Patented July 3, 1951

2,559,260

UNITED STATES PATENT OFFICE

2,559,260

METHOD OF IMPARTING WATER REPELLENCY TO FIBROUS MATERIALS AND RESULTING PRODUCT

John W. Schick, Camden, Howard D. Hartough, Pitman, and Darwin E. Badertscher, Woodbury, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

No Drawing. Application July 25, 1947, Serial No. 763,744

21 Claims. (Cl. 117—161)

1

The present invention relates to water-repellent fibrous materials and to methods of producing the same and, more particularly, to water-repellent textiles and to methods of producing the same.

In the textile-treating art the problem of producing water-repellent fibers has received considerable attention ever since cravenetted cloth was first available. More recently, the members of the textile-treating industry and the public have displayed increased interest in water-repellent textiles that retained their water-repellency even after laundering or dry-cleaning.

From the viewpoint of the textile finisher prior processes have not been completely satisfactory either because the finishing material was only soluble in organic solvents having relatively low flash points, or the treating process included operations during which the textile deteriorated or special equipment was required. Thus, for example, one of the most widely used so-called "permanent" water-proofing or water-repellent agents at the present time appears to be quaternary ammonium salts of the general type $R—CH_2-(NC_5H_5)\cdot HCl$ where R is a long chain alkoxy group or an amide of a long chain carboxylic acid and C_5H_5N is a pyridine radical. This material may be applied in aqueous solution thereby avoiding the disadvantage of the use of organic solvents but the treating process requires the use of special equipment for flashing drying and the use of temperatures of the order of 300 degrees Fahrenheit for 4 to 6 minutes to decompose the quaternary salt and to remove pyridine and acetic acid. The exposure of textiles to temperatures of the order of 300 degrees Fahrenheit even for 4 to 6 minutes is deleterious to textiles. Furthermore, washing and dry-cleaning of the so-treated textiles results in loss of water-proofing or water-repellent properties.

The recent U. S. Patent No. 2,411,860 provides a disclosure of the use of higher molecular ethenones or ketones which are used by dissolving them in organic solvents such as benzine, carbon disulfide, carbon tetrachloride and the like, followed by a preliminary drying and then by heat treatment at 230 degrees Fahrenheit (110 degrees centigrade). U. S. Patent No. 2,413,024 presents a description of the use of "Schiff's bases"; this term including anils which are condensation products of primary amines with either an aldehyde or a ketone. The preferred "Schiff's bases" are made of a ketone containing an aliphatic chain of at least 8 and preferably 8 to 20 carbon atoms, and a primary amine containing either an alkyl radical having at least 8 carbon atoms or an aryl radical. These anils are used either in alcoholic solution or as an aqueous emulsion.

It has now been discovered that certain nitrogenous resins containing 1 or more 5-membered heterocyclic radicals and, preferably, containing 1 or more thiophene radicals may be used to impart water-repellent properties to fibrous materials with the elimination of the disadvantages attendant upon the use of prior art materials. For example, these nitrogenous resinous materials preferably are used in aqueous solution, no special equipment is required for drying or baking and temperatures of the order of those used in home-laundering are satisfactory for heat treatment.

2

It is an object of the present invention to provide a means of imparting water-repellent properties to fibrous materials such as wool, cotton, cellulose wool, silk, rayon, hemp and various other artificial fibers of organic material employing as an impregnating material nitrogenous resinous material containing one or more 5-membered heterocyclic radicals, especially 5-membered heterocyclic radicals having a sulfur or an oxygen atom and, preferably, containing one or more thiophene radicals.

It is another object of the present invention to provide water-repellent fibrous material.

It is a further object of the present invention to provide water-repellent fibrous material containing nitrogenous resinous material having one or more 5-membered heterocyclic radicals in an amount sufficient to impart water-repellent properties to the so-treated fibrous material.

It is also within the scope of the objects of the present invention to provide water-repellent fibrous material containing the condensation product of thiophene, an aldehyde and ammonium chloride in amount sufficient to impart water-repellent properties to the so-treated fibrous material.

The present invention also has as an object the provision of means to provide water-repellent fibrous material containing nitrogenous resinous material having one or more 5-membered heterocyclic radicals in an amount sufficient to impart water-repellent properties to be so-treated fibrous material.

