WATER-RESISTANT AND OIL-RESISTANT FIBROUS SUBSTANCES, AND PROCESSES THEREFOR

Carlo G. De Marco, Coehlinute, and Gil M. Diaz, Fall River, Mass., assignors to the United States of America as represented by the Secretary of the Army
No Drawing. Filed Feb. 7, 1961, Ser. No. 86,832

30 Claims. (Cl. 117—123)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein, if patented may be manufactured and used by or for the Government for governmental purposes, without the payment to us of any royalty thereon.

This application is a continuation-in-part of our patent application Serial Number 844,830, filed October 6, 1959, now pending.

This invention relates to the production of wettable water-resistant and oil-resistant fibrous substances, and more particularly to the application to cotton and other textiles, other cellulosic substances such as paper, and to leather of a novel liquid composition of a mixture of chemical treating agents. We have discovered that our treatment confers a much greater degree of water resistence and oil resistance to such substances than could be achieved by the individual applications of any of the components of this liquid mixture, and particularly that the treated substances possess an unprecedented permanence in the retention of these desirable properties even after a large number of repeated launderings or other wettings.

Numerous attempts have been made in the course of textile research leading to the provisions of improved textiles for military and civilian use to confer water resistance and/or oil resistance on fabrics. While water resistance and oil resistance are obviously desirable properties of textiles tested for civilian use, it is even more important that military clothing for use in combat, in motor maintenance and other working conditions be both water-resistant and oil-resistant, and able to retain these properties unchanged after many repeated launderings. Commercial processes have not, up to now, made it possible to produce military clothing having the desired measure and permanence of water resistance and oil resistance.

We have unexpectedly discovered in the course of our research that a combination treatment with a liquid mixture of two types of commercially available textile treating agents confers permanent water resistance and oil resistance on textiles many times in excess of the water resistance and/or oil resistance that either type of textile treating agent is able to confer individually. As stated, the permanency of the treatment after many repeated launderings, conferred by the use of our invention is likewise more than adequate to meet rigid military requirements, which treatment in accordance with the knowledge of the trade, prior to our invention, was not able to provide.

We have likewise found that water-resistance and oil-resistance can be conferred on other fibrous substances such as paper and leather in accordance with the above-summarized principles of our invention. It is accordingly a principal object of our invention to provide a synergistic treatment for fibrous substances such as cotton textiles and other natural and synthetic textile fabrics as well as paper and leather which renders them permanently water-resistant and/or oil-resistant. Another object of our invention is the use of compositions whose active ingredients are commercially available textile-treating agents.

A further object of our invention is a process which can be practiced with regular machinery in use in the textile trade, and which does not necessitate special training for operators.

Another object of our invention is an air-permeable launderable textile fabric possessing superior permanent resistance to water and oil, and suitable for military and civilian clothing, as well as for covers and other industrial uses, under severe conditions of use.

Still other objects of our invention are water-resistant and oil-resistant paper and water-resistant and oil-resistant leather, and simple processes for making them in analogy to the textile treating processes of our invention.

Other objects and advantages of our invention will become readily apparent from the following description of our invention.

We now first proceed to describe the practice of our invention with particular reference to textile treatments.

Generally speaking, we accomplish the objects of our invention by treating textiles with a liquid mixture of (a) quaternary long-chain-carrying pyridinium compound, and (b) an organic fluorine compound, namely a polymerizable fluoro alkyl ester of acrylic acid or a Werner type chromium complex wherein trivalent nuclear chromium coordinated with a saturated perfluoro-mono-carboxylic acid.

As will be more fully explained hereinafter, two preferred pyridinium compounds for the practice of our invention are, respectively, octadecloxymethyl pyridinium chloride (steara oxy methyl pyridinium chloride) and stearamidomethyl pyridinium chloride. Octadecylxymethyl pyridinium chloride is a commercially available water-repellent compound produced by several chemical manufacturers, e.g., by Warwick Chemical Co. under the designation Norane R. Stearamidomethyl pyridinium chloride is a water-repellent compound produced by E. I. du Pont de Nemours & Co. under the designation Zelan AP. Both compounds have been tried on Army clothing fabrics and were found to offer good initial water resistance properties, which, however, is quickly reduced and then altogether lost after a few launderings; and they confer virtually no oil resistance.

