_{4-n}SiX_n$$

$$(YH)_{4-n}SiX_n + SO_2X_2 \xrightarrow[\text{Peroxide}]{\text{Benzoyl}} (YX)_{4-n}SiX_n$$

$$(YX)_{4-n}SiX_n + nRMgX \longrightarrow R_nSi(YX)_{4-n}$$

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 Rn—Si—Y$_{4-n}$—. It may also be hydrolyzed by water at temperatures as low as 60° C. to 80° C., forming these products.

The silicon-carbon linkage is hydrolyzable, but its ease of hydrolysis depends upon the numbe of carbon atoms of the —Y— group attached to the silicon atom. When Y is methylene, the linkage is hydrolyzed more or less rapidly by dilute alkali or acid at room temperature, and the hydrolysis is exothermic.

During treatment, apparently 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

$$Cellulose—O—Y—Si—Rn$$

Where two or more quaternary ammonium groups are present, cross linkages between cellulose molecules may be found.

Moreover, if Y is CH_2, this ether may also hydrolyze to give the radical ≡Si—Rn and the ether Cellulose O—CH_2—. The latter may form a cross-linkage with another cellulose molecule. The RnSi— radical may polymerize to form a silicone resin, a siloxane,

$$Rn—Si—O—Si—Rn$$

or a silanol, Rn—Si—OH_{4-n}. 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.

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:

Cellulose—O—Si—R_3

Cellulose—O—YSi—R_3

Cellulose—O CH_2O—Cellulose

Cellulose—O—Si—O—Cellulose
R_2

Cellulose—O CH_2—OH

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 molecules; the compounds give similar results with wool, regenerated keratin, 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), Vinyon and Saran polyvinyl resins, Orlon polyacrylonitrile, and the like.

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.

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 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% pickup of treating solution by weight of the material being treated. If a lower pickup 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 material has a pH between 5 and 7.5, preferably 6 to 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, stearamido-methylpyridinium 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° C. 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 overstretched 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 at both it and the silicon-carbon linkage.

It is not necessary to hydrolyze the silicon-carbon linkage. When it is stable to hydrolysis, permanent water-repellency, softness, dimensional stability, crease resistance 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.

When it is desired to hydrolyze the silicon-carbon 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-carbon linkage. In this procedure, the impregnated textile is dried, cured at a temperature between about 80° C. and about 200° C., impregnated with a solution adapted to hydrolyze the silicon-carbon linkage, such as dilute aqueous sodium hydroxide, and then warmed at 40° C. to 150° C. and cured a second time at temperatures from about 80° C. 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-carbon linkage may be made to occur first. These procedures are quicker and more economical, since in the latter case the hydrolysis of the silicon-carbon 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° C. 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° C. and 260° C. For decomposition of the quaternary ammonium salt, temperatures between 80° C. and 150° C. are preferred, while curing of the silicon-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° C. 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-carbon 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 mols of the amine per mol 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 hydrolyzing 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 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° C. to 100° C., depending upon the case 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° C. to 150° C., for from 15 minutes to several hours, and then cured at 80° C. 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.

SYNTHESIS

The compounds operable in this invention may be synthesized as follows, considering, for example, the simplest member of the series, trimethylsilylmethylene pyridinium chloride:

$$SiCl_4+CH_3MgBr\rightarrow CH_3SiCl_3$$

$$CH_3SiCl_3+SO_2Cl_2\rightarrow ClCH_2SiCl_3$$

$$ClCH_2SiCl_3+3CH_3MgBr\rightarrow (CH_3)_3SiCH_2Cl$$

$$(CH_3)_3SiCH_2Cl+N(tert)\rightarrow (CH_3)_3SiCH_2N(tert)Cl$$

Specifically, to 1.5 mols of silicon tetrachloride dissolved in ether was added dropwise 1.5 mols of methylmagnesium bromide also dissolved in ether, the addition being made in the absence of moisture. After heating for 3–4 hours, the magnesium salts precipitate was filtered out, the filtrate recovered, and ether removed by distillation.

About 2 mols of methyl trichlorosilane were dissolved in 2 mols of sulfuryl chloride, a small quantity, i. e., about 0.5 gram, of benzoyl peroxide added to the solution, and the reactants refluxed for about 8 hours. The chloromethyltrichlorosilane was separated by distillation.

This product was reacted, with slight excess of methyl magnesium bromide, in the manner set forth above, with the exception that the reaction was carried out in the cold. The resulting solution was fractioned and the trimethylchloromethyl silane recovered.

One mol of trimethylchloromethyl silane was then reacted at a temperature of about 100° C. with 1.2 mols of the tertiary amine, in this case pyridine, under anhydrous conditions to prevent premature hydrolysis. The resulting viscous liquid was trimethylsilylmethylene pyridinium chloride.

By selecting a Grignard reagent the alkyl radical of which has the proper number of carbon atoms, the R and Y groups may be made of the desired length.

