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3,296,264

FIBER-REACTIVE FLUOROALKYL DERIVATIVES OF AMINO-ALDEHYDE COMPOUNDS AND TEXTILES "SOIL PROOFED" THEREWITH

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No Drawing. Filed Sept. 30, 1963, Ser. No. 312,291
3 Claims. (Cl. 260—249.6)

The present invention relates to fiber-reactive fluoroalkyl derivatives of heterocyclic amido compounds and to textiles "soil proofed" therewith and more particularly to fiber-reactive fluoroalkyl derivatives of cyclic ureas, triazines and guanamines, compounds and textiles "soil proofed" with said fluoroalkyl derivatives.

The treatment of textiles including fibers, yarns, woven fabrics, felted fabrics, and the like has been practiced for many centuries. At first man was concerned with imparting to textiles the capability of resistance to wetting by water. Many empirically developed mixtures have been applied to cloths to provide the water-repelling rainwear which has in the past been known as "macintoshes." Everybody is acquainted with the coated fabric generally available as "oil cloth." These early coated fabrics presented one surface which was a continuous film of the coating material which filled the interstices of the cloth, changed the porosity of the cloth, and the air permeability of the cloth. 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 with various "cook-book" recipes such as rubber, linseed oil-rubber mixtures, empirical and esoteric 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 resisting wetting by water or more briefly water repellency.

Without understanding the basic principles of the mechanism of conferring water repellency to textiles such as surface free energy, contact angle, and spreading coefficient several unrelated practical developments arose during the period from 1935 to 1940 which changed the art of water-proofing textiles. In Germany, a series of paraffin wax emulsions were developed which, when padded onto textiles, produced a high contact angle of water drops on the surface and a high degree of shower resistance without changing the porosity or air permeability of the textile material as do the preparations recommended for water proofing prior to 1935. The fabrics treated with these paraffin-wax emulsions were not wettable by water and water-borne liquids and stains because of the change of the free energy of the fiber surfaces and not because the interstices of the woven fabrics were plugged. Thus, a practical improvement was made without an understanding of the reason for the advance in the art.

By the use of these new wax emulsion-metallic salts mixtures, it was then and is now possible to produce fabrics which have the feel and appearance of conventional fabrics but do not look like oil-cloths or fabrics having rubberized coating. The only practical limitation of such mixtures is the durability to washing and dry-cleaning. This class of water-proofing materials generally comprises a mixture containing:

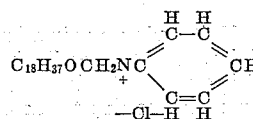
- (a) A paraffin wax or mixtures of vegetable wax esters such as carnauba, candelilla, or sugar cane wax.
- (b) An emulsifying agent, usually glue, gelatin, and rosin soaps.
- (c) An aluminum or zirconium salt, usually the formate or acetate. The primary function of the salt is to

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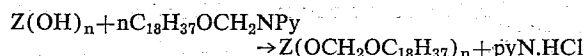
insolubilize the glue and other emulsifiers after the emulsion is deposited on the fabric.

A large variety of such products are still in use as low-cost, non-durable water repellants 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 repellants as contrasted with these non-durable water repellants, especially for cellulosic fibers was initiated by the need to overcome the deficiencies of these wax emulsion-metallic salt mixtures. The first major advance occurred in England where a product marketed under the trade name "Velan" was produced. This material was octadecyloxy-methyl pyridinium chloride, a quaternary ammonium compound made by the chloromethylation of octadecanol, followed by quaternization with pyridine to yield a product having a composition represented by the formula

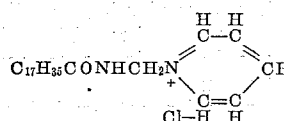


This compound, unlike other quaternaries, is unstable and under acid conditions reacts with surfaces containing active hydrogen, e.g., the hydrogen of a hydroxyl group in cellulose fibers. If the cellulose molecules be represented by $\text{Z}(\text{OH})_n$ then the reaction can be considered to be summarized by the equation:



where py is the balance of the pyridine ring. Fabrics treated with such a compound are durably water repellent, are porous, soft, and have the appearance of untreated fabrics.