Among commercially available fluorine compounds heretofore tested for use on textiles for military use are fluorooalkyl esters of acrylic acid such as those produced by Minnesota Mining & Mfg. Co. under the designation FC-148, and FC-154; these fluorooalkyl esters of acrylic acid are capable of polymerization in situ on the fabric. Another organic fluorine compound contemplated for use was FC-149 (perfluorinated octanoic acid Werner-type chromium complex), likewise produced by Minnesota Mining & Mfg. Co. The designation "FC" for the above-mentioned products of Minnesota Mining & Mfg. Co. is also referred to as "Fluorochemical." These "Fluorochemicals" offer good initial oil resistance, but insufficient initial water resistance to meet military requirements and even less water resistance after laundering; moreover, the oil resistance is quickly reduced below the point of military acceptability after a few launderings.

In the course of these and other tests, we have made the unexpected and surprising discovery that the foregoing drawbacks can be eliminated and a superior product obtained by treating the textile fabric with a liquid composition being a mixture of a quaternary long-chain radical-carrying pyridinium compound and of an organic fluorine compound of the general type about to be set forth. The quaternary pyridinium compound suitable
for use in such a composition has the general formula:

\[
\text{R.A.CH}_3
\]

\[
\text{R} = \text{Hal} + \text{Nu}
\]

\[
\text{CH}_2
\]

wherein \( \text{R} \) is an aliphatic hydrocarbon radical having at least about 12 carbon atoms, \( \text{A} \) is selected from \(-\text{O}-\) and \(-\text{CONH}-\), and \( \text{Hal} \) is halogen. This pyridinium compound is preferably in aqueous solution. The organic fluoride compound is preferably in emulsion form because of its low water-solubility; it is either a polymerizable fluoroalkyl ester of acrylic acid having at least about 9 fluoroine atoms and from about 4 to about 10 carbon atoms in the ester-forming radical, or a Werner-type chromium complex wherein trivalent nuclear chromium is coordinated with a saturated perfluoromonomocarboxylic acid having from about 5 to about 11 carbon atoms in the molecule. The aqueous emulsion of the organic fluoride compound and the aqueous solution of the pyridinium compound are combined in the form of an aqueous dispersion, preferably buffered.

We have found that a preferred ratio of pyridinium compound to organic fluoride compound is about 2:3 parts by weight of pyridinium compound per 1 part of organic fluoride compound; within the foregoing range an approximately 2:1 ratio is recommended. Acceptable results, in terms of performance, but not as effective as those obtained within the foregoing range, were also obtained with a ratio of about 1:4.5 parts by weight of pyridinium compound per 1 part of organic fluoride compound; however, oil-resistance is less satisfactory in the 4.5:1 ratio and falls below military performance requirements above that range. Conversely, water resistance of the treated fabric is not sufficiently effective for military requirements below a 1:1 ratio of pyridinium compound to organic fluoride compound.

Reverting now to the quaternary pyridinium compounds for use in the practice of our invention, we prefer chlorides for ready commercial availability, but also contemplate other halides such as bromides and iodides. The long-chain substituent on the pyridinium group is an aliphatic hydrocarbon radical connected to any oxo \((-\text{O})\) or amido \((-\text{CONH})\) group, which in turn is joined to the nitrogen atoms of the pyridinium group by \(-\text{CH}_2-\). The preferred aliphatic hydrocarbon radical is a saturated hydrocarbon radical having 17 or 18 carbon atoms for reasons of ready commercial availability and reliability of performance of the end product; however, other saturated or unsaturated long-chain aliphatic hydrocarbon radicals of 12 or more carbon atoms, such as dodecyl, tetradecyl, hexadecyl, eicosyl, docosyl, oleyl, are within the contemplation of our invention.

The polymerizable alkyl esters of acrylic acid for use in our invention in combination with the above-described pyridinium compounds are represented by the general formula

\[
\text{RCOR}
\]

where \( \text{R} \) is a perfluorinated alkyl group, the alkyl group having about 4 to 10 carbon atoms. These compounds are "partial polymers," i.e., capable of further polymerization on the fabric by curing in situ above room temperature. A preferred compound of this type is perfluorobutyl acrylate

\[
\text{H} \rightarrow \text{CHF}_2 \rightarrow \text{R}
\]

\[
\text{COOR}
\]

where the \( \text{R} \) group of the ester-forming radical has more than 4 carbon atoms, it need not be fully fluorinated, so long as at least about 9 fluoroine atoms are present in the ester-forming radical.

