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Information sheets "XERODERM LF" of Bayer

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Description

Background of the Disclosure

5 This invention, in one aspect, relates to a composition comprising a fluorochemical compound useful for treating leather, textiles, and cellulosic materials. In another aspect, the invention relates to a method for treating these materials with the composition. In a third aspect, this invention relates to leather, textiles and cellulosic materials treated with the composition.

10 Leather has a combination of properties which has long made it useful and desirable for many applications, e.g. footwear, garments, and upholstery, requiring protection, comfort, durability, and esthetics. Such properties include long term flexibility, toughness, breathability, insulation, conformability, soft feel, and luxurious appearance. However, due to its porous, fibrous structure, leather absorbs water and oil, and the consequent unsightly spotting and stains detract from its usefulness and appearance. There had been considerable effort expended to overcome these drawbacks of leather. See Kirk-Othmer, Encycl. of Chem. 15 Tech., Vol. 22, 1970, John Wiley & Sons, p 150, 151.

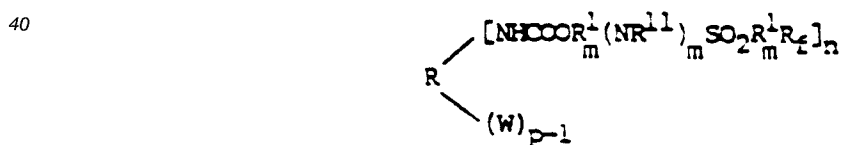
Leather has been frequently treated with various substances to impart greater water and oil repellancy. Because the desired result of such treatment may vary depending upon the user's expectation, it is much more practical for the ultimate consumer to apply the treating product rather than the manufacturer.

20 At present, products that are used by consumers to impart water and oil repellancy to leather include waxes, e.g., beeswax, carnauba wax, paraffin wax; greases, e.g., lanolin; oils, e.g., fish oil, mink oil, neat's-foot oil, silicones, e.g., dimethylpolysiloxane, silicone resins; and fluorochemicals, e.g., FC-326 Scotchgard® Brand Fabric Protector available from Minnesota Mining and Manufacturing Company, and FC-905 3M Brand Fluorochemical available from Minnesota Mining and Manufacturing Company.

25 The waxes, greases, oils, and silicones have been found to impart some degree of water and oil repellancy to leather; however, none of these are as effective as fluorochemicals in providing water and oil repellancy. Fluorochemicals, however, are somewhat less desirable to use than waxes or oils, generally because certain of the solvents needed to apply fluorochemicals to leather are deleterious to leather or dyes that have been applied to the leather. Furthermore, unlike waxes or oils, presently available fluorochemical compounds are not known to condition or clean leather.

30 Although there are many commercially available fluorochemicals which will impart water and oil repellancy to textiles, they are generally applied from solutions wherein the solvent is a chlorinated hydrocarbon, e.g., trichloroethane. Many consumers find chlorinated hydrocarbons objectionable for both health and environmental reasons.

35 DE-A-1,418,985 discloses fluorochemical compounds for treating paper, textile, leather and other articles. The compounds are incorporated in an emulsion or are dissolved in an organic solvent and are defined by a general formula which includes as one of many sub-classes of compounds those compounds defined by the formula:



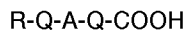
45 where R may be a hydrocarbon group, R¹ may be an alkyl group, R is a fluorinated aliphatic group, W may be an isocyanate, m is 0 or 1, 1 ≤ b ≤ 3, 1 ≤ p ≤ 6 and (2n + (p-1)) ≤ 6. Table III lists various aromatic isocyanate reactants which can be utilised to form W.

50 FR-A-2,106,269 discloses organic solvent-based compositions containing fluorochemical compounds for treating textile and cellulose fibres. The fluorochemical compounds are defined by a general formula which includes the sub-class of compounds defined by the formula:



where R¹ is a perfluoroalkyl group having 3 to 11 carbon atoms and R₃, R₄, and R₅ are independently alkyl, aryl, aralkyl or lower cycloalkyl groups.

EP-A-0,107,948 which forms part of the state of the art against the present application by virtue of Article 54(3) EPC, discloses a general formula which includes the sub-class of compounds represented by the formula

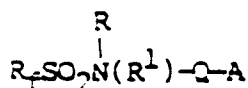


where

- R is a fluoroaliphatic radical
- Q is an organic linkage, and
- A is -NHCONH-, -CONH-, -OCO-, or -OCONH-.

Summary of the Invention

In one aspect the invention provides a method of treating a material selected from the group consisting of leather, textiles, and cellulose in order to provide enhanced water and oil repellancy thereto comprising the step of applying to said material a composition comprising a compound represented by the formula:



wherein:

R_f is saturated, monovalent, non-aromatic radical of up to 20 carbon atoms, containing a terminal perfluoromethyl group and at least three fully fluorinated connected carbon atoms in a straight, branched or cyclic chain, and optionally incorporating Cl substituents, subject to the proviso that not more than one atom of Cl is present in R, for every two carbon atoms present in (R_f + R + R¹).

R represents an alkyl radical having 1 to 4 carbon atoms,

R¹ represents an alkylene radical having 1 to 12 carbon atoms,

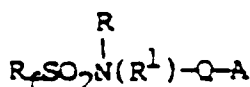
A represents a hydrocarbon or carboxylate group having from 5 to 36 carbon atoms, said group A being derived from a fatty acid and/or a fatty alcohol and having at least one unsaturated site, and, optionally being substituted with one or more hydroxyl (-OH) or carboxyl (-COOH) groups.

Q represents a member selected from the group consisting of



In another aspect the invention provides a composition for treating leather textiles, and cellulosic materials in order to provide enhanced water and oil repellancy thereto, said composition comprising:

(a) a compound represented by the formula



Wherein:

R_f is a saturated, monovalent, non-aromatic radical of up to 20 carbon atoms, containing a terminal perfluoromethyl group and at least three fully fluorinated connected carbon atoms in a straight, branched or cyclic chain, and optionally incorporating Cl substituents, subject to the proviso that not more than one atom of Cl is present in F, for every two carbon atoms present in (R_f + R + R¹);

R represents an alkyl radical having 1 to 4 carbon atoms,

R¹ represents an alkylene radical having 1 to 12 carbon atoms,

A represents a hydrocarbon or carboxylate group having from 5 to 36 carbon atoms, said group A being derived from a fatty acid and/or a fatty alcohol and having at least one unsaturated site, and,

optionally being substituted with one or more hydroxyl (-OH) or carboxyl (-COOH) groups,

Q represents a member selected from the group consisting of

5



and

10 (b) a vehicle that is not deleterious to said leather, dyes that have been applied to said leather, said textiles, or said cellulosic materials.