These and other objects and advantages will become apparent from the following description.

At the outset it is to be understood that the term "fibrous material" includes wool, cotton, linen, silk, rayon, nylon, hemp, jute and various artificial fibers of organic material in the form of threads, skeins or in woven form and also paper, sheeted cellulose, leather, fur and the like. Furthermore, the term "5-membered heterocyclic compounds" includes thiophene and derivatives of thiophene having stable electropositive nuclear substituents other than unstable $(OH)^-$ and $(NH)_2^-$ groups attached to the thiophene nucleus, furan, pyrrole, etc.

In the copending application for United States

Letters Patent Serial No. 636,511 filed December 21, 1945, now abandoned, in the names of Howard D. Hartough and Sigmund J. Lukasiewicz the production of nitrogenous resinous bodies containing one or more thiophene radicals, has been described. Therein it has been shown that when thiophene or a derivative thereof having at least one unsubstituted nuclear alpha carbon atom and 1 to 3 substitutes selected from the group consisting of alkyl and alkoxy groups and halogens is reacted with formaldehyde or a polymer thereof and an ammonium halide, resinous bodies are produced; when the molar ratio is within the limits 1:1:0.5 to 1:4:2 resinous bodies having a molecular weight of the order of 637 to 1137 (±10 per cent) are obtained. While these materials can be used with satisfactory results in treating fibrous materials to impart the characteristics of water-repellency thereto, it is preferred to employ analogous nitrogenous resinous bodies, the preparation of which is more fully described in the co-pending application for United States Letters Patent Serial No. 781,754, filed October 23, 1947, in the names of John W. Schick and Howard D. Hartough, which have been modified by condensing the heterocyclic compound as hereinbefore defined with formaldehyde or its polymers and an ammonium halide in the presence of an acid having an ionization constant greater than 1×10^{-5} as found in the table pages 1396–7 Lange's Handbook of Chemistry (5th ed.) such as acetic acid, arsenic acid, benzoic acid, haloalkanoic acids, citric acid, formic acid, fumaric acid, maleic acid, phosphoric acid, etc. Included among these modifiers are SO_2 which in aqueous solution forms $[HSO_3]^-$, and sodium bisulfite which likewise ionizes to form $[HSO_3]^-$.

In the following description of the novel method of imparting the property of water-repellency to fibrous material, the term "heterocyclic nitrogenous material" will be used to include the foregoing condensation products of thiophene and derivatives thereof of the class hereinbefore defined as well as nitrogenous resinous bodies formed by the condensation of pyrrole and furan with formaldehyde or its polymers and ammonium halide in the presence or absence of the $[HSO_3]^-$ radical.

Broadly described, the novel method of imparting the property of water-repellency to fibrous material comprises depositing an amount of the heterocyclic nitrogenous material on the fibrous material from an aqueous bath of a water-soluble form of the aforesaid nitrogenous material, converting the water-soluble form of the nitrogenous material to a water-insoluble form in an aqueous bath, removing a major portion of foreign non-nitrogenous material from the treated fibrous material, treating the impregnated fibrous material with formaldehyde, drying the formaldehyde treated impregnated fibrous material and heat treating the dried fibrous material at relatively low temperatures.

Fabrics such as woven "rayon" cloth, silk cloth, "nylon" cloth, woolen cloth, cotton gabardine and cotton poplin when treated in accordance with the principles of this novel process have been subjected to severe dry-cleaning tests. For example, treated fabrics have been immersed for 15 minutes in boiling benzene and retained the original degree of water-repellency. After immersion for 15 minutes in boiling carbon tetrachloride, treated fabrics have retained their water-repellent properties. Fabrics treated in accordance with the method described hereinbefore have successfully withstood ten hand launderings with soap and water without any observed loss in water-repellent properties.