A typical Werner-type chromium coordination complex of a perfluorinated monocarboxylic acid suitable for the practice of our invention in synergistic combination with a pyridinium compound of the class described is

\[
\text{R} \rightarrow \text{O}
\]

\[
\text{H}
\]

wherein \( \text{Hal} \) is halogen, e.g., chloro or fluoro. This is a compound of a trivalent chromium salt and perfluoro octanoic acid formed in accordance with the valence theory of Professor Alfred Werner; according to the Werner Theory, atoms may exert auxiliary valences as well as principal valences, in which case the auxiliary valences act to hold various groups to the atom which exerts such auxiliary valences, whereby the atom exerts the principal and auxiliary valences becomes the nuclear atom of a complex. The aforementioned graphic formula may be written more generally

\[
\text{R} \rightarrow \text{O}
\]

\[
\text{H}
\]

\[
\text{Hal}
\]

\[
\text{H}
\]

\[
\text{Hal}
\]

\[
\text{H}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]

\[
\text{R}
\]

\[
\text{O}
\]
cloth by means of 2 dips and 2 nips using conventional padding equipment. The fabric is then dried at a temperature of 240° F. for 2½ minutes and then cured for 1½ minutes at 350° F.

The treated fabric is then jig washed for 10 minutes in a solution containing .05% wetting agent (Du Ponton D) and .1% soda ash. The washing temperature is approximately 140° F. After washing, the fabric is dried at a temperature of about 300° F. The increase in fabric weight due to this application is about 5.0%. A rainroom comparison of this treated material with: (1) the same type of fabric containing a dry add-on of 4.0%, (not possible to effect a higher add-on) of the fluoroalkyl ester of acrylic acid alone and (2) the same type of fabric containing 5.2% dry add-on of the stearamidomethyl pyridinium chloride alone are as follows:

**Time (Hours) Required to Fall Rain Test (Simulated Rainfall of 1.0 In./Hr.)**

<table>
<thead>
<tr>
<th>Launderings</th>
<th>Fluoroalkyl Ester Alone</th>
<th>Pyridinium Compound Alone</th>
<th>Fluoroalkyl Ester + Pyridinium Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.0</td>
<td>0.9</td>
<td>124</td>
</tr>
<tr>
<td>1</td>
<td>6.0</td>
<td>8.0</td>
<td>124</td>
</tr>
<tr>
<td>2</td>
<td>6.0</td>
<td>8.0</td>
<td>124</td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>8.0</td>
<td>124</td>
</tr>
<tr>
<td>4</td>
<td>6.0</td>
<td>8.0</td>
<td>124</td>
</tr>
<tr>
<td>5</td>
<td>6.0</td>
<td>8.0</td>
<td>124</td>
</tr>
<tr>
<td>6</td>
<td>6.0</td>
<td>8.0</td>
<td>124</td>
</tr>
<tr>
<td>7</td>
<td>6.0</td>
<td>8.0</td>
<td>124</td>
</tr>
<tr>
<td>8</td>
<td>6.0</td>
<td>8.0</td>
<td>124</td>
</tr>
<tr>
<td>9</td>
<td>6.0</td>
<td>8.0</td>
<td>124</td>
</tr>
<tr>
<td>10</td>
<td>6.0</td>
<td>8.0</td>
<td>124</td>
</tr>
</tbody>
</table>

*Test terminated at this point.*

The launderings were performed in a rotary reversible cylinder washer standardized for use in Quantermaster mobile laundries. The following washing procedure was employed with the use of a powdered detergent:

**Operation** | **Water Level (In.)** | **Time (Min.)** | **Temperature (deg. F.)** | **Supplies** | **Spray Rating** | **Suter hydrostatic (Method 83/4) (cm.)** | **Dynamic Absorption (Percent) (Method 86/8) (in.)** | **Other** |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Surf</td>
<td>5</td>
<td>5</td>
<td>100</td>
<td>Detergent (6 oz.)</td>
<td>99</td>
<td>45.1</td>
<td>20.2</td>
<td>heavy</td>
</tr>
<tr>
<td>Do</td>
<td>5</td>
<td>5</td>
<td>100</td>
<td>Detergent (8 oz.)</td>
<td>70</td>
<td>70</td>
<td>0.2</td>
<td>heavy</td>
</tr>
<tr>
<td>Rinse</td>
<td>5</td>
<td>3</td>
<td>100</td>
<td>Detergent (2 oz.)</td>
<td>15</td>
<td>15</td>
<td>3.2</td>
<td>none</td>
</tr>
<tr>
<td>Do</td>
<td>5</td>
<td>3</td>
<td>100</td>
<td>Detergent (2 oz.)</td>
<td>15</td>
<td>15</td>
<td>3.2</td>
<td>none</td>
</tr>
<tr>
<td>Rinse</td>
<td>5</td>
<td>3</td>
<td>100</td>
<td>Sorb (2 oz.)</td>
<td>15</td>
<td>15</td>
<td>3.2</td>
<td>heavy</td>
</tr>
</tbody>
</table>