The fluorochemical compounds useful in this invention confer durable water and oil repellancy to leather while not adversely affecting the appearance, feel, hand, and other desirable qualities of the leather. The fluorochemical compounds useful in the practice of this invention are capable of providing up to about 30
15 times as much water repellancy to leather as the best commercially available leather treatment products.. The fluorochemical compounds are also useful for imparting water and oil repellancy to textiles, including both natural materials, e.g. cotton, silk, and synthetic materials, e.g. nylon, polyester. In addition the fluorochemical compounds have been found to be useful for imparting water and oil repellancy to cellulosic materials, e.g. wood, paper.

20 The sites of unsaturation in the fluorochemical compounds of the invention allow crosslinking after the composition is applied to the surface of the leather. The preferred solvents from which these fluorochemical compounds can be applied are not only not harmful to leather, but they are also capable of cleaning and conditioning the leather. In addition, the solvents perform the additional function of suppressing cross-linking of the fluorochemical compounds before the composition is applied to the leather. Upon evaporation of the
25 solvent after application of the composition, the fluorochemical compound cross-links to cure in air at normal room temperature.

The fluorochemical compounds of this invention can be applied from solvent that are not harmful to the health of the consumer, to leather itself, to dyes previously applied to leather, or to textiles and cellulosic materials. While not preferred, the fluorochemical compounds can also be applied from chlorinated
30 hydrocarbon solvents. Compositions of the present invention can be readily formulated into a variety of preparations for various modes of application to leather and/or textiles and/or cellulosic materials.

The fluorochemicals useful in this invention preferably contain at least 20 weight percent, preferably 25 to 50 weight percent, fluorine in the form of said fluoroaliphatic radical.

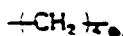
In the most preferred embodiments of the invention, R is -CH₃ and R¹ is -CH₂CH₂-,

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or

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The chain in the radical A may be straight, branched, or cyclic. The radical preferably contains two or more unsaturated sites. Compositions of the present invention containing fluorochemical compounds having
45 unsaturated sites are easy to formulate, because the fluorochemical compounds readily dissolve in solvents that are not harmful to leather. In addition, when these compositions are applied, the unsaturated fluorochemical compounds begin to cross-link as the solvent evaporates and continue to cross-link even several days after application. The aliphatic moiety A can be substituted with one or more pendant hydroxyl groups (-OH) or one or more pendant carboxyl groups (-COOH) or both.

50 The organic linking group, Q can have a wide variety of structures, serving as it does the function of bonding together in the same molecule the R, and A moieties. The Q linkages should be free of moieties, particularly hydrophilic groups, such as acid functional groups and salts thereof, e.g. -COOH and -COONa, polyoxyethylene, polyethyleneimine, and aliphatic hydroxyl groups, which would interfere with the ability of the fluorochemical compounds to impart the desired oil and water repellancy to the substrate treated
55 therewith in accordance with this invention.

However, it should be noted that Q for a specific fluorochemical compound useful in this invention will be dictated by the ease of preparation of such compound and the availability of the necessary precursors thereof.

The products of the present invention can be prepared by any of the following method:

(1) reacting a fluoroaliphatic sulfonamido alcohol with a fatty acid:

Alternatively, the fluoroaliphatic sulfonamido alcohols and the fatty acid can be replaced by a fluoroaliphatic sulfonamido carboxylic acid and a fatty alcohol respectively. Because of the nature of such intermediates and such reactions, the fluorochemicals so prepared and useful in this invention will often be mixtures of isomers and homologs.

The fluoroaliphatic reactants may be chemically combined with the aforementioned coreactants through the condensation of their hydroxyl or carboxyl groups with available carboxyl and hydroxyl groups in fatty acids or fatty alcohols to form an ester linkages or bridging radical or through the addition of their hydroxyl or carboxyl groups to an isocyanate group to form a urethane linkage and amine linkage respectively. The reaction of these fluoroaliphatic acids and alcohols with the coreactants may be carried out in a manner similar to that conventionally employed with nonfluorinated carboxyl or hydroxyl containing components.

The reaction (1), can be conducted by introducing the reactants into a vessel containing a catalyst. Catalysts that are suitable for the reactions include sulfuric acid and ion exchange resins. Commercially available ion exchange resins that are useful as catalysts in the reactions include Amberlite® IR 120, a strongly acidic, sulfonated polystyrene cation exchange resin, and Amberlite® 15, a strongly acid, sulfonic functional cation exchange resin, both of which are available from Mallinckrodt. The reaction medium can include a solvent or it can be solvent free. Solvents suitable for the reaction include xylene and mixtures of hydrocarbons. A commercially available mixture of hydrocarbons useful as a solvent for the reaction medium is sonar L, available from Exxon. The reaction is preferably conducted under an atmosphere of nitrogen and refluxed until no additional water is generated.

