CERTAIN PERFLUORO ALKANAMIDO-, PERFLUOROALKANOXY-, PERFLUOROALKYLOXY- AND PERFLUORO MERCAPTO-QUATERNARY AMMONIUM COMPOUNDS, THE CORRESPONDING PYRIDINIUM COMPOUNDS AND DERIVATIVES THEREOF

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U.S. Cl. 260--295

10 Claims

ABSTRACT OF THE DISCLOSURE

Highly fluorinated quaternary ammonium compounds containing between the fluoro moiety and the quaternized nitrogen one of three linkages selected from the group

\[ O - \overset{-}{N} - CH_2 - \overset{\sim}{S} - CH_2 - \overset{\sim}{O} - CH_2 - \]

which represent carboxamido, thioether and acid groups respectively are provided which are outstanding for producing water repellent, oil repellent and soil repellent finishes on textiles as well as resistance to staining.

The present invention is a continuation-in-part Ser. No. 301,628 now abandoned, filed Aug. 12, 1963, and relates to "soil-proofing" textiles and to the "soil-proofing" quaternary ammonium compounds used and, more particularly to "soil-proofing" textiles with perfluoro quaternary ammonium compounds and to the perfluoro quaternary ammonium compounds per se.

For centuries man has sought to alleviate the discomfort concomitant with exposure to rain. It was not until about 1935 that there was any attempt to discover the factors controlling resistance to wetting by water. Prior to this time, textile materials were coated fabrics with various "cookbook" recipes such as rubber, linseed oil-rubber mixtures, empirical and whimsical synthetic dopes and other compositions having no basis in a discovery of the physical properties of a preparation which would impart to a textile the capability of water-repellency.

A large variety of such products are still in use as low-cost, non-durable water repellents for textiles. Since neither thermosetting nor fiber reaction occurs when textiles are coated with such products, the treated textile is non-durable to washing and dry cleaning. Other than water repellency for rainwear fabrics, such mixtures provide fabrics with a fair degree of spot and stain resistance to water-borne chromophoric materials.

The search for durable or permanent water repellents as contrasted with these non-durable water repellents, especially for cellulose fibers was initiated by the need to overcome the deficiencies of these wax emulsion-metallic salt mixtures.

While durable water repellents had been initially developed for outerwear and raincoat applications, it was soon recognized that durable water repellents could be used as finishes for other purposes. In the period 1950 to 1956 these durable water repellent finishes were widely used on men's suits, dress goods, and upholstery materials. When offering these products to the textile finishing trade, promotional emphasis was not placed on water-repellency but on spot-and-stain resistance. This use has continued to the present time. It had been observed that fabrics treated with such durable water repellents had a high degree of resistance to soiling by water-borne soils and stains and were easier to launder. The primary limitation of these finishes was that they attracted rather than repelled oily soils, and the treated fabrics were not resistant to staining by oily materials such as oils, greases, gravy, mayonnaise, etc.

Although fabric finishes capable of providing water- and oil repellency and resistance to staining by water- and oil-borne stains are important for wearing apparel, upholstery and the like, the capability of resisting staining by oily particulate soil is of greater importance for aesthetic, if for no other reasons. That is to say, the finely divided environmental grime mixed with the oil exudations of the human skin, i.e., oily particulate soil, in the neckband and cuffs of a man's shirt, are far more often encountered than soiling with gravy or mayonnaise.