A major improvement of the "Velan" type material was made when the stearamidomethyl analog of "Velan"



commercially known as "Zelan" and "Norane R" was produced. The advantage of the stearamide product is greater initial water repellancy and greater durability to washing. Such products are still among the forefront of the leaders in rainwear fabric finishes.

In the search for other fabric-reactive or durable water repellants other classes of compounds have been developed. Illustrative of these other classes of water repellants are the silicone water repellants methylstearamide compositions ("permel," "Ahcovel NW"), hydrophobic resins ("Norane GG," "Ranadare R," "Argus DWR," octadecylketene dimer ["Aqualap"] and others.

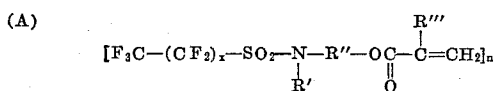
While durable water repellants had been initially developed for outerwear and raincoat applications, it was soon recognized that durable water repellants could be used as finishes for other purposes. In the period 1950 to 1956 these durable water repellent finishes were widely used on men's suitings, 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 repellants 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.

In the early part of the 1950 decade based on work done at Naval Research Laboratory by Fox and Zisman and from work done at a division of the Minnesota Mining and Manufacturing Co., the utility of certain fluoro-carbon based chemicals as fibrous finishes was announced. Fox and Zisman had demonstrated the physiochemical principle of low free energy surfaces and the relation of non-wetting with water or oils of surfaces treated with chemicals containing perfluoroalkyl groups.

The practical developments of "3M" culminated in the introduction of the first product for textile treating. This product is still known as FC-149 and is a classical Werner complex of a carboxylic acid made by reacting 1 mol of the acid with 2 mols of basic chromic chloride. The compound is water soluble and cationic in nature. It exhibits strong adhesion to anionic substrates such as cellulose and fiberglass. It also complexes with proteinaceous fibers such as wool, silk, and leather to give both water and oil repellent surfaces. It is generally believed that perfluorodecanoic acid is the base for this product.

Subsequently, "3M" made a product known as FC-208 available as a finish. It is generally believed that this finishing material is a perfluorosulfonamide polymer having a composition corresponding to the formula:



where x is an integer in the range of 3 to 13, R' is methyl, ethyl, propyl, butyl, amyl, hexyl, R'' is an alkylene radical having 1 to 12 carbon atoms and R''' is hydrogen, methyl, or ethyl.

The advent of these "perfluoro" finishes produced a great practical improvement in fabric finishes. Although of little merit for plain water repellency for outerwear purposes, the two products, i.e., the Werner Complex and the perfluorosulfonamide, offer a solution to the problem of providing fabrics with water-and-oil repellency and practical resistance to staining. Because of its hydrolytic instability the Werner complex has been limited to wool, leather, and upholstery finishes. The sulfonamide has become a leader in finishes for cotton, rayon, and non-cellulosic synthetic fiber.

Although important for water-and-oil repellency and resistance to staining by water-and-oil borne stains for wearing apparel, upholstery and the like, the capability of shedding oily particulate soil is of greater importance. That is to say, the finely divided environmental grime mixed with the oil exudations of the human skin, i.e., oily particulate soil, soil in the neckband and cuffs of a man's shirt, are far more often encountered than soiling with gravy or mayonnaise. Hence, while fabric finishes which repel water, oil, water-borne and oil-borne stains are of great importance, the capability of resisting staining by oily particulate soil is of greater importance for aesthetic reasons if for no other reason. Yet even the "perfluoro" finishes presently available do not have the capability of resisting staining by oily particulate soil. In fact they enhance such soiling.

It is manifest that controlled evaluating of fabric finishes in actual use is not possible. Consequently, it has been necessary to use evaluation methods subject to laboratory control which will simulate as closely as possible actual conditions under which water-repellency, oil-repellency, resistance to staining by water-borne and oil-borne stains, and resistance to staining by oily particulate soil of treated fabrics occurs. Such methods of evaluation are the following.