Water resistance data obtained on this material are as follows:

<table>
<thead>
<tr>
<th>Fluoroalkyl Ester Alone</th>
<th>Pyridinium Compound Alone</th>
<th>Fluoroalkyl Ester + Pyridinium Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray Rating (Method 83/4):</td>
<td>99</td>
<td>100</td>
</tr>
<tr>
<td>Initially</td>
<td>45.1</td>
<td>46.8</td>
</tr>
<tr>
<td>After 15 launderings</td>
<td>20.2</td>
<td>20.8</td>
</tr>
<tr>
<td>Suter hydrostatic (Method 83/4) (cm.):</td>
<td>3.2</td>
<td>15.6</td>
</tr>
<tr>
<td>Initially</td>
<td>20.6</td>
<td>22.3</td>
</tr>
<tr>
<td>After 15 launderings</td>
<td>20.6</td>
<td>22.3</td>
</tr>
</tbody>
</table>

The following details apply to the water resistance test methods used.

(a) Spray rating is principally a measure of surface repellency. It is conducted by means of a funnel connected to a spray nozzle which sprays water onto a test fabric specimen held by a metal hoop at a 45° angle. The percentage of test fabric area still remaining unwetted at the end of a 30-second test generally determines the spray rating; e.g., 100 denotes complete water repellency.

(b) Suter hydrostatic is primarily dependent upon fabric structure but applied repellent does have some effect. This test is carried out by directing water under variable hydrostatic pressure onto the fabric test speci-

The amount of hydrostatic pressure in centimeters needed to penetrate the fabric determines the test rating; thus, a highly water-penetration-resistant fabric will have a high numerical rating.

(c) Dynamic absorption is primarily a function of applied finish. As the results show, the material treated with the fluoroalkyl ester pyridinium finish exhibited little change in this property after 15 launderings. This test is carried out in a water-filled tumble jar. The percentage of water taken up by the fabric test specimen in terms of the original weight of the specimen determines the rating; thus, a highly water-resistant fabric will have a low numerical rating in this test.

These water resistance tests are in accordance with the methods of Federal Specification CCC-T-191b. For military performance characteristics the dynamic absorption test is the most important; as shown by the foregoing table, the amount of water absorbed by a fabric treated in accordance with our invention rises but slightly after 15 launderings (from 23.3 to 24.8), as compared with a two-fold rise in the case of test fabrics treated with either agent alone, thus showing the synergistic effect of the conjoint treatment.

Oil repellency-data obtained on this same material are listed below:

<table>
<thead>
<tr>
<th>Operation</th>
<th>Water Level (In.)</th>
<th>Temperature (deg. F.)</th>
<th>Supplies</th>
<th>Pyridinium Ester Alone</th>
<th>Pyridinium Compound Alone</th>
<th>Fluoroalkyl Ester Alone + Pyridinium Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil wicking test (height in.):</td>
<td>Initially</td>
<td>0.0</td>
<td>6.5</td>
<td>6.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 15 launderings</td>
<td>4.6</td>
<td>6.5</td>
<td>6.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil penetration test:</td>
<td>Initially</td>
<td>none</td>
<td>heavy</td>
<td>none</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 15 launderings</td>
<td>heavy</td>
<td>heavy</td>
<td>heavy</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These tests are as follows:

(1) The oil wicking test measures resistance to liquid travel. A fabric strip is suspended in mineral oil and maximum height of wetting at the end of a 24-hour period is recorded.

(2) The oil penetration test indicates resistance to oil passage. Degree of oil penetration is recorded when a 3 mg. drop of oil is placed on the fabric surface and a 1-pound weight is applied on top of the drop for 1 minute.