It has now been discovered that chlorine resistant fluoroquaternary ammonium compounds having compositions corresponding to the following formula provide textiles with water-repellency, oil-repellency, resistance to staining by water-borne and oil-borne stains and the ability to shed dry soil:

\[ R', R'' \text{ and } R''' \text{ are alkyl groups having 1 to 6 carbon atoms of which two adjacent carbon atoms can form with the nitrogen a heterocyclic group having 5 or 6 carbon atoms or aromatic groups. } R', R'' \text{ and } R''' \text{ can be the same or different, e.g., two or three, } R' \text{ and } R'' \text{ can be alkyl or cyclo-alkyl groups and the other can be an aromatic group. } \Omega \text{ is an alkyl, aryl, alkyl-aryl or cyclo-alkyl radical having three to twenty-one carbon atoms and } 7 \text{ to } 50 \text{ of hydrogen atoms of which hydrogen atoms 70 to 100 percent are replaced by fluoriine atoms and the terminal carbon group preferably has three fluorine atoms attached thereto; and } R_4 \text{ is alkyl, hydroxyalkyl, aryl, halo-alkyl, or haloaryl.}

As used herein, the term chlorine resistant refers to the ability of the compound on the fabric, after bleaching with chlorine, to resist yellowing and fabric damage which normally occurs when fabric treated with non-chlorine resistant fluoro-quaternary compound is bleached during laundering and then is ironed.

The term textiles as used herein refers to fibers, yarns, woven fabrics, felted materials composed in part or in whole of cellulosic material such as cotton, synthetic cellulosic material such as regenerated cellulose, proteinaceous material such as wool or synthetic fibers such as nylon, fiberglass, acrylic, polyester fibers and non-woven fabrics. In addition, solid materials such as paper, wood, leather and the like may also be treated where it is desired to impart oil, water or any soil repellency.

The quaternary ammonium compounds are made by the classical methods of organic chemistry. The methods of preparation of these quaternary ammonium compounds form no part of the present invention. Hence, the preparation of these quaternary ammonium compounds need not be described in detail. It suffices to describe the preparation of N-hydromethyl-perfluoroctanamidomethyl pyridinium acetate as illustrative of the preparation of these
quaternary ammonium compounds having compositions corresponding to the formula:

\[
\begin{align*}
\text{CF}_3(\text{CF}_2)_5\text{COCl} + 2\text{NH}_3 & \rightarrow \text{CF}_3(\text{CF}_2)_5\text{CONH}_2 + \text{NH}_4\text{Cl} \\
\end{align*}
\]

where \( \text{X}, \text{R}', \text{R}'', \text{R}''' \) and \( \text{Q} \) have the significance noted hereinbefore under Formula B.

As described in U.S. Pat. No. 2,727,923, the perfluoroalkanoic acid amides can be obtained by reacting the acid chloride with a dialkyl amine to produce the \( \text{N}- \)substituted fluorocarbon amide. On the other hand, the simple amides can be produced by reacting the perfluoroalkanoic acid chloride with ammonia. Thus, reaction of pentadecafluorooctanoic chloride with ammonia yields the perfluoroalkanoic amide in a manner which can be represented by the Equation 1:

\[
\text{(1) } \text{CF}_3(\text{CF}_2)_5\text{CONH}_2 + \text{CNH}_2 + \text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CF}_3(\text{CF}_2)_5\text{CONH}_2 + \text{H}_2\text{O}
\]

The perfluorooctanoamidomethyl pyridinium acetate is then made chlorine resistant by reacting it with formaldehyde. The reaction can be represented by the Equation 2:

\[
\text{(2) } \text{CF}_3(\text{CF}_2)_5\text{CONH}_2 + \text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CF}_3(\text{CF}_2)_5\text{CONHCl} + \text{CH}_2\text{OH}
\]

Thus, 0.1 mol of pentadecafluorooctanamide, 0.15 mol of pyridine, 0.15 mol of 91 percent paraformaldehyde and fifty parts water by weight of glacial acetic acid were charged into a three neck flask having a stirrer and a condenser. The contents of the flask were heated to 112° C. After about thirty minutes at 112° C, all of the paraformaldehyde had dissolved to yield a clear yellow solution. After an additional one and one-half hours at a temperature in the range of 112° C. to 126° C., the reaction mixture was cooled to room temperature. The reaction vessel was settled out and was recovered. The reaction product was reacted with one mol equivalent of formaldehyde to make it chlorine resistant.

