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HYDROXYMETHYLATED, FLUOROACYLATED AMINOHYDROXY AROMATIC COMPOUNDS

Domenick Donald Gagliardi, East Greenwich, R.I., assignor to Colgate-Palmolive Company, New York, N.Y., a corporation of Delaware

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3 Claims. (Cl. 8—116.2)

The present invention relates to hydroxymethylated fluoroacylated aminohydroxy aromatic compounds to the reaction products of the aforesaid hydroxymethylated aromatic compounds and substrates having active hydrogen in the surface produced in the presence of acid catalysts and to solid substrates having attached thereto the polymers produced by alkaline catalysis of a monomer of hydroxymethylated fluoroacylated aminohydroxy aromatic compound.

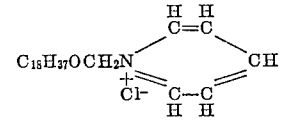
While man has used woven textiles for raiment for more than two thousand years, it was not until about one hundred years ago that he sought to make woven textiles water repellent. The first and, in the light of recent knowledge of the basic principles of surface free energy, contact angle and spreading coefficient, unsophisticated "water-proofing" agents were various mixtures compounded according to "cookbook" recipes which, when applied to woven textiles, coated the surface and filled the interstices of the woven fabric with air-impervious and water-repellent material. This served to provide rainwear such as the Macintosh and the sou'wester but was not completely satisfactory for other uses.

In the period 1935 to 1940 in Germany especially at Chemische Fabricke Pferze with an empirical approach and without understanding the basic principles of water repellency, a series of wax emulsions was developed which, when padded onto textiles, produced a high contact angle of water drops on the surface of the textile and a high degree of shower resistance without changing the porosity or air permeability of the textile material. The fabrics so treated were not wettable by water or by water-borne stains because of the change in free energy of the fiber surfaces and not because, as in prior art treatments of closing the interstices of the fabric with deposits of treating material. By the use of the new wax emulsion-metallic salts compositions, it became possible to produce fabrics which had the feel and appearance of conventional untreated fabrics but did not look like oil-clothes, or rubberized coated fabrics. The primary practical limitation of such compositions was and still is the lack of durability to washing and dry cleaning. Products of this type generally comprise a composition containing (a) a paraffin wax or mixtures of vegetable wax esters such as carnauba, candelilla, or sugar cane wax; (b) an emulsifying agent, generally glue, gelatin, and rosin soaps; and (c) an aluminum or zirconium salt, usually the formate or acetate. The primary function of the salt is to insolubilize the glue and other emulsifiers after the emulsion is deposited on the fabric.

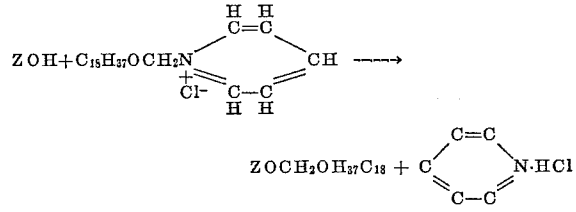
A large variety of such products are still used as low-cost, non-durable water repellents for textiles. Since neither thermosetting nor fiber reaction occurs with such products, they all are non-durable to washing and dry cleaning. Other than water repellency for rainwear fabrics, such products produce fabrics which have a fair degree of spot-and-stain resistance to water-borne stains.

The search for durable or permanent water-repellent finishing materials especially for cellulosic fibers was initiated because of the deficiencies of the afore-discussed wax emulsions. The first major improved product was offered in England under the trade name of "Velan." "Velan" was octadecyloxymethyl pyridinium chloride, a quaternary ammonium compound made by the chloromethylation of

octadecanol followed by quaternization with pyridine and having a composition corresponding to the formula:

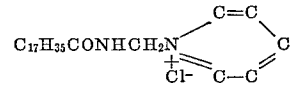


This structure, unlike other quaternary ammonium compounds, is unstable and under acid conditions reacts with surfaces containing active hydrogen, e.g., the hydrogen of a hydroxyl group in cellulose fibers. If Z be the core of the cellulose fiber and OH be an hydroxyl group in the surface thereof, then the reaction can be represented by the formula:



Fabrics treated with a compound such as "Velan" are durably water repellent, are porous, soft, and appear like untreated fabrics.