Where the alkyl group of the alkyl trichlorosilane contains 3 or more carbon atoms, the process is complicated by the fact that all of the possible chloro-substituted compounds, i. e., α-chloro-, β-chloro-, γ-chloro- and so on, are produced as a result of the reaction with sulfuryl chloride. In all cases, however, that fraction having highest boiling point is the one to be used. If, for example, propyltrichlorosilane is reacted with sulfuryl chloride, α-chloro-, β-chloro-, and γ-chloropropyltrichlorosilane having boiling points of 157° C., 162° C. and 178° C., respectively, are obtained. When the mixture is fractionated in a conventional column, the ratio of yields was about 1:3.5:3.

As has been mentioned heretofore, it has not been possible to produce by the above process an organohalogenosilane in which Y has two carbons. It appears that when the chlorine atom is attached to a carbon atom in a position β to the silicon, the beta C—Cl bond is just as reactive as the Si—Cl bond, so that in step 3 of the synthesis, the compound breaks down into ethylene, evolved as a gas, and the tetra-alkyl silane.

Example I

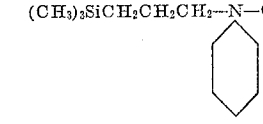
Trimethylsilylmethylene pyridinium chloride,

$$(CH_3)_3Si—CH_2NC_5H_5Cl$$

is dissolved in water to form a six per cent solution. The pH is adjusted to 8 by addition of a small amount of triethanolamine. A cotton twill fabric is padded with the solution at room temperature to a 100% pickup 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° C.–65° C. Next, the fabric is removed from the padder and heated in an oven at 60° C. in a moist atmosphere for two hours. It is then dried and cured by heating at 150° C. 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 II

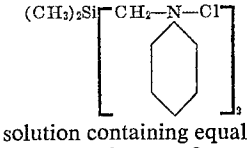
Trimethylsilylpropylene pyridinium chloride,



is dissolved in an aqueous alcohol solution to form an eight per cent solution. A viscose rayon fabric is padded with this solution to a hundred per cent pickup by weight. The fabric is then passed through a bath containing one per cent 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 140° 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 III

Dimethylsilyldi(methylene pyridinium chloride),



is dissolved in a solution containing equal parts of pyridine and water or ethanol to form a five per cent solution. This solution is padded on a wool fabric to a 100% pickup by weight. The fabric is dried at 50° C. and then baked at 130° C. for five minutes. The cured fabric is immersed in a 0.5% ammonium 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° C. 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 IV

An aqueous treating solution is prepared containing five per cent by weight of each of: Diethylsilyldi(methylene pyridinium chloride),

$$(C_2H_5)_2Si[CH_2NC_5H_5Cl]_2$$

and trimethylsilylmethylene pyridinum chloride,

$$(CH_3)_3Si—CH_2N—C_5H_5Cl$$

An acetate rayon gabardine fabric is padded with the solution to 100% pickup by 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 0.5% aqueous sodium hydroxide, and 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 150° C. for 20 minutes. The resulting fabric is water repellent, crease resistant and dimensionally stable.

Example V

Trimethylsilyldecamethylene pyridinium chloride,

$$(CH_3)_3SiC_{10}H_{20}—N—C_5H_5Cl$$

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% pickup by weight. The fabric is dried at 60° C. and then baked at 130° C. for 3 minutes, and then dried. It is then water-repellent.

Example VI

Dimethylpropylsilylmethylene pyridinium bromide,

$$C_3H_7(CH_3)_2SiCH_2N—C_5H_5Br$$

is dissolved in water to form a 10% solution. A rayon fabric is padded with this solution to a 100% pickup 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.

Example VII

Six grams of benzylmethylsilyldi(octamethylene pyridinium chloride),

$$C_6H_5CH_2(CH_3)Si—(C_8H_{16}—NC_5H_5Cl)_2$$

is dissolved in 94 grams of water to form a six per cent solution by weight. A cotton fabric is padded with this solution to a 100% pickup by weight, dried at 50° C. and then baked at 110° C. for one-half hour. The product obtained is permanently water repellent and also shows a high degree of dimensional stabilization.

Example VIII

Tri-(β-phenylethyl)silylpropylene pyridinium chloride,

$$(C_6H_5CH_2CH_2)_3Si—CH_2CH_2CH_2NC_5H_5Cl$$

is 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% pickup by weight and dried at 60° C. The dry fabrics are heated at 115° C. for ten minutes and then baked at 130° C. for 25 minutes, and rinsed. The products show a high degree of permanent water repellency, crease resistance and dimensional stability.

Example IX

Dimethylnapthylmethylsilylhexamethylene pyridinium chloride of the formula,

$$C_{10}H_7CH_2(CH_3)_2SiC_6H_{12}NC_5H_5Cl$$

is dissolved in water to form an eight per cent solution by weight. A rayon-cotton gabardine fabric is padded with this solution to a 100% pickup, dried at 80° C., and then baked at 110° C. for 5 minutes. The cured fabric is padded with a two per cent sodium hydroxide solution at 60° C., allowed to remain in the bath for 20 minutes, and then warmed, while still wet, at 60° C. for two hours and finally cured at 160° C. for 10 minutes. The resulting fabric is permanently water repellent and dimensionally stable.