The prior art perfluoro-quaternary ammonium compounds described in U.S. Pat. No. 2,727,923 (Formula C) and U.S. Pat. No. 3,147,065 (Formula D) are not to be confused with the chlorine resistant fluoro-quaternary ammonium salts of this invention (Formula E):

\[
\text{(C) } \text{CF}_3(\text{CF}_2)_5\text{CONH}_2 + \text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CF}_3(\text{CF}_2)_5\text{CONH}_2 + \text{H}_2\text{O}
\]

where \( \text{n} \) has an integer value of 3 to 9 and the \( \text{R}'\text{s} \) are alkyl groups (which can be the same or different) that contain 1 to 5 carbon atoms.

\[
\text{(D) } \text{CF}_3(\text{CF}_2)_5\text{CONHCH}_2X
\]

wherein \( X \) is chlorine or bromine; \( R \) is a divalent radical selected from the group consisting of:

\[
\text{CH}_2\text{CHCl} \quad \text{CH}_2\text{Cl}
\]

and

\[
\text{(CH}_3)_2\text{CH}
\]

and

\[
\text{R}' \text{ is an integer from 1 to 10; and } \text{n} \text{ is an integer from 3 to 12.}
\]

\[
\text{CF}_3(\text{CF}_2)_5\text{CONH}_2 + \text{CH}_2\text{OH} + \text{H}_2\text{O}
\]

where \( \text{n} \) has an integer value of 3 to 21 even when \( \text{R}', \text{R}'' \) and \( \text{R}''' \) are the same as \( \text{R}', \text{R}'' \) and \( \text{R}''' \) in Formula C, and \( \text{R}', \text{R}'' \) and \( \text{R}'' \) and \( \text{R} \) and \( X \) having the meaning set forth in Formula B.

The quaternary ammonium compounds of the present invention react with the active hydrogen in the surface of the substrate even at low temperatures, e.g., 300° F. and lower and are substrate- or fiber-reactive. In addition, the quaternary ammonium compounds of the present invention endow the substrates to which they are affixed with water repellency when the number of carbon atoms in \( Q \) in the formula:

\[
\text{(E) } \text{CF}_3(\text{CF}_2)_5\text{CONRCH}_2N\text{R'} + \text{H}_2\text{O}
\]

is at least three. Furthermore, the quaternary ammonium compounds of the present invention have the highly desirable property of being chlorine resistant so that substrates to which they are affixed, in addition to being provided with water, oil and soil repellency properties, and are highly resistant during and after laundering, bleaching and ironing to yellowing and fabric damage.

By employing other starting materials, it is possible to readily prepare other compounds of the invention. Thus, one mol equivalent of \( \text{CF}_3 \) fluoroalcohol reacted with one mole equivalent of paraformaldehyde and one equivalent of morpholine when dissolved in xylene and heated to azotrope off the water to yield a reaction product which, after the xylene is removed by vacuum stripping, then reacted with one mole equivalent of benzyl chloride for about 3 hours, will yield another compound of the present invention. The product obtained is solid, is dispersible in hot water and when applied to textiles, provides desirable repellencies. The reaction can be represented by Equations 4 and 5:

\[
\text{(4) } \text{HCF}_2(\text{CF}_2)_5\text{CH}_2\text{OH} + \text{CH}_2\text{O} + \text{HNC}_2\text{H}_4\text{O} \rightarrow \text{HCF}_2(\text{CF}_2)_5\text{CH}_2\text{OCH}_2\text{NC}_2\text{H}_4\text{H}_2 + \text{H}_2\text{O}
\]

\[
\text{(5) } \text{HCF}_2(\text{CF}_2)_5\text{CH}_2\text{OH} + \text{CH}_2\text{H}_3\text{Cl} \rightarrow \text{HCF}_2(\text{CF}_2)_5\text{CH}_2\text{OH} + \text{H}_2\text{O}
\]