The absence of oil wicking and penetration after 15 launderings in the fabrics treated in accordance with the present invention is evidence of the synergistic effect of our contemplated treatment. Analogous protection is afforded against other organic base liquids, such as motor oil, grease, vegetable oils and animal oils.

**EXAMPLE II**

Example I was repeated, except that octadecylxyloxy methyl pyridinium chloride (stearyloxyethyl pyridinium chloride) was substituted for stearamidomethyl pyridinium chloride. Rainroom values are as follows:

**Time (Hours) Required to Fall Rain Test (Simulated Rainfall of 1.0 In./Hr.)**

<table>
<thead>
<tr>
<th>Launderings</th>
<th>Fluoroalkyl Ester Alone</th>
<th>Pyridinium Compound Alone</th>
<th>Fluoroalkyl Ester + Pyridinium Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.5</td>
<td>7.5</td>
<td>134</td>
</tr>
<tr>
<td>1</td>
<td>6.5</td>
<td>7.5</td>
<td>134</td>
</tr>
<tr>
<td>10</td>
<td>6.0</td>
<td>7.5</td>
<td>134</td>
</tr>
<tr>
<td>20</td>
<td>6.0</td>
<td>7.5</td>
<td>134</td>
</tr>
</tbody>
</table>

*Test terminated at this point.*
Oil repellency data obtained on this same material are listed below:

<table>
<thead>
<tr>
<th>Fluoroalkyl Ester Alone</th>
<th>Pyridinium Compound Alone</th>
<th>Fluoroalkyl Ester + Pyridinium Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil wicking test (Height in.):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initially</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>After 15 launderings</td>
<td>4.8</td>
<td>6.6</td>
</tr>
<tr>
<td>Oil penetration test:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initially</td>
<td>none</td>
<td>heavy</td>
</tr>
<tr>
<td>After 15 launderings</td>
<td>none</td>
<td>heavy</td>
</tr>
</tbody>
</table>

Water resistance data determined in accordance with test methods of Federal Specification CCC-T-191b were as follows:

<table>
<thead>
<tr>
<th>Fluoroalkyl Ester Alone</th>
<th>Pyridinium Compound Alone</th>
<th>Fluoroalkyl Ester + Pyridinium Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spicy Rotting (Method 53H3):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initially</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>After 15 launderings</td>
<td>0</td>
<td>70</td>
</tr>
<tr>
<td>Water Extractable (Method 3310) (wt. %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initially</td>
<td>20.2</td>
<td>46.5</td>
</tr>
<tr>
<td>After 15 launderings</td>
<td>17.4</td>
<td>28.4</td>
</tr>
<tr>
<td>Dynamic abrasion (Percent) (Method 5000):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initially</td>
<td>21.2</td>
<td>25.4</td>
</tr>
<tr>
<td>After 15 launderings</td>
<td>25.0</td>
<td>62.0</td>
</tr>
</tbody>
</table>

EXAMPLE III

Examples I and II were repeated with a 5 oz. cotton poplin fabric and again with a 3 oz. nylon Taelon fabric. These treated fabrics likewise exhibit a vast improvement from the standpoint of water resistance and oil resistance following as many as 15 launderings, as compared with the results accomplished by applying either the pyridinium compound or the organic fluoro compound alone, the add-on was about 3%.

EXAMPLE IV

In another test, a cationic emulsion of perfluorobutyl acrylate was substituted for the non-ionic emulsion of Example I. The same result was obtained as in Example I.

Our invention may also be applied to natural, synthetic or blended fabrics, either unfinished or previously finished with a crease-resistant and/or fire-retardant finish.

A highly desirable property of a clothing textile is air permeability. Our treatment has no adverse effect on air permeability of the fabric.

The following examples illustrate the application of our invention in the production of water-resistant and oil-resistant paper and leather, respectively.

EXAMPLE V

120 grams of stearamidomethyl pyridinium chloride product are dissolved in 1,085 grams of water. Separately, 21 grams of sodium acetate, anhydrous are dissolved in 661 grams of water. In each case the water is maintained at a temperature of 110° to 130° F. The acetate and the stearamidomethyl pyridinium chloride are then combined and the temperature maintained within the range stated. A 213 gram non-ionic (FC-208) emulsion consisting of 59.6 grams of fluoroalkyl ester of acrylic acid such as perfluorobutyl acrylate 36.2 grams of acetone and 171.2 grams of water is then added to the stearamidomethyl pyridinium chloride-sodium acetate dispersion. The temperature of the final dispersion is maintained between 110 and 130° F.