Example X

A sufficient quantity of octadecyldimethylsilyldodecamethylene pyridinium fluoride,

$$C_{18}H_{37}(CH_3)_2Si—(CH_2)_{12}NC_5H_5F$$

is dissolved in a mixture of equal weights of pyridine and water to form a five per cent solution, which is then applied to a rayon fabric. The fabric is dried at 55° C. and cured at 150° C. for 15 minutes. The cured cloth is rinsed and dried. The product is permanently water repellent and dimensionally stable.

Example XI

A six per cent aqueous solution of dioctadecylsilyldi-(methylene pyridinium chloride),

$$(C_{18}H_{37})_2Si—(CH_2N—C_5H_5Cl)_2$$

is applied to a cotton fabric using the procedure set forth in Example X. The treated fabric shows excellent water repellency and dimensional stability.

The following is claimed:

1. Compounds having the formula:

$$RnSi[YN(tert)X]_{4-n}$$

where n is an integer of 1 to 3; R is selected from the group consisting of alkyl and aralkyl radicals; Y is an aliphatic hydrocarbon radical other than an ethylene radical; X is a halogen selected from the class consisting of bromine, fluorine and chlorine and N(tert)X represents a substituent group having no replaceable amine hydrogen and in which the nitrogen has a valence of five.

2. Compounds having the formula:

$$RnSi[YN(tert)X]_{4-n}$$

where n is an integer from 1 to 3; R is an alkylene radical containing from 1 to 10 carbon atoms other than an ethylene radical; Y is an alkyl radical containing from 1 to 10 carbon atoms; N(tert)X represents a substituent group having no replaceable amine hydrogen and in which the nitrogen has a valence of five; and X is chlorine.

3. Compounds having the formula:

$$(CH_3)_nSi[CH_2N(tert)Cl]_{4-n}$$

where n is an integer from 1 to 3 and N(tert)Cl represents a substituent having no replaceable amine hydrogen and in which the nitrogen has a valence of five.

4. A compound having the formula:

$$(CH_3)_nSi[(CH_2)_yN(tert)X]_{4-n}$$

where n is an integer from 1 to 3; y is an integer from 3 to 10; N(tert)X is a substituent group having no replaceable amine hydrogen and in which the nitrogen has a valence of five and X is chlorine.

5. A compound having the formula:

$$(CH_3)_3SiCH_2CH_2CH_2N(tert)Cl$$

where N(tert)Cl is a substituent group having no replaceable amine hydrogen and in which the nitrogen has a valence of five.

6. A compound having the formula:

$$(CH_3)_3SiCH_2N(tert)Br$$

where N(tert)Br is a substituent group having no replaceable amine hydrogen and in which the nitrogen has a valence of five.

7. A process of treating organic textile materials for the purpose of improving the crease resistance, dimensional stability, water repellency and flame resistance thereof, which comprises impregnating said textile material with a compound of claim 2 and subsequently subjecting the impregnated material to a heat treatment at a temperature within the range from about 40° C. to 250° C., lower than will damage the textile but high enough to decompose the compound to form organic silicon-containing residue and permanently bond said residue to the textile.

8. A process of treating organic textile materials for the purpose of modifying the physical characteristics thereof which comprises impregnating said material with a compound in accordance with a compound of claim 1, hydrolyzing the silicon-bridging radical link of said compound, and then subjecting said material to a heat treatment at between about 40° C. and 250° C.

9. The process for treating organic textile materials in order to improve the water repellency, dimensional stability, flame resistance and crease resistance thereof, which comprises impregnating said material with a solution of the compound of claim 1, drying said material at a temperature from about 30° C. to 80° C., and subjecting said impregnated material to a heat treatment at a temperature of about 80° C. to 150° C. in order to decompose the quaternary ammonium salt while leaving the Si—Y linkage intact.

10. The process for treating organic textile materials

in order to improve the characteristics thereof, which comprises impregnating said material with a solution of the compound of claim 1, drying said material at a temperature less than 100° C., subjecting said material to a heat treatment at a temperature of about 100° C. to 200° C. to decompose the quaternary ammonium salt, impregnating said material with a hydrolyzing medium, and then subjecting said material to a second heat treatment at a temperature of about 100° C. to 250° C. in order to bond the reaction product to said material.

11. The process for treating organic textile materials to improve the physical characteristics thereof which comprises impregnating said material with a solution of the compound of claim 1, the pH of said impregnating solution being at about 5 to 10, maintaining said material in a

humid atmosphere at a temperature less than 80° C., drying said material, and subjecting said material to a heat treatment at a temperature of about 100° C. to 250° C.

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