Similarly, one mol equivalent of perfluorooctanoic acid when refluxed with one mol equivalent of paraformaldehyde, one mol equivalent of pyridine and an excess of glacial acetic acid by refluxing yields a water-soluble product which when applied to cotton fabric produces satisfactory oil repellency. The reaction can be represented by Equation 6:

\[
\text{(6) } \text{CF}_3(\text{CF}_2)_5\text{COOH} + \text{CH}_2\text{O} + \text{H}_2\text{COOH} + \text{CH}_2\text{H}_3\text{Cl} \rightarrow \text{CF}_3(\text{CF}_2)_5\text{COOC} + \text{H}_2\text{O}
\]

Another product may be obtained by reacting one mol equivalent of perfluoroctyl mercaptan and one mol equivalent of paraformaldehyde in an excess of benzene by passing dry HCl gas into the mixture until the paraformaldehyde disappears. The water is the azotroped off and an intermediate product is obtained which when reacted with one mol equivalent of triethylamine provides an exothermic reaction. The reaction is heated until the theoretical chloride content has formed and the
mixture then cooled, and the compound of the invention crystallizes out and the crystals may be removed by filtering off the supernatant liquid and drying the crystals. When dissolved in water and added to cotton fabric the product provides desirable oil, water and dry soil repellencies to fabrics. The reaction for the preparation can be represented by Equations 7 and 8.

(7) \[ \text{C}_4\text{H}_8\text{CHSH} + \text{CH}_2\text{O} + \text{HCl} \rightarrow \text{C}_4\text{H}_8\text{CHSCHCl} + \text{H}_2\text{O} \]

(8) \[ \text{C}_4\text{H}_8\text{CHSCH}_2\text{Cl} + \text{N(C}_3\text{H}_5)_2 \rightarrow \text{C}_4\text{H}_8\text{CHSCH}_2\text{N(C}_3\text{H}_5)_2 \cdot \text{Cl}^- \]

Yet another product may be obtained by mixing one mole of pentadecafluoroacetyl alcohol with one mole of p-hydroxy benzoic acid in toluene, sodium methoxide is added as a catalyst and the mixture is heated to reflux temperature. Reflux is continued using an azeotropic separator to remove water as it is formed during esterification:

\[ \text{C}_2\text{F}_5\text{CHOH} + \text{HOOCC} \rightarrow \text{OH} \]
\[ \text{C}_2\text{F}_5\text{CHOCC} \rightarrow \text{OH} + \text{H}_2\text{O} \]

When the reaction is completed, one mole of paraformaldehyde is added to the solution. Then HCl gas is bubbled through the solution until the paraformaldehyde dissolves and the chloromethyl ether of perfluoroacetyl phenol ester has formed:

\[ \text{C}_2\text{F}_5\text{CHOOCC} \rightarrow \text{OCH}_2\text{Cl} + \text{H}_2\text{O} \]

The solution is cooled and one mole of triethyl amine is added slowly to form the fluorinated quaternary. This crystallizes out of solution as it is formed:

\[ \text{C}_2\text{F}_5\text{CHOOCC} \rightarrow \text{OCH}_3\text{N(CH}_3)_2 \cdot \text{Cl}^- \]

The resulting product is filtered, washed with cold alcohol and dried. When applied to textiles at 0.5 - 3.0% concentration it produces water, oil and soil repellency.

Still another product may be obtained by mixing one mole of perfluorobenzamide with one mole of paraformaldehyde and one mole of morpholine in xylol solution. The mixture is refluxed and water collected in an azeotropic separator. After 18 grams of water are collected, the solution is cooled to room temperature:

\[ \text{C}_2\text{H}_5\text{CONH} + \text{CH}_2\text{O} + \text{HN} \rightarrow \text{CH}_3\text{NH} \]
\[ \text{C}_2\text{H}_5\text{CONHCH}_3 \rightarrow \text{O} + \text{H}_2\text{O} \]

Then one mole of ethyl bromide is added. After heating at 50° C. for several hours, the crystalline quaternary settles out. It is filtered and washed and then dissolved in water. To the aqueous solution is added one mole of 37% formaldehyde. The solution is heated at 50°C. until the free formaldehyde content is less than 1%. The N-hydroxymethyl derivative is therein formed:

\[ \left( \text{C}_2\text{H}_5\text{CONHCH}_3 \right)^+ \cdot \text{Br}^- \]

When applied to fabrics and cured at 300° F. for 5 minutes, this produces a soil retardant finish.