This dispersion was applied to a 47 gram sample of blotting paper (AATCC Standard White Blotting Paper) by means of conventional textile laboratory padding equipment. The paper was then dried at a temperature of 240° F. for 2½ minutes and then cured for 1½ minutes at a temperature of 350° F. The increase in weight was approximately 4% based on the dry weight of the fabric.

A comparison of this treated material with the same type of paper, untreated, is as follows:

| Absorption Time |
|-----------------|-----------------|-----------------|
| Treated, hrs. | Untreated, sec. |
| Water Resistance | 8+ | 12 |
| Oil Resistance | 8+ | 10 |

The paper was tested for water absorption and oil absorption according to the methods cited in Federal Specification UU-P-31.

EXAMPLE VI

240 grams of stearamidomethyl pyridinium chloride product are dissolved in 2,042 grams of water. Separately 24 grams of sodium acetate, anhydrous are dissolved in 265 grams of water. In each case the water is maintained at a temperature of 110° to 130° F. The acetate and the stearamidomethyl pyridinium chloride are then combined and the temperature maintained within the range stated. A 429 gram non-ionic (FC-208) emulsion consisting of 120 grams of fluoroalkyl ester of acrylic acid such as perfluorobutyl acrylate. 72 grams of acetone and 237 grams of water is then added to the stearamidomethyl pyridinium chloride-sodium acetate dispersion. The temperature of the final dispersion is maintained between 110 and 130° F.

This dispersion was applied to 4 samples of chrome tanned glove leather 6 inches wide and 14 inches long, which had been previously extracted with chloroform for 5 hours to remove grease. The application consisted of 2 dips and 2 nips using conventional textile padding equipment. The leather pieces were then dried at 240° F. for 5 minutes and then cured for 1½ minutes at 350° F.

The treated leather was then washed for 10 minutes in a solution containing 0.5% wetting agent (Duponol D) and 1% soda ash. The washing temperature was approximately 140° F. After washing, the sample was dried at a temperature of about 300° F. After drying the leather was staked. The increase in weight due to this application is about 4%.

A comparison of this treated material with the same type of leather, untreated, is as follows:

| Water Resistance: Quartermaster Tap Tester (dry): |
|--------------------------------------------------|-----------------|-----------------|
| Treated | 1,875 | 1,875 |
| Untreated | 715 | 715 |

The Quartermaster tap tester operates on the principle of exposing one surface of the leather to water under a ½ pound weight. The end point of test is the time required for water to penetrate the sample as determined by electrical contact.

In the oil resistance test, approximately .5 gm. of white mineral oil is placed on the surface of the leather and then the oil is tapped manually. This is an accepted test procedure.

It will thus be seen that we have provided a synergistic treatment for rendering natural and synthetic textiles and other fibrous substances, such as paper and leather water-resistant and oil-resistant, with particularly superior performance results after many repeated launderings or wetting. While we have described several practical examples of the practice of our invention in terms of application to cotton and nylon fabrics, it will be understood that it is equally applicable to other natural and synthetic fab-
ric, either blended or unblended, such as wool, silk, cellulose acetate, rayon (Viscose), acrylonitrile polymers and copolymers of the Orlon and Dynel type, etc., and blends of the foregoing. Likewise, while the specific examples of the foregoing specification describe certain commercially available textile-treating agents in synergistic combination, as well as preferred conditions for their use, it will be clear to the expert that the results of our invention may be achieved by suitable substitutions and alterations within the skill of technologists having ordinary experience. Still other changes and modifications within the scope of our invention will also readily occur to the expert and are deemed to be encompassed within the scope of our invention, which we now proceed to describe by the appended claims.

We claim:

1. Process for rendering a fibrous substance water-resistant and oil-resistant, comprising applying to said fibrous substance a pyridinium compound having the general formula

\[
R \cdot \text{CH}_2 \cdot N \cdot \text{Hal}
\]

wherein \( R \) is an aliphatic hydrocarbon radical having at least about 4 carbon atoms, \( A \) is selected from —OH and —CONH—, and \( \text{Hal} \) is halogen, and an organic fluorine compound being a member of the group consisting of a polymerizable fluoroalkyl ester of acrylic acid having at least about 4 fluorine atoms and from about 4 to about 10 carbon atoms in the ester-forming radical and a Werner-type chromium complex wherein trivalent nuclear chromium is coordinated with a saturated perfluoro-monocarboxylic acid having from about 5 to about 11 carbon atoms in the molecule, said pyridinium compound being present in a ratio of about 1-4.5 parts by weight per 1 part by weight of said organic fluorine compound; and curing said substance above room temperature.