Du Pont and Warwick Chemical Co. produced a product which was a major improvement of "Velan." The improved product was the stearamidomethyl analog of "Velan" having a composition corresponding to the formula:



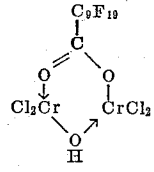
which is available commercially as "Zelan" and "Norane R." The advantage of the stearamide product is greater initial water repellency and greater durability to washing. Such products are leaders in rainwear fabric finishes.

In the search for other fiber reactive or durable water repellents, other classes of materials have now evolved as represented by silicone water repellents, methylol stearamide compositions ("Permel," "Ahcovel NW"), hydrophobic resins ("Norane GG," "Ranedare R," "Argus DWR"), octadecylketene dimer ("Aquapel"), and others.

While durable water-repellent finishes had been initially developed for outerwear- and rainwear-type applications, in the period 1950 to 1956 such products began to be used widely on men's suitings, dress goods, and upholstery materials. In this exploitation of these finishes emphasis was placed not on water repellency but on resistance to spotting and staining by waterborne stains. This use continues. It had been observed that fabrics treated with such durable water repellents had a high degree of resistance to soiling by water-borne soils and stains and were easier to launder. The principal limitation of such finishes was that they attracted rather than repelled oily soils and the fabrics were not repellent to staining by oil materials such as oils, greases, gravy, mayonnaise, etc.

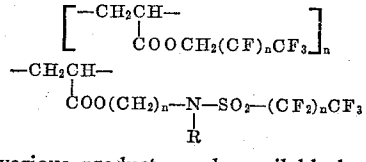
In the early part of the decade of 1950 to 1960 based on work done at the Naval Research Laboratory by Fox and Zisman and work done by the Kellogg division, later to become a part of the operations of Minnesota Mining and Manufacturing Company, the latter announced the utility of certain fluorocarbon based chemicals as finishes for various fibers. Fox and Zisman had demonstrated the physicochemical principle of low free-energy surfaces and the relation to non-wetting with water and oil of surfaces treated with chemicals containing perfluoroalkyl groups.

The practical developments of Minnesota Mining and Manufacturing Company resulted in the first product directed to textile finishing. This was and still is the product known as FC–149. FC–149 is a classical Werner complex of a carboxylic acid made by reacting one mol of the carboxylic acid with 2 mols of basic chromic chloride to obtain a reaction product having a composition represented by the formula:



The compound is water soluble and cationic in nature. It shows strong adhesion to anionic substrates such as cellulose and fiberglass. It also complexes with proteinaceous materials such as wool, silk, and leather to yield both water- and oil-repellent surfaces.

A second general class of products developed by Minnesota Mining and Manufacturing Company (often referred to as "3M") comprise latices of perfluorochemicals. For example, some of these are believed to have a composition corresponding to the formulae:



These various products made available by "3M" produced a great practical improvement in fabric finishes. Although of some merit for plain water repellency for outerwear finishing, the two products offered a solution to obtaining water and oil repellency and practical resistance to staining. Because of its hydrolytic instability, the Werner complex product has been limited to wool, leather, and upholstery finishes. The acrylate products have become prominent in finishing cotton, rayon, and synthetic fibers.

Thus, while the progress in the art of imparting water-repellency to textiles has been noteworthy, the soiling problem has not been solved. Recognizing the need for reproducible results, those concerned with research in this field have developed a test for water repellency, a test for oil repellency, a test for resistance to water-borne and oil-borne stains and, for household furnishings, the most important: a test to evaluate "particulate soil" repellency.

Water repellency.—Resistance to wetting (spray test) AATCC Standard Test Method 22–1952

This test method 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 applied. 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.