In the preferred procedure for imparting the property or characteristic of water-repellency to woven fabrics of cotton, wool, linen and various artificial fibers of organic nature, the fabric is immersed in an aqueous about 1 to 25 weight per cent, preferably about 6 to 10 weight per cent, solution of the hydrochloride of the nitrogenous condensation product of thiophene until the fabric has adsorbed a substantial amount of the solution. The impregnated fabric is then transferred to an aqueous alkaline bath in which the hydrochloride of the nitrogenous condensation product is converted to the free base. Suitable alkaline materials for this purpose are sodium acetate, sodium hydroxide, sodium carbonate, disodium acid phosphate (Na_2HPO_4) or any suitable material of the buffer type capable of producing aqueous solutions having a pH of the order of that of 10 weight per cent sodium acetate. Thereafter, the treated cloth is rinsed in cold water or otherwise treated to remove foreign non-nitrogenous material such as the inorganic salts resulting from the conversion of the hydrochloride to the free base. After the removal of the contaminating foreign material the fabric is treated with formaldehyde. At the present time the most facile means of treating the fabric with formaldehyde appears to comprise immersing the fabric in an aqueous alkaline solution of formaldehyde, for example, a solution containing about 12 weight per cent formaldehyde and about 1 weight per cent sodium hydroxide. Thereafter, excess solution is removed, the treated fabric dried and heat treated at relatively low temperatures of the order of about 230 to about 260 degrees Fahrenheit. When otherwise desirable and when foreign non-nitrogenous material has not been removed sufficiently in previous operations, the impregnated cloth is treated to remove inorganic salts when such are present. It is important to remove inorganic salts from the treated cloth since residual salts destroy or greatly impair the water-repellency imparted to the fabric.

The specific procedure followed in treating fabrics for the purpose of evaluating the water-repellency of the treated fabric was as follows:

A 7 inches by 7 inches piece of a coarse weave cotton poplin was immersed in a filtered aqueous solution containing 12 weight per cent of a nitrogenous resinous condensation product of a 5-membered heterocyclic compound in the form of soluble salt, formaldehyde and ammonium halide for about 3 to about 4 minutes at about 30 to about 40 degrees centigrade (86–104 degrees Fahrenheit). The time of contact between the cloth and the aqueous bath varies with the type of cloth and must be sufficient to ensure substantially complete wetting of the fabric with the solution. The cloth was allowed to drain and then was immersed in a 10 weight per cent aqueous sodium acetate bath for at least 5 minutes. Thereafter, the cloth was rinsed in cold water to remove an adhering but not adsorbed precipitated resin. After rinsing in cold water, the treated cloth was immersed in a 36 weight per cent aqueous formaldehyde solution for one or two minutes and excess solution removed. The treated fabric was then dried (cured) at standard temperatures used in textile manufacturing for drying, such as about 212 to about 250 degrees Fahrenheit. The heat

treated cloth was then treated to remove inorganic salts by washing with soap and water and subjected to the spray test described in the 1942 Year-Book of the American Association of Textile Chemist and Colorist, vol. XIX, page 260.

Fabrics woven from "rayon," silk, "nylon," wool, cotton, including cotton gabardine and cotton poplin, were treated in the manner described hereinbefore with the condensation product obtained by reacting 5 moles of thiophene, 6 moles of aqueous 36 weight per cent formaldehyde, 2.5 moles of ammonium chloride and 2.5 moles of sodium bisulfite and tested for spray rating as indicated hereinbefore with the following results:

TABLE I

Treated fabric:	Spray test rating
Rayon	80
Silk	80
Nylon	100
Wool	90
Cotton gabardine	80
Cotton poplin	90
"Byrd" cloth	90

A 7 inches by 7 inches piece of coarse weave cotton poplin was treated as described hereinbefore using various thiophene condensation products obtained by reacting thiophene with formaldehyde or paraformaldehyde and ammonium chloride or hydroxylamine hydrochloride in the presence of sodium bisulfite in the proportions indicated in Table II. The cloth treated with the various thiophene-nitrogen resinous condensation products had the spraying ratings indicated in Table III after one to ten washings.