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
100 -----	No sticking or wetting of the upper surface.
90 -----	Slight random sticking or wetting of the upper surface.
80 -----	Wetting of the upper surface at spray points.
70 -----	Partial wetting of the whole of the upper surface.
50 -----	Complete wetting of the whole of the upper surface.
0 -----	Complete wetting of the whole of the upper and the lower surfaces.

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 80±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 hoop 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 the two hydrocarbon liquids, mineral oil ("Nujol") and n-heptane. ("Nujol" is the tradename for white mineral or paraffin 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 0.875 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.

Oil Repellency Rating	Percent Heptane (by volume)	Percent "Nujol" (by volume)
100+-----	60	40
100-----	50	50
90-----	40	60
80-----	30	70
70-----	20	80
50-----	0	100
0-----		No hold out to "Nujol".

The standard oil-heptane mixtures are contained in small stoppered 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 oc-

curs. 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 refractivity 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 hereinafter the term "O+" 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:

Appearance:	Rating
No stain visible -----	5
Slight stain -----	4
Easily noticeable stain -----	3
Considerable stain -----	2
Very heavily stained -----	1

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

(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 characterizations of the stains employed.

Water stains:

1. Instant tea ¹.
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. Oleomargarine ².
9. La Rosa tomato sauce.
10. "Jergen's" lotion.

¹ 8 cc. dry powder/200 cc. water applied at 160° F.

² Melted and applied at 160° F.

In reporting the relative resistance to staining and ease of stain removal in laundering, the staining values for water-borne and oil-borne stains were averaged separately.

In all cases the stains were allowed to dry on the fabrics for twenty-four hours before laundering.

OILY PARTICULATE SOIL REPELLENCY

(GRC dry soil test)

Fifteen to twenty 6" x 8" numbered specimens (normally 80 x 80 cotton), including at least one untreated control, are tumbled for thirty minutes with 10 percent of "Cyanamid Soil" based on the weight of the fabric. The tumbling is carried out in a 5-liter capacity "Five-Minute Home Cleaner" at 44 r.p.m.; six No. 8 neoprene

rubber stoppers are distributed among the specimens to increase the mechanical action. At the end of tumbling, the specimens are removed and each shaken separately up and down fifteen times by hand to remove surface dirt.

The specimens are then cut in two (to produce two 4" x 6" pieces). One-half is washed with 50 grams of "Fab" in a cotton cycle with a 5-pound dummy load, then hung to dry and lightly ironed under a clean cotton cloth.

The degree of soiling is determined with a Photovolt Reflectance Meter (Tri Blue Filter). Six readings per specimen are made and the arithmetic average reported.

The "Cyanamid Soil" described below is the same as that recommended by Minnesota Mining and Manufacturing Co. The following dry ingredients are blended thoroughly, dried in a forced draft convection oven for eight hours at 50° C., then milled for twenty-five hours with ceramic balls and stored in a polyethylene bag.

"CYANAMID SOIL"

Material:	Percent by weight
Peat moss -----	38
Cement -----	17
Kaolin clay ¹ -----	17
Silica, 200 mesh ² -----	17
Furnace black ³ -----	1.75
Red iron oxide ⁴ -----	0.50
Mineral oil -----	8.75

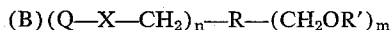
¹ "Peerless" R. T. Vanderbilt.

² Davidson Chemical Co.

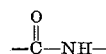
³ "Molacco" Benny and Smith Co.

⁴ C. K. Williams Co.