Appearance of test specimen:	Rating
No sticking or wetting of the upper surface	100
Slight random sticking or wetting of the upper surface	90
Wetting of the upper surface at the spray points	80
Partial wetting of the whole of the upper surface	70
Complete wetting of the whole of the upper surface	50
Complete wetting of the whole of the upper and lower surfaces	0

When measuring the spray rating, especially of finishes of the present invention, it is not unusual to encounter a test specimen with sufficient hydrophobic properties to confine the area of wetting and yet permit wetting through. Thus, it becomes necessary to have a rating for this condition. The following illustrates this modification of the standard wetting evaluation:

A spray rating number of 70/0 is reported for a spray pattern comparable to the standard "70" rating but the under surface is also wetted to some extent. The 70 of the numerator indicates equivalence with the standard test pattern for a rating of 70. The zero in the denominator indicates wetting to the under surface of the cloth at the wet areas.

The test specimens having a minimum size of 7" x 7" 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 degrees to the horizontal. Two hundred and fifty milliliters of water at 80°±2° F. is poured into the funnel attached above the spray nozzle. The spray lasts twenty-five to thirty 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 degrees.

Oil repellency tests.—3M oil repellency test: "3M Textile Chemicals" (Appendix A, Test Methods, page 1)

The Minnesota Mining and Manufacturing Company oil repellency test is based upon the different penetrating properties of the two hydrocarbon liquids, mineral oil ("Nujol") and n-heptane. The "Nujol"-heptane proportions for each rating were selected by 3M so as 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 (supra):

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	----------	(1)

[1] No hold out to Nujol.

The standard oil-heptane mixtures are contained in small stoppered medicine dropper bottles. A drop of each mixture is placed on the fabric. The appearance of the test oil is observed through the drop. Note is made whether wetting or penetration has occurred. The number corresponding to that mixture containing the highest percentage of heptane which does not penetrate nor 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 of zero oil/heptane rating, the symbol 0+ has been used to indicate a modicum of resistance to wetting by oil.

Stain Repellency.—Standing tests in anti-soiling evaluation of the resistance of textile fabrics to water- and oil-borne stains

The following procedures were established in the application of liquid staining materials more nearly approaching the materials producing water- and oil-borne stains to which household furnishings in actual daily use.

(a) The fabrics are stretched lightly on 12" x 31" frames. All or part of the frame area is used depending

upon the amount of fabric available. The frames are supported at both ends with the fabric about 8 inches above a horizontal black surface. The fabric touches nothing.

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

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

Appearance:	Rating
No visible stain	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 these ratings.)

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

The following two lists describe the numbering system and organization of the stains on the fabrics:

Water stains	Oil stains
(1) Instant tea [a]	(6) Wesson Oil
(2) Sheaffer's 232 blue-black Skrip	(7) Gulf Supreme Motor oil 20/20
(3) A & P Concord grape juice	(8) Oleomargarine [b]
(4) Ann Page salad mustard	(9) La Rosa tomato sauce
(5) Bosco chocolate syrup	(10) Jergen's lotion

[a] Eight cubic centimeters of dry powder per 200 cubic centimeters of water applied at 160° F.
[b] Melted and applied at 160° F.

Those skilled in the art will recognize that, while these stains are not scientifically compounded, they are stains to which household furnishings are exposed in the use attendant upon everyday life.

When reporting the relative resistance to staining and relative ease of removing stain in laundering, the values from water-borne stains and oil-borne stains are averaged and reported. In all cases the stains are allowed to dry on the fabrics for twenty-four hours before washing.

Household furnishings is a term used herein to designate all articles in the home of prince or pauper which are washed regularly at relatively frequent intervals or semi-occasionally at relatively irregular infrequent intervals. Household furnishings include bed linen, i.e., sheets, pillow cases, blankets, tablecloths, napkins, curtains, draperies, underthings, shirts, dresses, sox, handkerchiefs, blouses, skirts, slipcovers, and the like. It will be recognized that the term "household furnishings" is inclusive but not exclusive.