TABLE II

Water-repellent agents

	Reagents	Mole Ratio
A	Thiophene, 36% formalin soln., NH_4Cl, and $NaHSO_3$.	5:5:5:1.
B	Thiophene, paraformaldehyde, NH_4Cl	1:3:1.
C	Thiophene, 36% formalin soln., $NH_2OH \cdot HCl$, and $NaHSO_3$.	2:2:1:1.
D	Thiophene, 36% formalin soln., NH_4Cl, and $NaHSO_3$.	3:5:5:3.
E	Thiophene, 36% formalin soln., NH_4Cl, and $NaHSO_3$.	5:5:5:1.
F	Thiophene, paraformaldehyde, NH_4Cl, and $NaHSO_3$.	2:6:2:1.
G	Thiophene, paraformaldehyde, NH_4Cl, and $NaHSO_3$.	1:3:0.75:0.25.
H	Thiophene, paraformaldehyde, NH_4Cl, and $NaHSO_3$.	4:8:4:1.
I	Thiophene, paraformaldehyde, NH_4Cl, $NaHSO_3$.	4:16:4:1.

TABLE III

Water-repellent agents

SPRAY TEST

Ref. No	A	B	C	D[d]	D[e]	E	E	F	G	G	H	I
1st wash	50	50	50	70	80	-----	70+	50	----	----	----	---
2nd wash	80	80	70+	80++	80	-----	-----	----	----	----	----	---
3rd wash	80	80	50	80	80	80+	70+	50	----	----	----	---
4th wash	-----	-----	70	-----	-----	-----	-----	----	----	----	----	---
5th wash	[a] 70+	[b] 80	-----	[b] 80	80	70+	[c] 70	[b] 50	80	50	70	70
6th wash	-----	-----	-----	-----	-----	-----	70+	----	----	----	----	---
7th wash	[b] 70+	[c] 70	-----	[c] 80	70	-----	-----	----	----	----	----	---
8th wash	-----	-----	-----	70+	80	-----	-----	----	----	----	----	---
9th wash	[c] 70	-----	-----	70+	----	-----	-----	----	----	----	----	---
10th wash	-----	-----	-----	-----	----	-----	-----	----	----	----	----	---

[a] Benzene soak for 2 min. (26° C.).
[b] Benzene soak for 15 min. (26° C.).
[c] Benzene soak for 15 min. (80° C.).
[d] Benzene treated cloth.
[e] Washed cloth.
[f] Carbon tetrachloride soak for 15 min. (26° C.).
[g] Carbon tetrachloride soak for 15 min. (80° C.).

Another means of determining the water-repellency of fibrous material is the measurement of contact angles between a drop of water and a treated fiber. Those skilled in the art will understand that the larger the contact angle, the smaller the attractive force between the fiber and a droplet of water, and, therefore, the better the water-repellency of the fiber. The values of contact angles of untreated cloth, cloth treated as described hereinbefore and cloth treated with quaternary ammonium salts of the general type $R—CH_2—(NC_5H_5) \cdot HCl$ mentioned hereinbefore are given in Table IV.

TABLE IV

Type Fabric	Contact Angle in Degrees		
	Untreated	Treated with novel amine resin	Treated with $R-CH_2-(NC_5H_5) \cdot HCl$
Cotton Poplin	90	156	154
Silk	90—	156	150
Nylon	90—	140	154
Rayon	20	148	148
Wool	120	148	142

The data submitted in Table IV clearly establish that the products produced by the means described herein have the same order of water-repellency as that imparted by the presently most widely used quaternary ammonium salts of the general type $R—CH_2—(NC_5H_5) \cdot HCl$ discussed hereinbefore.

The amount of nitrogenous resinous material containing at least one heterocyclic radical and preferably at least one heterocyclic radical containing a sulfur or an oxygen atom is exemplified by the values given in Table V for nitrogenous resinous material containing at least one thiophene molecule.

TABLE V

Type Fabric	Weight Per cent of resin deposited thereon	Spray Rating
Cotton Poplin	0.64	50—
	2.4	80
	5.0	80
	11.5	80
Rayon	3.1	70
Silk	7.9	80
Nylon	0.46	90+
Wool	1.6	80

Illustrative of some of the nitrogenous resinous materials containing at least one heterocyclic

radical are those prepared in the manner described hereinafter and used in the treatment of fibrous material as described hereinbefore.

EXAMPLE I

About one mole of pyrrole was treated with about 2 moles of ammonium chloride, about one mole of sodium bisulfite and about 3 moles of 36 per cent formaldehyde solution. The temperature rose to 70 degrees centigrade, and was controlled there by means of an ice bath. The reaction mixture was stirred for about one hour. Most of the reaction mixture was soluble in hot water. Treatment of poplin in the manner described hereinbefore imparted a slight amount of water-repellency to the cloth.