The effectiveness of the treatments is determined by means of the following tests:

**WATER REPELLENCY**

(Resistance to wetting (spray test), AATCC standard test method 22-1952)

This test is applicable to any textile fabric. It measures the resistance of fabrics to wetting by a water spray and the results depend primarily on the degree of hydrophobicity inherent in the fibers and yarns and subsequent treatments to which the fabric is subjected. Water is sprayed against the taut surface of a test specimen. Evaluation of the wetted pattern is readily brought about by comparing the wetted pattern with standard wetting pattern pictures:

Rating: Characterized by—

<table>
<thead>
<tr>
<th>Rating</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>No sticking or wetting of the upper surface.</td>
</tr>
<tr>
<td>90</td>
<td>Slight random sticking or wetting of the upper surface.</td>
</tr>
<tr>
<td>80</td>
<td>Wetting of the upper surface at spray points.</td>
</tr>
<tr>
<td>70</td>
<td>Partial wetting of the whole of the upper surface.</td>
</tr>
<tr>
<td>50</td>
<td>Complete wetting of the whole of the upper surface.</td>
</tr>
<tr>
<td>0</td>
<td>Complete wetting of the whole of the upper and the lower surfaces.</td>
</tr>
</tbody>
</table>

The test specimens of minimum size of 7” x 7” (seven inches by seven inches) are conditioned at 70° F. and 65 percent relative humidity for a minimum of four hours before testing.

The test specimen, fastened securely and wrinkle-free in a metal hoop having a diameter of 6 inches, is placed and centered 6 inches under a standard spray nozzle at an angle of 45° to the horizontal. Two hundred and fifty milliliters of water at 70°±2° F. is poured into a funnel attached above the spray nozzle. The spray lasts 25 to 30 seconds at the end of which time the loop is taken by one edge and the opposite edge tapped smartly once against a solid object with the wet side facing the solid; this procedure is repeated with the hoop reversed 180°.

**OIL REPELLENCY**

("3M Textile Chemicals" Appendix A—Test Methods, page 1)

The Minnesota Mining oil repellency test is based on the different penetrating properties of two hydrocarbon liquids, mineral oil ("Nujol") and n-heptane. ("Nujol" is the trademark for white mineral or paraffin number corresponding to that mixture containing the oil being a mixture of hydro-carbons having a density for "light" oil in the range of 0.83 to 0.860 and for "heavy" oil in the range of 0.873 to 0.905.) The "Nujol-heptane" proportions for each rating were selected by "3M" to give oily stain resistance somewhat comparable to the water-borne stain resistance corresponding to each of the spray ratings of the AATCC Standard Test Method 22-1952.

<table>
<thead>
<tr>
<th>Oil repellency rating</th>
<th>Percent heptane (by volume)</th>
<th>Percent Nujol (by volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100+</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>90</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>85</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>80</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>75</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>70</td>
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</tr>
<tr>
<td>65</td>
<td>25</td>
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<td>80</td>
</tr>
<tr>
<td>55</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>45</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

1 No hold out to Nujol. Percent

The standard oil-heptane mixtures are contained in small stopped medicine-dropper bottles. A drop of each mixture of "Nujol" and heptane is placed on the fabric. The appearance of the test oil is observed through the drop. Note is made whether wetting or penetration occurs. The
number corresponding to that mixture containing the highest percentage of heptane which does not penetrate or wet the fabric after three minutes is considered the oil repellency rating of the system.