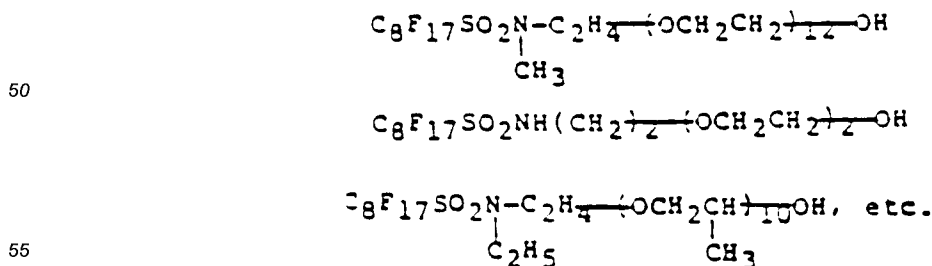
Monofunctional alcohols useful in this invention include the N-alkanol perfluoroalkanesulfonamides described in U.S. Patent 2,803,656, which have the general formula



wherein R_f is a perfluoroalkyl group (including perfluorocycloalkyl) having 4 to 10 carbon atoms, R^1 is an alkylene radical having 1 to 12 carbon atoms, and R is a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms. These monofunctional alcohols are prepared by reactions of an acetate ester of halohydrin with a sodium or potassium salt of the corresponding perfluoroalkanesulfonamide. Illustrative alcohols include the following:

- N-ethyl N-(2-hydroxyethyl)perfluorooctanesulfonamide,
- N-propyl N-(2-hydroxyethyl)perfluorooctanesulfonamide,
- N-ethyl N-(2-hydroxyethyl)perfluoroethanesulfonamide,
- N-ethyl N-(2-hydroxyethyl)perfluorododecanesulfonamide,
- N-ethyl N-(2-hydroxyethyl)perfluorocyclohexylethanesulfonamide,
- N-propyl N-(2-hydroxyethyl)perfluorobutylcyclohexanesulfonamide.
- N-ethyl N-(2-hydroxyethyl)perfluoro-4-dodecylcyclohexanesulfonamide,
- N-ethyl N-(2-hydroxyethyl)perfluoro-2-methylcyclohexanesulfonamide,
- N-ethyl N-(6-hydroxhexyl)perfluorooctanesulfonamide,
- N-methyl N-(11-hydroxyundeoyl)perfluorooctanesulfonamide,
- N-methyl N-(4-hydroxybutyl)perfluorobutanesulfonamide,
- N-(2-hydroxyethyl)perfluorooctanesulfonamide, etc.

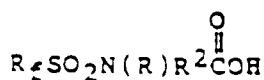
Further useful monofunctional alcohols include the N-[-hydroxypoly(oxaalkylene)]perfluoroalkane sulfonamides of U.S. Patent 2,915,554, such as



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Suitable carboxyl-containing fluoroaliphatic reactants include the monofunctional perfluoroalkanesulfonamidoalkylene-carboxylic acids of U.S. Patent 2,809,990, which have the general formula:

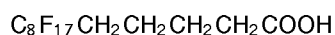
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10 wherein R_1 is a perfluoroalkyl (including perfluorocycloalkyl) group having from 4 to 10 carbon atoms, R is hydrogen or an alkyl group having from 1 to 4 carbon atoms and R^2 is an alkylene group having from 1 to 12 carbon atoms. Illustrative acids include the following:

- 15 N-ethyl N-perfluorooctanesulfonyl glycine,
- N-perfluorooctanesulfonyl glycine,
- N-perfluoropentanesulfonyl glycine,
- 15 N-perfluorodecane sulfonyl glycine,
- 3-(perfluorooctanesulfonamido) propionic acid,
- 11-(N-methyl N-perfluorooctanesulfonamido) undecanoic acid,
- 11-(N-ethyl N-perfluorooctanesulfonamido) undecanoic acid,
- N-ethyl N-perfluorocyclohexylsulfonyl glycine,
- 20 N-ethyl N-perfluorocyclohexylethanesulfonyl glycine,
- N-butyl N-perfluoro-4-dodecylcyclohexanesulfonyl glycine.
- N-ethyl N-perfluoro-2-methylcyclohexanesulfonyl glycine.
- N-hexyl N-perfluorooctanesulfonyl glycine,
- N-ethyl N-perfluorobutanesulfonyl glycine, etc.

25 Still other carboxyl containing fluorocarbon reactants include the perfluoro-substituted aliphatic acids, described in U.S. Patent 2,951,051, such as



30 5-perfluorobutyl pentanoic acid, 11-perfluorooctylhendecanoic acid, etc as well as the unsaturated perfluoroalkane aliphatic acids, e.g. $R_1CH=CH-(CH_2)_7CH_2CO_2H$, also described in U.S. Patent 2,951,051.

Fatty acid and fatty alcohol reactants useful in the practice of this invention preferably have at least one to three unsaturated sites, and more if available. Representative examples of fatty acids suitable for the practice of this invention include, but are not limited, to, linseed fatty acid, linolenic acid, eleostearic acid, 35 ricinoleic acid, oleic acid, linoleic acid, sorbic acid, dimer acid, and mixtures thereof. Representative fatty alcohols that are suitable for the practice of this invention are the analogs of the fatty acids mentioned above.

Reactions schemes that can be used for preparing the compounds of the present invention are set forth below:

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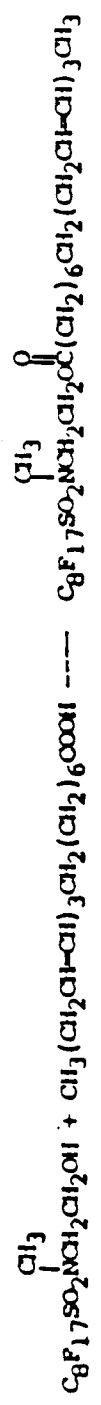
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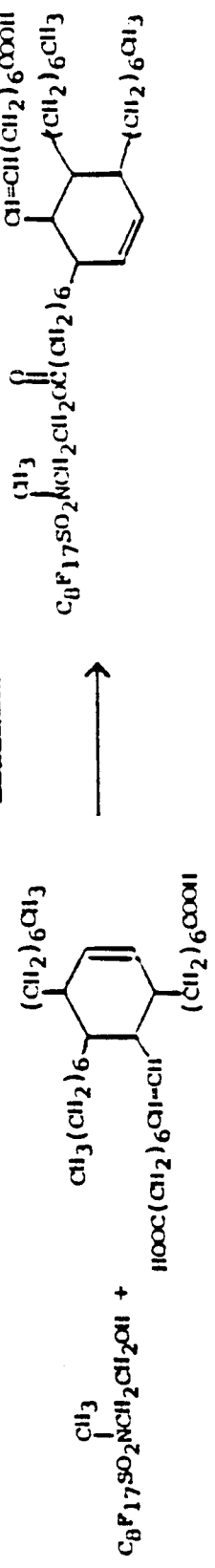
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Scheme 1