EXAMPLE II

About one mole of furan was heated at about 70 degrees centigrade in a stirring autoclave at about 15 to 20 pounds per square inch pressure with about one mole of ammonium chloride, about one mole of sodium bisulfite and about three moles of 36 per cent aqueous formaldehyde solution. After ten minutes the pressure fell to zero, indicating complete reaction of the furan and the heating was continued for about three hours. Deposition of this material on fabric in the manner described hereinbefore indicated that water-repellency was imparted to the fabric.

Resinous materials were prepared in the manner described in copending application Serial No. 636,511 from the materials listed in Table VI in the proportions indicated.

TABLE VI

Product	Thiophene	Ammonium Halide	Formaldehyde (as 36% Formalin)	Sodium Bisulfite
A.....moles..	3	4	6	1
B.....do....	3	4	9	0.8
C.....pounds..	16.5	16	[1] 80	15

[1] An excess to compensate for loss due to conversion of formaldehyde to dimethylformal because of high methanol content.

The spray ratings of common fabrics impregnated with the nitrogenous-resinous materials A, B and C of Table VI from a 12 weight per cent aqueous solution are given in Table VII.

TABLE VII

Fabric	Product A		Product B		Product C	
	Weight Per Cent Resin Deposition	Spray Rating	Weight Per Cent Resin Deposition	Spray Rating	Weight Per Cent Resin Deposition	Spray Rating
Cotton	5.6	80	----	70	2.9	80+
Rayon	3	----	----	50	3.1	70
Wool	4	70—	----	70	7.9	80
Silk	6.4	50	----	70	1.6	90

The launderability of the water-repellent fabrics was determined by subjecting cotton poplin made water-repellent by impregnation with product C of Table VI.

TABLE VIII

Time (min.)	Temp., ° F.	Spray Rating
0	----	80+
30	63	80
30	100	70
30	140	50

At this time it does not appear that the water-repellency of fabrics is improved substantially by the addition to the impregnating bath of such compounds as dodecyl and octadecylamine in amounts of about 1 weight per cent. That is to say, the spray ratings of fabrics treated in impregnating baths containing only the water-soluble derivative of the nitrogenous resinous material containing at least one thiophene radical was not improved by impregnating other portions of the fabrics in baths containing 1 weight per cent of dodecyl or octadecylamine in addition to the nitrogenous resinous thiophene material. Similarly, the impregnated fabrics treated in baths containing stearamide or lauryl alcohol did not have substantially improved spray ratings. Furthermore, at this time it does not appear that results are substantially improved by preparing a modified thiuram disulfide from nitrogenous resinous thiophene material, carbon disulfide and hydrogen peroxide in situ in the impregnating bath nor by preparing a chloramine from nitrogenous resinous thiophene material and sodium hypochlorite in the impregnating bath.

Fire-retarding and moth proofing of textiles with cupric phosphate does not impair the water-repellency of the textiles to any noticeable degree as to washability or spray rating. Cotton poplin was impregnated with $Cu_3(PO_4)_2$ from aqueous solution containing 5 weight per cent copper acetate and 10 weight per cent trisodium phosphate. The data for cotton impregnated with $Cu_3(PO_4)_2$ and product C of Table VI are given in Table IX:

TABLE IX

Time in Washing Machine at 140° F. (min.)	Spray Rating	
	One Treat of 5% Cu^{++}	Three Treats of 5% Cu^{++}
0	80	70
15	70+	70
30	70	70

Substituted thiophenes may replace thiophene in the preparation of the nitrogenous resinous thiophene material, the preparation of which is described in the copending applications mentioned hereinbefore. Thus, the nitrogenous resinous thiophene material obtained from 3-methylthiophene imparts water-repellency to cotton poplin sufficient to give a spray rating of 80 while the product obtained from tertiary butyl-3-thienyl thioether gave a spray rating of 70 on cotton poplin. Furthermore, the heterocyclic compound furan or thiophene can be replaced in part by a phenol in the preparation of nitrogenous resinous materials for imparting water-repellency to textile materials. For ex-

ample, a material which imparted sufficient water-repellency to cotton poplin to provide a spray rating of 70 was prepared as follows:

About 2.5 moles of thiophene, about 0.5 mole of phenol, about 4 moles of ammonium chloride, about 0.8 mole of sodium bisulfite and about 9 moles of 36 per cent aqueous formaldehyde solution were mixed and refluxed for about two hours. The water-soluble hydrochloride was used in an impregnating bath as described hereinbefore to impregnate cotton poplin which after treatment had a spray rating of 70.