The change in the optical reflectivity of the drop is often an indication of wetting. In some cases wetting can be better determined by observing the other side of the fabric. In some cases reported hereafter the term "O-1" has been used to indicate a modicum of resistance to wetting by oil.

**STAIN REPELLENCY**

The following procedures have been used to establish the degree of resistance to staining by water-borne and oil-borne stains of fabrics.

(a) The fabrics were stretched lightly on 12" x 31" frames. All or part of the frame was used depending upon the amount of fabric available. The frames were supported at both ends with the fabric about 8 inches above a black surface. The fabric touched nothing.

(b) Three inch medicine droppers were used to draw the stains from the containers. A 1 cubic centimeter calibration was established and marked on the exterior of each dropper. The stains were squeezed vertically downward from a height 2 inches above the cloth.

(c) After five minutes the unabsorbed stain was wiped off the fabric with two sweeps of "Kleenex" and the stains rated as follows:

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>No stain visible</td>
<td>5</td>
</tr>
<tr>
<td>Slight stain</td>
<td>4</td>
</tr>
<tr>
<td>Easily noticeable stain</td>
<td>3</td>
</tr>
<tr>
<td>Considerable stain</td>
<td>2</td>
</tr>
<tr>
<td>Very heavily stained</td>
<td>1</td>
</tr>
</tbody>
</table>

(The spread or lack of spread is not necessarily reflected in the rating.)

(d) Duplicate sets of stains were applied in separate areas so that one-half of the fabric could be washed. In most instances, the wash was carried out with 50 grams of "FAB," a cotton cycle, and a dummy load to total 5 pounds in a Norge Home Automatic Washer.

(e) The following two lists describe the numbering and the gross characteristics of the stains employed.

**Water Stains:**

1. Instant tea
2. Sheaffer's 232 blue-black skrip
3. A & P Concord grape juice
4. "Ann Page" salad mustard
5. "Bosco" chocolate syrup

**Oil Stains:**

6. Wesson oil
7. Gulf "Supreme" motor oil 20/20
8. Olomargarine
9. La Rosa tomato sauce
10. "Jergen's lotion"

Since the perfluoro-quaternary ammonium compounds of the present invention are soluble in water, it is preferred to affix the compound to the substrate from an aqueous solution of the quaternary ammonium compound. Thus, the substrate particularly a substrate having active hydrogen in the surface thereof, for example, cellulose, wool, silk and in general natural or synthetic proteinaceous materials, nylon, etc., is immersed in a solution containing 2 to 3 percent of the perfluoro quaternary ammonium compound, present usually as a salt of acetic acid, hydrochloric acid, and the like, separated from the aqueous solution, wrung to 80 to 100 percent wet pick-up, dried and preferably heat treated at an elevated temperature for a time inversely proportioned to temperature in the range of 250° to 350° F., e.g., for five to ten minutes at 300° F. In this manner about 0.15 to 3 percent of the perfluoro quaternary compound can be affixed to the textile substrate.

Illustrative of the reaction between a substrate having active hydrogen in the surface and the present perfluoro quaternary compound is the reaction with the active hydrogen of a hydroxy group of cellulose ZOH where Z is the cellulose radical and OH is a hydroxy group.

\[Z-OH + Q-X-CH(N+)-R'' \rightarrow Z-O=\text{NH}+X+Q+R''\]

where Q has the same significance Formula E supra.

Illustrative of the resistance to soiling by water, oil, water-borne, and oil-borne materials are the following data obtained when treating cotton with pentadecylfluorooctadecylmethyl pyridinium acetate.
3,510,494

vention provides novel perfluoro quaternary ammonium compounds which are reactive with active hydrogen in the surface of a substrate having active hydrogen to produce a coated fiber or fabric or in general a coated textile in which at least a portion of the coating is attached to the substrate by chemical bonds. Consequently, these novel quaternary compounds provide substantive coatings for textiles having active hydrogen in the surfaces thereof. Such coatings moreover do not form chloramines when bleached with chlorine and do not yellow or degrade the fibers. In addition, the compounds of the invention as previously stated can also be used to treat materials not having active hydrogen in the surface.