As everyone will recognize while the aforedescribed controlled staining tests are extremely useful for evaluating the effectiveness of various textile finishes, the incidence of staining a shirt front with salad oil (Wesson Oil) is only occasional whereas the staining of the collar and cuffs of a man's shirt with the finely divided soil of the environment mixed with the oily exudations of the healthy human skin is a moment-to-moment occurrence. Hence, important as the aforedescribed tests are, a test to evaluate the resistance of a finish to the pick-up of such soil, hereinafter designated "oily particulate soil," i.e., a test to evaluate the ability to shed oily particulate soil and the ease with which such oily particulate soil is removed by laundering under controlled conditions of soiling is of greater importance. Such a controlled test providing reproducible results has been developed and is designated the "GRC" Dry Soil Test.

GRC Dry Soil Test

Fifteen to twenty 6" x 8" numbered specimens (usually 80 x 80 cotton), including at least one untreated control, are tumbled for thirty minutes with 10 percent "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 the tumbling, the specimens are removed and each shaken up and down separately 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 soil is determined with the "Photovolt Reflectance Meter" (Tri-Blue Filter). Six readings per specimen are taken. The average of the six readings is reported.

Cyanamid Soil

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

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

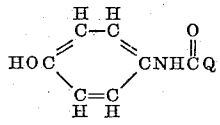
[1] R. T. Vanderbilt "Peerless."
[2] Davison Chemical Company.
[3] Benny & Smith Co. "Molacco."
[4] C. K. Williams Co.

It has been found that hydroxymethylated, fluoroacylated derivatives of aminohydroxy aromatic compounds having at least two active nuclear hydrogens impart to confer upon or endow textiles, i.e., fibers, yarns, fabrics, and the like composed of cellulosic, including natural such as cotton and regenerated proteinaceous including natural such as wool and synthetic fiber and particularly fibers having active hydrogen in the surface. It is to be observed that the compounds of the present invention can also be used for coating materials which do not have active hydrogen in the surface such as the polyalkylenes, e.g., polypropylene, and metals such as steel.

In general, the compounds of the present invention are prepared by methods of classical chemistry. Thus, an aromatic compound having one benzene ring or two or more fused rings is reacted in known manner to obtain the hydroxy compound. The latter is then reacted in known manner to obtain the amino hydroxy compound. While the single ring compounds are limited to a single amino and a single hydroxy group, i.e., paraaminophenol having two active nuclear hydrogens, the aromatic compounds having two or more fused rings can have one or a plurality of hydroxy groups and one or a plurality of amino groups provided the resulting compound has two active nuclear hydrogens. Thus, for example, the dimethylol derivative of paraaminophenol is illustrative of the single ring compounds while aminoalphanaphthol or 4-aminonaphthol is illustrative of the multi-ring compounds which can be used as starting materials for the preparation of the mono-methylol or dimethylol compounds of the present invention.

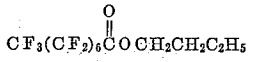
Illustrative of the preparation of a perfluoroacyl derivative of paraaminophenol having the generic formula:

(1)



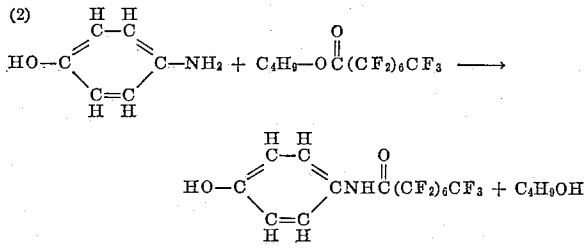
where Q is an alkyl group having 3 to 21 carbon atoms in which at least 70 percent of the 5 to 43 hydrogen atoms has been replaced with fluorine atoms and the terminal, i.e., omega carbon atom has at least two and preferably three fluorine atoms.