Scheme 2



The fluorochemical compounds useful in the practice of this invention can be dissolved in an appropriate organic solvent or mixture of organic solvents, and applied directly from the resulting solution. Solvents that are suitable for dissolving the fluorochemicals include chlorinated hydrocarbons, e.g. tetrachlorethane, trichloroethane, isoparaffinic hydrocarbons, alcohols, e.g., isopropyl alcohol, ketones, e.g., methyl isobutyl ketone, and mixtures thereof. Although chlorinated hydrocarbons can be used to dissolve the fluorochem-

icals, they are not recommended because they can damage leather and dyes that are used on leather. Furthermore, chlorinated hydrocarbons can be objectionable to user of the composition of this invention. The composition can be applied in any of several alternative formulations, including, for example, aerosols, water/oil emulsions, and anhydrous gels. Aerosols will require a propellant, e.g. isobutane. Anhydrous gels will require a gelling agent, e.g. aluminum oleate. Water/oil emulsions will require water and an emulsifying agent, e.g. sorbitan sesquioleate. Water/oil emulsions and anhydrous gels can further employ mild solvents, e.g. isoparaffinic hydrocarbons, which can serve the dual purpose of carrying the fluorochemical and acting as a cleaning aid for the leather. Conditioners and softeners, e.g. mineral oil, can also be included in compositions of the present invention.

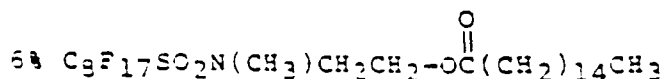
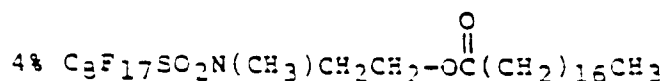
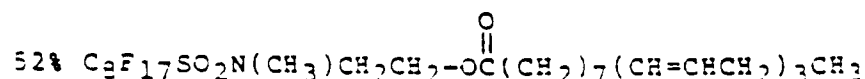
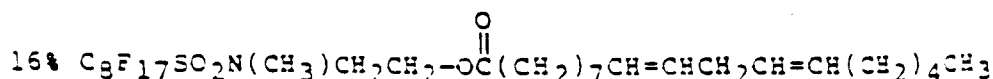
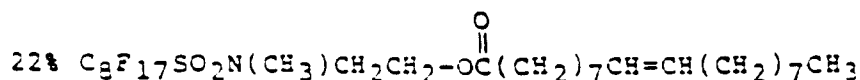
The composition of this invention can be used to treat such leather articles as show uppers, garments, gloves, luggage, handbags, upholstery, and the like. The composition is particularly useful for leathers having porous surfaces, such as natural smooth leathers having no finish and suede leathers. The composition can also be used with finished skins, e.g. those having a sprayed on leather finish. The composition can also be used to treat textile articles such as clothing, shoes, and the like. The composition is especially useful for articles comprising leather and textiles, e.g. shoes, fashion accessories. In addition, the composition can be used to treat cellulosic materials such as wood and paper.

The amount of the fluorochemical deposited on the leather can vary, but functionally stated that amount will be sufficient to impart oil and water repellency to the leather. Generally that amount will be about 0.05 to 1.0 percent by weight, preferably 0.1 to 0.2 percent by weight based on the weight of the leather after it is dried. More can be applied, but a greater effect will probably not be noticed. With such amounts of fluorochemical deposited on the leather, the leather will have oil and water repellency that is durable, that is, the repellency will last a long time during active use of the article made from such finished leather, the fluorochemical penetrating to a significant depth into the leather. Such durable repellency is obtained without adversely affecting the appearance, feel, hand, flexibility, breathability, or other desirable properties of leather. And such desirable properties are obtained not only by treated cattlehide in accordance with this invention but other finished hides and skins, such as sheepskin and pigskin. The amount of fluorochemical required to impart water and oil repellency to textiles and cellulosic materials is substantially similar to that amount required to impart those properties to leather.

Objects and advantages of this invention are shown in the following examples, Examples 1-11 illustrating the preparation of various fluorochemicals of this invention, Examples 12-13 illustrating the effectiveness of various fluorochemicals in the treatment of leather, and Examples 14-16 illustrating various formulations into which the fluorochemicals can be incorporated.

Example 1

In a one-liter, three-necked round-bottomed flask equipped with a reflux condenser and fitted with a Dean Stark water trap were charged 250 g (0.449 mole) N-methyl(perfluorooctane)sulfonamidoethyl alcohol, 153 g (0.550 mole) linseed fatty acid, 20 g Amberlyst® 15 cation exchange resin, and 150 g xylene solvent. The resulting mixture was stirred and refluxed in an atmosphere of nitrogen at 144 °C for about 16 hours to complete the reaction, as indicated by the water given off as a by-product. The resulting product solution contained the following components in the weight ratio indicated:



Examples 2-7

Following the general procedures of Example 1, and using the appropriate or corresponding precursor fluorochemical alcohol and fatty acid, all in the appropriate molar ratios, there were prepared the 5 fluorochemical products represented by the formulas shown in Table I.

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Table I

Ex. No.	Fluorochemical	Unsaturated Fatty Acid	Formula of Product
2	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OH$	Eleostearic	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OC(=O)(C_{11}H_2)_{7-}C_{11}H=C_{11}H=C_{11}H=C_{11}(C_{12})_3C_{11}H_3$
3	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OH$	Ricinoleic	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OC(=O)(C_{11}H_2)_{7-}C_{11}H=C_{11}H_2C(OH)(C_{12})_5C_{11}H_3$
4	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OH$	Oleic	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OC(=O)(C_{11}H_2)_{7-}C_{11}H=C_{11}(C_{12})_7C_{11}H_3$
5	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OH$	Linoleic	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OC(=O)(C_{11}H_2)_{7-}C_{11}H=C_{11}H_2C_{11}H=C_{11}(C_{12})_4C_{11}H_3$
6	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OH$	Sorbic	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OC(=O)C_{11}H_2C_{11}H_2C_{11}H=C_{11}H_2C_{11}H_3$
7	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OH$	Linolenic	$C_8F_{17}SO_2N(C_{11}H_3)C_{12}H_{25}OC(=O)(C_{11}H_2)_{7-}(C_{11}H=C_{11}H_2)_{3-}C_{11}H_3$

Example 8

Into a two liter three-necked flask equipped with a large magnetic stirring bar and a reflux condenser fitted with a Dean-Stark water collector were charged 145.0 g (0.5 equiv.) of dimer acid (Hystrene® 3695, acid equiv. wt. 290), 139.3 g (0.25 equiv.) of N-methyl perfluorooctanesulfonamidoethyl alcohol and 14.3 g Amberlyst 15® cation exchange resin, and 290 ml xylenes. The reaction mixture was refluxed on a heating mantle with vigorous stirring for two hours, at which time approximately 4.2 ml water was collected.