While the present invention has been described by means of the foregoing examples, it is to be understood that the invention is not limited thereto, reference being had to the claims for a definition of the scope of the invention.

What is claimed is:
1. A water-soluble, chlorine-resistant fluoro-quaternary ammonium compound of the formula

\[
\begin{array}{c}
\text{Q-} \\
\text{X-} \\
\text{R'} \\
\text{R''} \\
\text{AN} \\
\end{array}
\]

where:

(1) \(X\) is \(-\text{C-N-}\); (2) \(R', R'', \text{ and } R''\) are each alkyl radicals of 1 to 6 carbon atoms, or two of said radicals together with the nitrogen form morpholine with the proviso that when two of said terms \(R', R''\) and \(R''\) represent morpholine the term \(X\) represents

\[
\begin{array}{c}
\text{O} \\
\text{X} = \text{O-N-} - \text{O-} - \text{O-} \\
\end{array}
\]

or all of the three said radicals together with the nitrogen form pyridine;

(3) \(Q\) is alkyl of 3 to 21 carbon atoms of which at least 70% of the hydrogens are replaced by fluoride and the terminal group is \(\text{CF}_3\) or \(\text{CF}_2\) or perfluorophenyl;

(4) \(R_4\) is lower alkyl, hydroxyl lower alkyl or phenyl; and

(5) \(\text{AN}^{-}\) represents a chloride, bromide or acetate ion.

2. A water-soluble chlorine resistant fluoro-quaternary ammonium compound as set forth in claim 1 wherein the terminal carbon group is \(\text{CF}_3\).

3. A water-soluble chlorine resistant fluoro-quaternary ammonium compound as set forth in claim 1 wherein \(Q\) is pentadecafluorooctyl.

4. A water-soluble chlorine resistant fluoro-quaternary ammonium compound as set forth in claim 1 wherein \(R', R'', \text{ and } R''\) are pyridine.

5. A water-soluble chlorine resistant fluoro-quaternary ammonium compound as set forth in claim 1 wherein the compound is \(N\)-lower alkyl, perfluorooctanamido-methyl pyridinium acetate.

6. A water-soluble chlorine resistant fluoro-quaternary ammonium compound as set forth in claim 1 wherein the compound is a perfluorooctanamidomethyl pyridinium salt of an acid selected from the group consisting of acetic, hydrochloric sulfuric and nitric.

7. A water-soluble, chlorine-resistant fluoro-quaternary ammonium compound as set forth in claim 1 wherein \(R', \text{ and } R''\) together with the nitrogen form a morpholine ring and \(R''\) is ethyl.

8. A water-soluble, chlorine-resistant fluoro-quaternary ammonium compound as set forth in claim 7 wherein \(X\) is

\[
\begin{array}{c}
\text{O} \\
\text{O-N-} \\
\end{array}
\]

9. A water-soluble chlorine-resistant fluoro-quaternary ammonium compound as set forth in claim 1 wherein the compound is \(N\)-(pentadecafluoroctyl thiomethyl) tri-ethyl ammonium chloride.

10. A water-soluble chlorine-resistant fluoro-quaternary ammonium compound as set forth in claim 1 wherein the compound is \(N\)-(pentadecafluorooctanoyloxymethyl) pyridinium acetate.

References Cited

UNITED STATES PATENTS

<table>
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<th>Inventor</th>
<th>Title</th>
</tr>
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<tbody>
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<td>3/1950</td>
<td>Crossley</td>
<td>-------</td>
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<td>8-116.2</td>
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<td>3,420,840</td>
<td>1/1969</td>
<td>Tesoro et al.</td>
<td>260-296</td>
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260–247.2, 247.1, 247.7, 294.8, 487, 561, 562, 567.6, 404.5; 8–116.2