Thus, 0.1 mol of the butyl ester of perfluorooctanoic acid



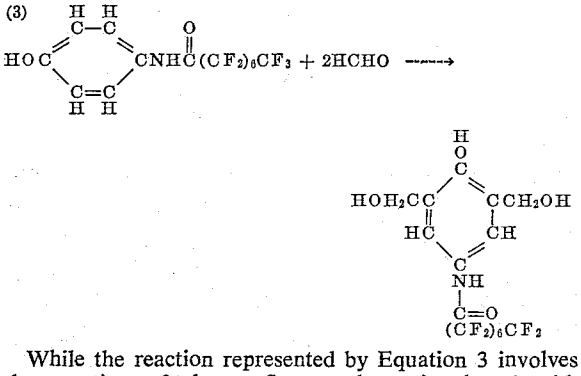
is mixed with 0.1 mol of p-aminophenol, $NH_2C_6H_4OH$, and 225 parts by weight of methyl ethyl ketone. The reaction mixture was heated to reflux temperature (80° C.) for 3.5 hours to effect ammonolysis. The reaction can be represented by the equation:

(2)

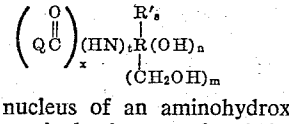


The reaction mixture was stripped at elevated temperature to remove all solvents, i.e., methylethylketone and butyl alcohol. To 25 parts by weight of the stripped residue were added 5.5 parts by weight of a 55 percent methanol solution of formaldehyde. The pH of the mixture was adjusted to 11.4 by the additon of caustic soda and the reaction mixture heated two hours at reflux to effect methylolation. The methylolation of the perfluoroctoyl-p-aminophenol can be represented by the equation:

(3)

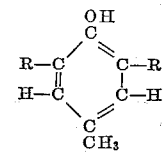


While the reaction represented by Equation 3 involves the reaction of the perfluoroacyl-p-aminophenol with formaldehyde in the molal ratio of 1 to 2, those skilled in the art will understand that the perfluoroacyl-p-aminophenol can be reacted with formaldehyde in the molal ratio of 1 to 1. Accordingly, the methylol derivatives of perfluoroacylaminohydroxy aromatic compounds having two active hydrogens have the generic formula:



where R is the nucleus of an aminohydroxy aromatic compound having a single ring, two fused rings, or three fused rings, Q has the same significance as in Formula 1, R′ is hydrogen or alkyl having one to five carbon atoms, n is 1 or 2, m is one or two, t is one or two, s an integer 6, 8, or 10 minus $(m+n+t)$, x is the same as t.

The novel perfluoroacyl aminohydroxy monomethylol and dimethylol compounds are not to be confused with prior disclosed compounds as simple methylol phenols. For example, in U.S. Patent No. 2,468,530, the after treatment of viscose rayon to reduce the swelling value and increasing the water resistance and wet strength of viscose rayon with mono- and di-substituted derivatives of mono- and di-substituted phenols such as paracresol mono- and di-alcohols represented by the formula:

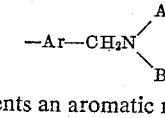


where R is H or CH_2OH. However, these resins do not confer surface water or oil repellency to textile fibers.

The perfluoroacyl derivatives of aminohydroxy aromatic compounds are not to be confused with the perfluorinated cyclohexyl carboxylic acid and cyclohexyl acetic acid derivatives described in U.S. Patent No. 2,593,737 having the composition represented by the generic formula R—Z where R is a saturated polycarbon fluorocarbon radical containing at least three carbon atoms and Z is a monocarboxyl radical or a carbon-containing derivative radical hydrolyzable thereto such as $C_6F_{11}COOH$, undecafluorocyclohexyl carboxylic acid.

In U.S. Patent No. 2,495,239 a method for treating cellulose is described. The patented method comprises condensing in alkaline medium para-tertiary-amyl phenol and formaldehyde in the molecular ratio of 1:2 and reacting the condensation product with cellulose material containing free hydroxyl groups and subjecting the cellulosic reaction products to thermal treatment to form resiniform bridge linkages between the cellulose chains.

A process of rendering textile fabrics, yarns, and fibers waterproof without materially altering the general appearance of the fabric is described in U.S. Patent No. 2,257,088. These results are produced by the use of compounds having the general structure



in which Ar represents an aromatic nucleus of the benzene or naphthalene series carrying a nuclearly bound oxygen and at least one hydrocarbon substituent of the aliphatic or cycloaliphatic series which contains eight or more carbon atoms and which is bound to the aromatic nucleus directly or through an ether, carbonyl, carboxyl, or carbamido linkage. The nuclearly bound oxygen may be part of hydroxyl group or a part of a side chain. A and B represent members of the group consisting of open chain, lower aliphatic groups when taken singly and when taken together divalent groups which jointly with the nitrogen form a heterocycle.