It has now been discovered that fiber-reactive fluoroalkyl derivatives of amino-aldehyde compounds, i.e., fluoroalkyl derivatives of monocyclic ureas and thioimino compounds having compositions corresponding to the formula:

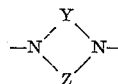


where Q is a fluoroalkyl group having four to twelve (inclusive) carbons atoms in which at least 70 percent to 100 percent of the (2n+1) hydrogen atoms (n=4 to 12) has been replaced by fluorine atoms and at least two and preferably three fluorine atoms are attached to the terminal or omega carbon atoms; X is



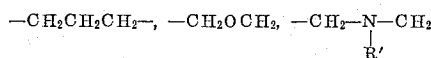
or —O—, R' is hydrogen, CH₃—, C₂H₅—, C₃H₇—; m is one to five dependent upon the functionality of the amido residue; n is at least one; (m+n) is two to six inclusive; R is a divalent radical selected from the group:

Monocyclic ureas



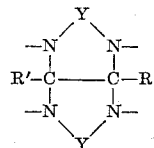
where

Y is: C=O, C=NH, C=S; and Z is —CH₂CH₂—,



R' has the significance given hereinbefore,

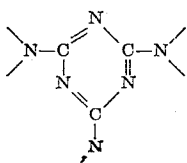
Diheterocyclic ureas



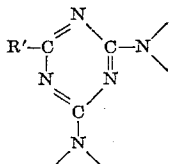
where Y and R' have the significance given hereinbefore.

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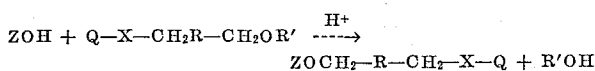
Triazines



Guanamines

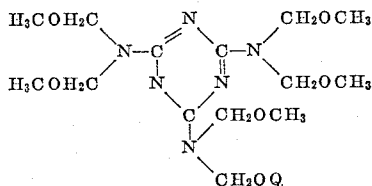


There can be one ($Q-X-CH_2$) group or as many as five, depending upon the functionality of the amido residue. There must always be at least one ($-CH_2OR'$) group remainin gfor reaction with the fiber, e.g., with cellulose (ZOH)



or when more than two ($-CH_2OR'$) groups are present for the formation of a thermosetting resin. Both of these reactions, i.e., with the active hydrogen of the fiber or the formation of a thermosetting resin, are catalyzed by acidic catalysts such as zinc nitrate, magnesium chloride, oxalic acid, ammonium chloride, and the like.

The fluoroalkyl group Q is derived from alcohols or amides. The fluoroalkyl cyclic amido compounds are prepared either by ether interchange or by direct fluoroalkylation. Thus, fluoroalkoxymethyl-penta (methoxymethyl) melamine



where Q is $-CH_2(CF_2)_6CF_3$ has been prepared by reacting hexa (methoxymethyl) melamine and pentadecafluorooctyl alcohol in equimolar proportions using about 0.05 part by weight of 85 percent orthophosphoric acid as the ether interchange catalyst. The reaction mixture was heated from 103° C. to 153° C. in about thirty minutes during which time an amount of methanol was collected indicating the replacement of one methyl group by the pentadecafluorooctyl group and the formation of the pentadecafluorooctoxymethylpenta (methoxymethyl) melamine. Pentadecafluorooctoxymethylpenta (methoxymethyl) melamine and the other fluoroalkyl derivatives of amino-aldehyde compounds within the scope of formula (B) supra are reactive with textile materials having active hydrogen atoms in the surfaces thereof.

Equimolar amounts of C_{11} trihydropyridyl alcohol ($CHF_2(CF_2)_9CH_2OH$) and tetramethylolacetylene monourein were condensed using 85 percent phosphoric acid as the condensation catalyst. An amount of water was stripped indicating the formation of the C_{11} trihydropyridyl trimethylolacetylene monourein.

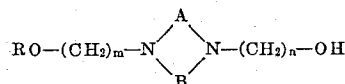
The C_{11} trihydropyridyl, trimethylolacetylene monourein was padded on 80 x 80 cotton from 3 percent isopropanol solution (Run No. 1) and from 3 percent isopropanol solution in the presence of a zinc complex as a catalyst (Run No. 2). The degree of "soil proofing" con-

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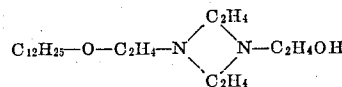
ferred on the textile is indicated by the values reported in the following table.