Similarly, the thiophene polymers described in the copending application in the name of George C. Johnson, and particularly the trimer described therein, may be used. The aforesaid trimer imparts a spray rating of 50 to cotton poplin when applied as described hereinbefore.

Material capable of imparting the property of water-repellency to textile fibers when applied to textile fibers in the manner described hereinbefore can be prepared as described in the following illustrative, but not limiting, examples:

Example III

A mixture of about 84 parts by weight of thiophene (about 1 mole), about 162 parts by weight of an aqueous 36 weight per cent solution of formaldehyde (about 2 moles), about 54 parts by weight of ammonium chloride (about 1 mole) and about 115 parts by weight of 85 per cent ortho-phosphoric acid (about 1 mole) were warmed at about 35 degrees centigrade, for about 3.5 hours. The reaction proceeded similarly to the reactions in which sulfur dioxide was employed. The polymeric material may be used to impart water-repellency to textile fibers.

Example IV

About 168 parts by weight of thiophene (about 2 moles), about 70 parts by weight of hydroxylamine hydrochloride (about 1 mole), and about 104 parts by weight of sodium bisulfite (about 1 mole), were mixed. To the foregoing mixture were added about 162 parts by weight of aqueous 36 per cent solution of formaldehyde (about 2 moles) with external cooling. During the addition of the formaldehyde, the temperature rose to about 50 degrees centigrade. After the heat of reaction had subsided, the mixture was warmed to about 72 degrees centigrade at which temperature reflux again became vigorous. After refluxing had subsided (about 10 to 15 minutes) the pale yellow solution was cooled, diluted with water and deposited on cotton poplin to produce a water-proofed textile.

Although the production of water-repellent fibrous material has been illustrated hereinbefore by a description of the treatment of woven textiles, it will be understood by those skilled in the art that these materials can be treated in the form of threads, and skeins. It will also be understood by those skilled in the art that cellulosic material such as paper and cardboard likewise can be treated. The paper can be treated either before being formed into sheets or boards by introducing the fibers into the impregnating bath or baths and then forming the sheet or board in the usual manner or the sheet or board may be based through an impregnating bath or baths or the solution of resinous material and the solution of formaldehyde sprayed on the formed sheet or board.

We claim:

1. A method of imparting water-repellency to fibrous material which comprises contacting organic fibrous material with an aqueous solution containing a water-solublue hydrohalide of a nitrogenous condensation product having at least one nucleus of a 5-membered heterocyclic compound, said nitrogenous condensation product having been obtained by condensing a 5-membered heterocyclic compound with formaldehyde and a member of the group consisting of ammonium halide and hydroxylamine halide in the presence of an acid having an ionization constant greater than 1×10^{-5} but not greater than about 1.7×10^{-2}, said 5-membered heterocyclic compound being selected from the group consisting of thiophene, furan and pyrrole removing said organic fibrous material carrying said water-soluble derivative of said nitrogenous condensation product from said solution, contacting said organic fibrous material with an alkaline medium in which said organic fibrous material is substantially insoluble, contacting said organic fibrous material carrying said condensation product with formaldehyde, subjecting the so-treated organic fibrous material to elevated temperatures of about 212° to about 260° F., and removing sufficient non-nitrogenous foreign material that the water-repellency of the so-treated organic fibrous material is not seriously impaired.

2. The method of imparting water-repellency to organic fibrous material as described and set forth in claim 1 in which the nitrogenous condensation product is derived from a thiophene radical having one unsubstituted nuclear alpha position.

3. The method of imparting water-repellency to organic fibrous material described and set forth in claim 1 in which the nitrogenous condensation product is derived from a thiophene radical having two unsubstituted nuclear alpha positions.