The mixture was diluted with xylenes, filtered with suction on a Buchner funnel, and the filtrate evaporated on a hot water bath in vacuo using a rotary evaporator. An amber-colored grease (283 g) with a melting range of 51 °-55 °C was obtained. The material was very soluble in chloroform and acetone, and isopropanol with warming. A gel formed upon cooling of the isopropanol solution.

Example 9

In this example, samples of leather were treated with various fluorochemical compositions in accordance with this invention and the properties of the treated leather tested. For comparison, similar tests were made on untreated samples or on samples treated with products not within the scope of the invention.

In testing the leather samples for water repellancy, a Bally Penetrometer Model 5022 (a dynamic testing machine for shoe leather uppers) was used, in which test the test piece was alternatively buckled and stretched by a machine, like an upper leather in actual use, while in contact with water on one side.

The leather-treating test method was as follows:

- (1) Smooth, natural-tanned cowhide was first cut to form a pad having the dimensions 6.0 cm by 7.3 cm (2-3,8 in by 2-7/8 in).
- (2) The pad was then weighed.
- (3) The treating composition was then applied to the face side of the bag and worked into the leather thoroughly.
- (4) The treated pad was allowed to dry in air for at least 24 hours.
- (5) The treated pad was weighed to determine the coating weight.
- (6) The treated pads were then evaluated with the Bally Penetrometer.

The quantities measured were:

- (a) The time until water first penetrates from one side of the test piece to the other.
- (b) The weight increase, in percent of the test piece weight, caused by water absorption during predetermined time intervals.

The results of the treatments are shown in Table II.

TABLE II

Treating agent	Penetration time (min)	Water absorption (percent)
Product of Example 1	15	3.5
Product of Example 2	15	11.3
Product of Example 3	15	13.7
Product of Example 4	15	15.4
Product of Example 5	15	14.7
Product of Example 6	15	10.4
Product of Example 7	15	3.7
Product of Example 8	14	5.1
C ₈ F ₁₇ SO ₂ N(CH ₃)CH ₂ CH ₂ OH	15	98.05
Stearic acid + C ₈ F ₁₇ SO ₂ N(CH ₃)CH ₂ CH ₂ OH	15	41.1
Wax S (Technical montanic acid) + C ₈ F ₁₇ SO ₂ N(CH ₃)CH ₂ CH ₂ OH	15	31.3

From the foregoing Table, it is apparent that the products of Examples 1-8 impart to leather a high degree of resistance to water. These products were formed from the reaction of a fluorochemical alcohol with unsaturated fatty acids, isocyanates, or a combination of both. N-methyl perfluorooctanesulfonamidoethyl alcohol, by itself, provided no enhanced water resistance. The reaction product of saturated aliphatic acids, e.g., stearic acid. Wax S, with N-methyl perfluorooctanesulfonamidoethyl alcohol provided a lower degree of water resistance than did the products of this invention.

Example 10

This example compares the efficacy of the product of the present invention with commercially available water-repellants for leather. The following ingredients, in the amounts indicated, were mixed in a beaker to form a gel-type leather treating composition:

Ingredient	Amount (% by weight)
Product of Example 1	5.0
Aluminum stearate	1.5
Aluminum soap (Alumagel®, available from Witco Chemical Co.)	2.5
Isoparaffinic hydrocarbon (Isopar L. available from Exxon)	76.0
Mineral oil	15.0

This treating agent, referred to as Formulation A, was compared with the commercially available leather treating agents listed in Table III. The leather-treating test method was the same as that employed in Example 12, and the results of the treatment comparison is shown in Table III.

TABLE III

Treating Agent	Buckling time (min)	Water absorption (Percent)
Formulation A	10	5.3
Biwell® - a formulation comprising carnauba wax, lanolin, fish oil, and denatured alcohol	10	41.1
Kiwi® - a formulation comprising a silicone compound and petroleum distillates	10	68.8
Ultra-seal® - a formulation comprising a silicone compound in a petroleum solvent	10	96.9
Mink oil - a formulation comprising pure mink oil, extra fancy beef tallow, and zinc stearate	10	98.3
Sno-seal® - a formulation comprising beeswax, but containing no lanolin or oils	10	107.2
Control (no treatment)	10	97.6

From the foregoing Table, it is apparent that the product of the present invention is much better than commercially available products with respect to water repellancy.

Example 11

This Example describes a leather treatment composition that can be applied as a clear liquid. The following ingredients in the amounts indicated were introduced into a beaker:

Ingredient	Amount (parts by weight)
Product of Example 1	5
Mineral oil	15
Isopropyl alcohol	5
Isoparaffinic hydrocarbon (Isopar L)	75

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Example 12

This Example describes a leather treatment composition that can be applied as an aerosol foam. The following ingredients in the amounts indicated were introduced into a container suitable for aerosol compositions:

Ingredient	Amount (parts by weight)
Product of Example 1	5
Mineral oil	15
Isopropyl alcohol	3
Aluminum soap (Alumagel®)	3.5
Non-ionic fluorochemical surfactant (fluoroaliphatic polymeric ester, FC-740, Minnesota Mining and Manufacturing Company)	0.5
Isoparaffinic hydrocarbon (Isopar L)	73
Isobutane	11.2

Example 13

This Example describes a leather treatment composition that can be applied as an aerosol spray. The following ingredients in the amounts indicated were introduced into a container suitable for aerosol compositions:

Ingredient	Amount (parts by weight)
Product of Example 1	5
Mineral oil	15
Isopropyl alcohol	6
Isoparaffinic hydrocarbon (Isopar L)	74
Isobutane	11.2

Example 14

This Example describes a leather treatment composition that can be applied as a water/oil emulsion. The following ingredients in the amounts indicated were introduced into a beaker:

Ingredient	Amount (parts by weight)
Product of Example 1	4
Mineral oil	4
Isoparaffinic hydrocarbon (Isopar L)	26
Styrene isoprene elastomeric gelling agent (5% Kraton® 1107, available from Shell, in isopar L)	20
Sorbitan sesquioleate emulsifying agent (Arylacel® 83, ICI Americas, Inc.)	1
Propylene glycol	3
Water	42

Example 15

In this example, samples of textiles were treated with the following composition in accordance with this invention and properties of the treated textiles tested.