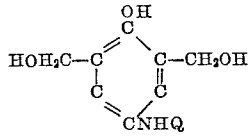
In direct contrast to the materials described in the foregoing U.S. patents, the compounds of the present invention are high melting point waxes which either react with active hydrogen in the substrate in the presence of an acid catalyst such as oxalic, phosphoric, and zinc nitrate, or form a coating on the substrate be it fibrous such as cotton, wool, nylon, polyethylene, wood, steel, aluminum, glass, or other ceramic having no active hydrogen when an alkaline catalyst such as NaOH, borax, and potassium methoxide is used.

Thus, for example, the dimethylol perfluorooctanoylaminophenol, the preparation of which has been described hereinbefore, can be suspended in water containing an acid catalyst, a fibrous material immersed in the water, the treated fibrous material squeezed to at least 80 percent wet pick-up and the treated fibrous material heat-treated at a temperature in the range of 250° to 300° F. for a period of time inversely proportional to the tem-

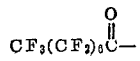
perature and for example five to ten minutes at 300° F. (80 percent wet pick-up is a term meaning that the fibrous material contains 80 percent by weight based on the weight of the fibrous material of the aqueous suspension. Hence, when the suspension contains 1 percent by weight of the methylol derivative, the fibrous material contains 0.8 percent of the methylol derivative. Similarly, the methylol derivative can be dissolved in a suitable solvent, for example, xylene containing an acid catalyst, the fibrous material immersed in the solution of the methylol derivative, the fibrous material squeezed to the predetermined wet pick-up in the fibrous material, the solvent removed and the treated fibrous material heat treated as previously described.

On the other hand, any solid substrate with or without active hydrogen can be treated to provide the solid substrate with a coating of the polymerized methylol derivative. Thus, an aqueous suspension or a solution in a suitable organic solvent such as xylene cotaining an alkaline catalyst for example $NaOCH_3$, ZnO, and triethanolamine can be applied to the solid substrate in any suitable manner as by dipping, spraying, spreading, or other means, the excess, if any, removed, and the treated solid substrate heat treated at elevated temperatures of at least 250° F. but below the decomposition temperature of the substrate or the methylol polymer for a period of time inversely proportional to the temperature, for example, at 300° F. for five to ten minutes.

Indicative of the water- and oil-repellency and the resistance to soiling by oily particulate soil is the treatment of cotton with the bis-formaldehyde adduct to perfluorooctanoyl-p-aminophenol:



where Q is



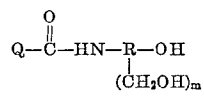
Treatment applied—3% product plus 0.5% $Zn(NO_3)_2.6H_2O$

Oil repellency obtained	100
Reflectance:	
Before wash	33
After wash	62

Accordingly, the present invention provides (1) novel mono- and di-methylolamino hydroxy aromatic compounds, (2) fibrous or solid substrates having associated therewith polymerized mono- and di-methylol aminohydroxy aromatic compounds, and (3) perfluoroacyl aminohydroxy aromatic compounds.

What is claimed is:

1. The reaction product produced by the acid catalyzed reaction of an fibrous substrate having active hydrogen in the surface therewith with a methylolperfluoroacylaminohydroxy aromatic reactant, corresponding to the formula:



where R is an aromatic residue selected from the group consisting of benzene and naphthalene nuclei; Q is an alkyl group having three to twenty-one carbon atoms in which at least 70 percent of the 5–43 hydrogen atoms have been replaced with fluorine atoms; and *m* is the integer 1 or 2.

2. The reaction product of claim **1** produced by the reactant, monomethylol N - pentadecafluorooctanoyl-p-aminophenol.

3. The reaction product of claim **1** produced by the reactant, dimethylol N-pentadecafluorooctanoyl-p-aminophenol.

No references cited.

NORMAN G. TORCHIN, *Primary Examiner.*

J. C. CANNON, *Assistant Examiner.*