4. The method of imparting water-repellency to organic fibrous material described and set forth in claim 1 in which the nitrogenous condensation product has more than two thiophene radicals and more than two unsubstituted nuclear alpha positions.

5. The method of imparting water-repellency to organic fibrous material as described and set forth in claim 1 in which the water-soluble derivative of the nitrogenous condensation product is the hydrochloride.

6. The method of imparting water-repellency to organic fibrous material as described and set forth in claim 1 in which the alkaline medium is an aqueous alkaline bath.

7. The method of imparting water-repellency to organic fibrous material as described and set forth in claim 1 in which after contacting the organic fibrous material with an alkaline medium, the so-treated organic fibrous material is contacted with an aqueous bath containing formaldehyde.

8. The method of imparting water-repellency to organic fibrous material as described and set forth in claim 1 in which the non-nitrogenous foreign material is removed from the organic fibrous material before contacting with formaldehyde.

9. The method of imparting water-repellency to organic fibrous material as described and set forth in claim 1 wherein the water-soluble derivative of the nitrogenous condensation product is the hydrohalide, said condensation product is obtained by condensing thiophene, formaldehyde and ammonium halide in the presence of the ion

HSO_3^- and the water-soluble derivative converted to a water-insoluble derivative in an aqueous alkaline bath having a pH of the order of that of 10 weight per cent sodium acetate.

10. Water-repellent fibrous material comprising organic fibrous material carrying nitrogenous resinous material containing at least one 5-membered heterocyclic radical per unit of polymer, said nitrogenous resinous material having as its principal component the reaction product of formaldehyde, a material selected from the group consisting of hydroxyl substituted ammonium halide and ammonium halide and a 5-membered heterocyclic compound selected from the group consisting of thiophene, furan and pyrrole having at least one unsubstituted nuclear alpha carbon atom.

11. Water-repellent fibrous material comprising organic fibrous material coated with nitrogenous resinous material containing at least one thiophene radical per polymer unit, said nitrogenous resinous material having as its principal component the reaction product of formaldehyde, a material selected from the group consisting of hydroxyl substituted ammonium halide and ammonium halide and a compound having an unfused thiophene radical.

12. Water-repellent fibrous material comprising organic fibrous material coated with nitrogenous resinous material containing at least one furan radical per polymer unit, said nitrogenous resinous material having as its principal component the reaction product of formaldehyde, a material selected from the group consisting of hydroxyl substituted ammonium halide and ammonium halide and a compound having an unfused furan radical.

13. Water-repellent fibrous material as set forth and described in claim 10 wherein the organic fibrous material is woven material.

14. Water-repellent fibrous material as set forth and described in claim 11 wherein the organic fibrous material is woven material.

15. Water-repellent fibrous material as set forth and described in claim 12 wherein the organic fibrous material is woven material.

16. Water-repellent fibrous material as set forth and described in claim 10 wherein the organic fibrous material is at least in part cellulosic.

17. Water-repellent fibrous material as described and set forth in claim 11 wherein the organic fibrous material is at least in part cellulosic.

18. Water-repellent fibrous material as described and set forth in claim 12 wherein the organic fibrous material is at least in part cellulosic.

19. Water-repellent fibrous material as set forth and described in claim 10, said water-repellent organic fibrous material having a contact angle of at least 140 degrees.

20. Water-repellent fibrous material as set forth and described in claim 10, said water-repellent fibrous material carrying at least 0.5 weight per cent of said nitrogenous condensation product.

21. Water-repellent fibrous material comprising organic fibrous material carrying nitrogenous resinous material prepared by the condensation of phenol, thiophene and ammonium chloride and having a ratio of phenol radicals to thiophene radicals of about 1 to 5.

JOHN W. SCHICK.
HOWARD D. HARTOUGH.
DARWIN E. BADERTSCHER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,306,924	Zerweck et al.	Dec. 29, 1942
2,369,948	D'Alelio	Feb. 20, 1945
2,453,085	Caeser et al.	Nov. 2, 1948
2,453,086	Caeser	Nov. 2, 1948

OTHER REFERENCES

Ser. No. 314,449, Zerweck et al. (A.P.C.), published April 20, 1943.

Holdren and Hixon, J. A. C. S., 68, 1198 (1946).