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Ingredient	Amount (% by weight)
Product of Example 1	15.0
Isoparaffinic hydrocarbon (Isopar L)	69.0
Isopropyl alcohol	5.0
Zirconium salt of mixed aliphatic acids (Troymax Zirconium 18, Troy Chemical Corporation, Inc., Newark, N.J.)	0.048
Manganese salt of mixed aliphatic acids (Troymax Manganese 12, Troy Chemical Corporation, Inc., Newark, N.J.)	0.077
1,10 Phenanthroline (Activ-8®, R.T. Vanderbilt Company, Inc., Norwalk, CT.)	0.037
Propane	10.8

In testing the textile samples for water repellancy, a spray test (AATCC-22-1967) was employed. This test was conducted as follows:

- (1) The test specimen (17.8 × 17.8 cm), conditioned at 65 ± 2% relative humidity and 21 ± 1 °C for a minimum of four hours before testing, was fastened in a 15.2 cm metal hoop to present a smooth wrinkle-free surface.
- (2) The hoop was then placed on the stand of the AATCC Spray Tester.
- (3) Two hundred fifty ml of distilled water at 27 ± 1 °C was poured into the funnel of the tester and allowed to spray into the test specimen, which took 2-30 seconds.
- (4) Upon completion of the spraying period, the hoop was taken by one edge and the opposite edge tapped against a solid object, then rotated 180 ° and tapped once more on the point previously held.
- (5) After tapping, the wet or spotted pattern was compared with a standard rating chart.

The results of the treatment and the rating scale are shown in Table IV

TABLE IV

Test fabric	Rating ¹	
	Untreated	Treated
Cotton	0	80
Silk	0	80
Wool	80	80
Chlorinated wool	0	80
Nylon	0	70
Polyester	0	80
Acrylic	0	80

- ¹
- 100 = No sticking or wetting of upper surface
 - 90 = Slight random sticking or wetting of upper surface
 - 80 = Wetting of upper surface at spray points
 - 70 = Partial wetting of whole of upper surface
 - 50 = Complete wetting of whole of upper surface
 - 0 = Complete wetting of whole of upper and lower surfaces.

From the foregoing Table, it is apparent that the product of Example 1 imparts to various textiles a high degree of resistance to water.

Example 16

In this example, wooden tongue depressors were treated with the following compositions in accordance with this invention and properties of the treated articles tested.

EP 0 140 525 B2

COMPOSITION A	
Ingredient	Amount (% by weight)
Product of Example 1	14.8
Isoparaffinic hydrocarbon (Isopar L)	64.1
Mineral oil	6.2
Isopropyl alcohol	3.5
Zirconium salt of mixed aliphatic acids (Troymax Zirconium 18)	0.048
Manganese salt of mixed aliphatic acids (Troymax Manganese 12)	0.077
1,10 Phenanthroline (Active-8®)	0.037
Propane	11.2

COMPOSITION B	
Ingredient	Amount (% by weight)
Product of Example 1	15.0
Isoparaffinic hydrocarbon (Isopar L)	69.0
Isopropyl alcohol	5.0
Zirconium salt of mixed aliphatic acids (Troymax Zirconium 18)	0.048
Manganese salt of mixed aliphatic acids (Troymax Manganese 12)	0.077
1,10 Phenanthroline (Active-8®)	0.037
Propane	10.8

The effectiveness of these compositions for water repellancy was tested by measuring the weight percent of water absorbed by the untreated and treated tongue depressors.

The tongue depressors were immersed in a water bath having a temperature of 15.6 °C (60 °F) for 45 minutes. Upon removal, the excess water was removed by shaking. The percentage of water absorbed was determined by weighing the tongue depressors before and after immersion, and multiplying the difference divided by original weight by 100.

The results are shown in Table V.

TABLE V

Untreated

Initial weight (g)	Weight increase (g)	Percent water absorbed
3.163	1.272	40.2
3.220	1.401	43.5
3.329	1.367	41.1
3.142	1.115	35.5

Treated with Composition A

Initial weight (g)	Coating weight (g)	Weight increase (g)	Percent water absorbed
3.285	0.123	0.487	14.3
3.158	0.200	0.475	14.1
3.227	0.113	0.530	15.7
3.269	0.181	0.463	13.4

TABLE V

Treated with Composition B

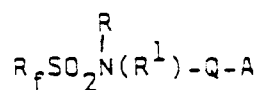
Initial weight (g)	Coating weight (g)	Weight increase (g)	Percent water absorbed
3.063	0.055	0.547	17.5
3.205	0.053	0.572	17.5
3.007	0.080	0.580	18.8
3.077	0.095	0.625	19.7

From the foregoing Table, it can be seen that the product of Example 1 imparts a high level of water repellancy to wood.

Various modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope of this invention.

Claims

1. Method of treating a material selected from the group consisting of leather, textiles, and cellulose in order to provide enhanced water and oil repellancy thereto comprising the step of applying to said material a composition comprising a compound represented by the formula:



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wherein:

R_f is saturated, monovalent, non-aromatic radical of up to 20 carbon atoms, containing a terminal perfluoromethyl group and at least three fully fluorinated connected carbon atoms in a straight, branched or cyclic chain, and optionally incorporating Cl substituents, subject to the proviso that not more than one atom of Cl is present in R_f for every two carbon atoms present in ($R_f + R + R^1$);

R represents an alkyl radical having 1 to 4 carbon atoms,

R^1 represents an alkylene radical having 1 to 12 carbon atoms,

A represents a hydrocarbon or carboxylate group having from 5 to 36 carbon atoms, said group A being derived from a fatty acid and/or a fatty alcohol and having at least one unsaturated site, and, optionally being substituted with one or more hydroxyl (-OH) or carboxyl (-COOH) groups,

15

Q represents a member selected from the group consisting of

20



2. The method of claim 1 wherein the composition further includes at least one organic solvent as a vehicle for said compound.