2. Process according to claim 1, wherein said pyridinium compound is octodecyleoxymethyl pyridinium chloride.

3. Process according to claim 1, wherein said pyridinium compound is stearamidomethyl pyridinium chloride.

4. Process according to claim 1, wherein said organic fluorine compound is perfluorobutyl acrylate.

5. Process according to claim 2, wherein said organic fluorine compound is perfluorobutyl acrylate.

6. Process according to claim 3, wherein said organic fluorine compound is perfluorobutyl acrylate.

7. Process according to claim 1, wherein said organic fluorine compound is octodecyleoxymethyl pyridinium chloride being present in a ratio of about 2-3 parts by weight per 1 part by weight of said fluoroalkyl ester; and curing said substance above room temperature.

11. Process for rendering a fibrous substance water-resistant and oil-resistant, comprising applying to said substance a stearamidomethyl pyridinium halide and a polymerizable fluoroalkyl ester of acrylic acid having at least about 9 fluorine atoms and from about 4 to about 10 carbon atoms in the ester-forming radical, said pyridinium halide being present in a ratio of about 2-3 parts by weight per 1 part by weight of said fluoroalkyl ester; and curing said substance above room temperature.

12. Process according to claim 10 wherein said halide is a chloride.

13. Process according to claim 11, wherein said halide is a chloride.

14. Process according to claim 10, wherein said ester-forming radical is perfluoroalkyl.

15. Process according to claim 11, wherein said ester-forming radical is perfluoroalkyl.

16. Process according to claim 10, wherein said compounds are applied to said fibrous substance in a proportion of about 2-7 percent total dry solids weight based on the dry weight of the untreated substance.

17. Process according to claim 11, wherein said compounds are applied to said fibrous substance in a proportion of about 2-7 percent total dry solids weight based on the dry weight of the untreated substance.

18. Process according to claim 1, wherein said fibrous substance is a textile.

19. Process according to claim 1, wherein said fibrous substance is paper.

20. Process according to claim 1, wherein said fibrous substance is leather.

21. Process according to claim 10, wherein said fibrous substance is a textile.

22. Process according to claim 11, wherein said fibrous substance is a textile.

23. A water-resistant and oil-resistant fibrous substance produced by the process of claim 1, said substance retaining its water resistance and oil resistance after repeated wettings.

24. A water-resistant and oil-resistant fibrous substance produced by the process of claim 10, said substance retaining its water resistance and oil resistance after repeated wettings.

25. A water-resistant and oil-resistant fibrous substance produced by the process of claim 11, said substance retaining its water resistance and oil resistance after repeated wettings.

26. A water-resistant and oil-resistant textile produced by the process of claim 1, said textile retaining its water resistance and oil resistance after repeated launderings.

27. A water-resistant and oil-resistant textile produced by the process of claim 10, said textile retaining its water resistance and oil resistance after repeated launderings.

28. A water-resistant and oil-resistant textile produced by the process of claim 11, said textile retaining its water resistance and oil resistance after repeated launderings.

29. Water-resistant and oil-resistant paper produced by the process of claim 1, said paper retaining its water resistance and oil resistance after repeated wettings.

30. Water-resistant and oil-resistant leather produced by the process of claim 1, said leather retaining its water resistance and oil resistance after repeated wettings.

References Cited in the file of this patent

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Issuer</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,200,944</td>
<td>Wood</td>
<td>May 14, 1940</td>
</tr>
<tr>
<td>2,356,161</td>
<td>Iker</td>
<td>Aug. 22, 1944</td>
</tr>
<tr>
<td>2,642,416</td>
<td>Ahlbrecht et al.</td>
<td>June 16, 1953</td>
</tr>
<tr>
<td>2,803,615</td>
<td>Ahlbrecht et al.</td>
<td>Aug. 20, 1957</td>
</tr>
</tbody>
</table>

FOREIGN PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Issuer</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>477,991</td>
<td>Great Britain</td>
<td>Jan. 10, 1937</td>
</tr>
</tbody>
</table>