Run No.	Percent Catalyst	Cured at Room Temperature		
		Repellencies, Oil	Reflectance	
			B	A
Untreated Cotton:				
1	0	0	26	77
2	1.5	80	43	81
		80	36	81

The heterocyclic nitrogen bases of the present invention are not to be confused with what seems to be similar compositions previously known to the art. For example in U.S. Patent No. 2,421,707 there are disclosed a group of wetting, detergent, and dispersing agents which may be represented by the general formula:

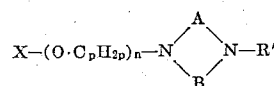


where R is an alkyl or acyl radical having about five to about twenty-three carbon atoms, A and B are ethylene radicals, and m and n are integers in the range of two to five. Illustrative of the patented compounds is the lauryl ether of n,n'-dialkanol piperazine,



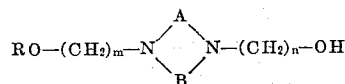
A "soil-proofing" textile finishing agent is not suggested by nor the same as, wetting detergent and dispersing agents.

In U.S. Patent No. 2,508,652 similar piperazine and alkyl substituted piperazines conforming to the general formula



where X is R or $R-CO$; A and B are unsubstituted ethylene radicals or ethylene radicals having one to four short chain alkyl substituents of not more than two carbon atoms; R is a long-chain aliphatic radical such that the carbon content of X is from six to twenty-four carbon atoms; R' is a short-chain alkyl or acyl radical; and n is 1 to 9, are described. These piperazines are said to be suitable for softening fabrics, fixing colors, removing grease and oil, and penetrating and in ore flotation as addition agents. In other words, these piperazines are of the nature of surfactive agents with no suggestion that such materials when applied to textiles will shed oily particulate soil.

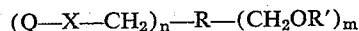
Novel detergents conforming to the general formula:



where R is an alkyl or acyl radical having five to twenty-three carbon atoms; A and B are ethylene radicals wherein any number of hydrogen atoms (none, one or more) are replaced by alkyl radicals; and m and n are integers in the range of two to five are disclosed in U.S. Patent No. 2,634,239. It is trite to remark that detergents are not suggestive of "soil-proofing" finishing agents.

What is claimed is:

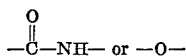
1. Heterocyclic nitrogen base having the composition corresponding to the formula



where Q is a fluoroalkyl group having four to twelve (inclusive) carbon atoms in which at least 70 percent to 100 percent of the $(2n+1)$ hydrogen atoms ($n=4$ to 12)

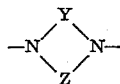
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has been replaced by fluorine atoms and at least two and preferably three fluorine atoms are attached to the terminal or omega carbon atom; X is



R' is hydrogen, CH₃—, C₂H₅—, C₃H₇—; m is one to five dependent upon the functionality of the amido residue; n is at least 1; (m+n) is two to six inclusive, R is a divalent radical selected from the group

Monocyclic ureas

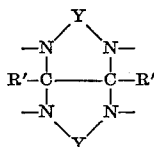


where

Y is C=O, C=NH, C=S, and Z is —CH₂CH₂—, —CH₂CH₂CH₂—, —CH₂OCH₂—, —CH₂—N—CH₂—
R'

R' has the significance given hereinbefore,

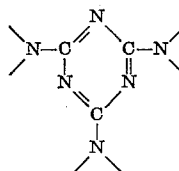
Diheterocyclic ureas



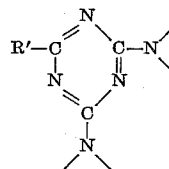
where Y and R' have the significance given hereinbefore

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Triazines



Guanamines



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2. Pentadecafluorooctoxymethylpenta (methoxymethyl) melamine.
3. C₁₁ - trihydroperfluoroalkyltrimethylolacetylene diureine.

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