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3. The method of claim 2 wherein the composition further includes a propellant.

4. The method of claim 2 wherein the composition further includes a gelling agent.

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5. The method of claim 4 wherein the composition further includes water.

6. The method of claim 5 wherein the composition further includes an emulsifying agent.

35

7. The method of claim 1 wherein the material being treated is leather.

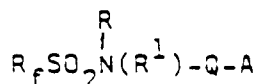
8. Article made from a material selected from the group consisting of leather, textiles, cellulose, and combination thereof bearing a coating applied by the method of claim 1.

40

9. Composition for treating leather, textiles, and cellulosic materials in order to provide enhanced water and oil repellancy thereto, said composition comprising:

(a) a compound represented by the formula

45



Wherein:

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R_f is a saturated, monovalent, non-aromatic radical of up to 20 carbon atoms, containing a terminal perfluoromethyl group, and at least three fully fluorinated connected carbon atoms in a straight, branched or cyclic chain, and optionally incorporating Cl substituents, subject to the proviso that not more than one atom of Cl is present in R_f for every two carbon atoms present in ($R_f + R + R^1$);

55

R represents an alkyl radical having 1 to 4 carbon atoms.

R^1 represents an alkylene radical having 1 to 12 carbon atoms.

A represents a hydrocarbon or carboxylate group having from 5 to 36 carbon atoms, said group A being derived from a fatty acid and/or a fatty alcohol and having at least one unsaturated site, and,

optionally being substituted with one or more hydroxyl (-OH) or carboxyl (-COOH) groups,
 Q represents a member selected from the group consisting of

5



(b) a vehicle that is not deleterious to said leather, dyes that have been applied to said leather, said
 textiles, or said cellulosic materials.

10

10. The composition of claim 9 wherein said vehicle comprises at least one organic solvent for said
 compound.

11. The composition of claim 10 wherein said vehicle further comprises a propellant.

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12. The composition of claim 10 wherein said vehicle further comprises a gelling agent.

13. The composition of claim 12 further including water.

20

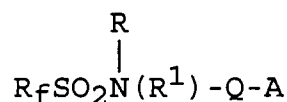
14. The composition of claim 13 further including an emulsifying agent.

Patentansprüche

25

1. Verfahren zum Behandeln eines Werkstoffs, der aus der Gruppe ausgewählt ist, die aus Leder, Textilien
 und Zelluloseprodukten besteht, um ihm stärkeres Wasser- und Ölabweisungsvermögen zu verleihen,
 in dem auf den Werkstoff eine Zusammensetzung aufgetragen wird, die mindestens teilweise aus einer
 Verbindung der Formel

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35

besteht, in der

R_f ein gesättigtes einwertiges nichtaromatisches aliphatisches Radikal mit bis zu 20 Kohlenstoffatomen
 ist, das eine endständige Perfluoromethylgruppe, mindestens, drei vollständig fluoridierte, miteinander
 verbundene Kohlenstoffatome in einer geraden, verzweigten oder zyklischen Kette und gegebenenfalls
 Cl-Substituenten enthält, wobei R_f pro zwei in (R_f + R + R¹) enthaltene Kohlenstoffatome nicht mehr als
 ein Cl-Atom enthält,

40

R ein Alkylradikal mit 1 bis 4 Kohlenstoffatomen darstellt,

R¹ ein Alkylradikal mit 1 bis 12 Kohlenstoffatomen darstellt,

R² ein Alkylradikal mit 1 bis 4 Kohlenstoffatomen darstellt,

45

A eine Kohlenwasserstoff- oder Carboxylatgruppe darstellt, die 5 bis 36 Kohlenstoffatome besitzt und
 die von einer Fettsäure oder einem Fettalkohol abgeleitet ist, mindestens einen ungesättigten Bin-
 dungsplatz besitzt und gegebenenfalls mit einer oder mehreren Hydroxylgruppen (-OH) oder Carboxyl-
 gruppen (-COOH) substituiert ist,

Q ein Glied darstellt, das aus der Gruppe ausgewählt ist, die aus

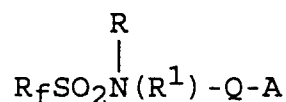
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besteht.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Zusammensetzung ferner mindestens ein organisches Lösungsmittel als Träger für die genannte Verbindung enthält.
3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß die Zusammensetzung ferner ein Treibmittel enthält.
4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß die Zusammensetzung ferner ein Geliermittel enthält.
5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß die Zusammensetzung ferner Wasser enthält.
6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die Zusammensetzung ferner ein Emulgiermittel enthält.
7. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das zu behandelnde Material Leder ist.
8. Gegenstand aus einem Werkstoff, der aus der Gruppe ausgewählt ist, die aus Leder, Textilien, Zelluloseprodukten und Kombinationen derselben besteht, und der mit einem nach dem Verfahren nach Anspruch 1 aufgetragenen Überzug versehen ist.
9. Zusammensetzung zum Behandeln von Leder, Textilien und Zelluloseprodukte, um ihnen ein stärkeres Wasser- und Ölabweisungsvermögen zu erteilen, wobei die Zusammensetzung enthält
(a) eine Verbindung der Formel



in der

R_f ein gesättigtes einwertiges nichtaromatisches aliphatisches Radikal mit bis zu 20 Kohlenstoffatomen ist, das eine endständige Perfluoromethylgruppe, mindestens, drei vollständig fluoriierte, miteinander verbundene Kohlenstoffatome in einer geraden, verzweigten oder zyklischen Kette und gegebenenfalls Cl-Substituenten enthält, wobei R_f pro zwei in $(\text{R}_f + \text{R} + \text{R}^1)$ enthaltene Kohlenstoffatome nicht mehr als ein Cl-Atom enthält,

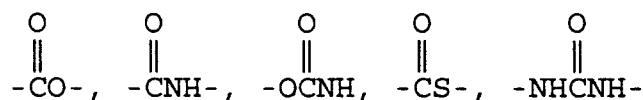
R ein Alkylradikal mit 1 bis 4 Kohlenstoffatomen darstellt,

R^1 ein Alkylradikal mit 1 bis 12 Kohlenstoffatomen darstellt,

R^2 ein Alkylradikal mit 1 bis 4 Kohlenstoffatomen darstellt,

A eine Kohlenwasserstoff- oder Carboxylatgruppe darstellt, die 5 bis 36 Kohlenstoffatome besitzt und die von einer Fettsäure oder einem Fettalkohol abgeleitet ist, mindestens einen ungesättigten Bindungsplatz besitzt und gegebenenfalls mit einer oder mehreren Hydroxylgruppen (-OH) oder Carboxylgruppen (-COOH) substituiert ist,

Q ein Glied darstellt, das aus der Gruppe ausgewählt ist, die aus



besteht, und

(b) einen Träger, der für das Leder, die auf das Leder aufgetragenen Farbstoffe, die genannten Textilien oder die genannten Zelluloseprodukte unschädlich ist.

10. Zusammensetzung nach Anspruch 9, dadurch gekennzeichnet, daß der Träger mindestens teilweise aus mindestens einem organischen Lösungsmittel für die genannte Verbindung besteht.

11. Zusammensetzung nach Anspruch 10, dadurch gekennzeichnet, daß der Träger ferner ein Treibmittel enthält.

5 12. Zusammensetzung nach Anspruch 10, dadurch gekennzeichnet, daß der Träger ferner ein Geliermittel enthält.

13. Zusammensetzung nach Anspruch 12, die ferner Wasser enthält.

10 14. Zusammensetzung nach Anspruch 13, die ferner ein Emulgiermittel enthält.

Revendications

15 1. Procédé pour traiter un matériau choisi parmi l'ensemble comprenant le cuir, les textiles et les matières cellulosiques, pour leur conférer un caractère hydrophobe et oléophobe amélioré, qui comprend l'étape consistant à appliquer sur ce matériau une composition comprenant un composé représenté par la formule suivante :



dans laquelle

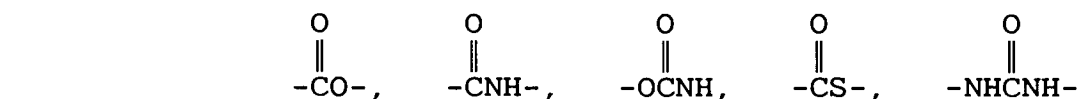
25 R_f est un radical non aromatique monovalent, saturé, ayant jusqu'à 20 atomes de carbone, contenant un groupe perfluorométhyle terminal et au moins trois atomes de carbone liés entièrement fluorés, en une chaîne droite, ramifiée ou cyclique, et comprenant éventuellement des substituants Cl, du moment qu'au plus un atome de Cl est présent dans R_f pour deux atomes de carbone présents dans ($\text{R}_f + \text{R} + \text{R}^1$),

30 R est un radical alkyle ayant de 1 à 4 atomes de carbone,

R^1 est un radical alkylène ayant de 1 à 12 atomes de carbone,

A est un groupe hydrocarboné ou carboxylate ayant de 5 à 36 atomes de carbone, ce groupe A dérivant d'un acide gras et/ou d'un alcool gras et comportant au moins un site insaturé, et étant éventuellement substitué par un ou plusieurs groupes hydroxyle (-OH) ou carboxyle (-COOH),

35 Q est un élément choisi parmi l'ensemble comprenant :



45 2. Procédé selon la revendication 1, dans lequel la composition comprend en outre au moins un solvant organique servant de véhicule pour le composé.

3. Procédé selon la revendication 2, dans lequel la composition contient en outre un propulseur.

4. Procédé selon la revendication 2, dans lequel la composition contient en outre un agent de gélification.

50 5. Procédé selon la revendication 4, dans lequel la composition contient en outre de l'eau.

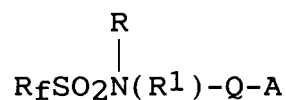
6. Procédé selon la revendication 5, dans lequel la composition contient en outre un émulsifiant.

7. Procédé selon la revendication 1, dans lequel la matière à traiter est le cuir.

55 8. Article fabriqué en une matière choisie parmi l'ensemble comprenant le cuir, les textiles, les cellulosiques et leurs combinaisons, portant un revêtement appliqué par le procédé selon la revendication 1.

9. Composition pour traiter le cuir, les textiles et les matières cellulosiques pour leur conférer de meilleures propriétés oléophobes et hydrophobes, cette composition comprenant :
 (a) un composé représenté par la formule suivante :

5



10

dans laquelle

R_f est un radical non aromatique monovalent, saturé, ayant jusqu'à 20 atomes de carbone, contenant un groupe perfluorométhyle terminal et au moins trois atomes de carbone liés entièrement fluorés, en une chaîne droite, ramifiée ou cyclique, et comprenant éventuellement des substituants Cl, du moment qu'au plus un atome de Cl est présent dans R_f pour deux atomes de carbone présents dans ($\text{R}_f + \text{R} + \text{R}^1$),

15

R est un radical alkyle ayant de 1 à 4 atomes de carbone,

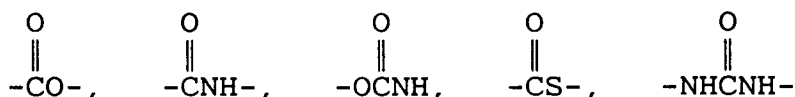
R^1 est un radical alkylène ayant de 1 à 12 atomes de carbone,

A est un groupe hydrocarboné ou carboxylate ayant de 5 à 36 atomes de carbone, ce groupe A dérivant d'un acide gras et/ou d'un alcool gras et comportant au moins un site insaturé, et étant éventuellement substitué par un ou plusieurs groupes hydroxyle (-OH) ou carboxyle (-COOH),

20

Q est un élément choisi parmi l'ensemble comprenant :

25



30

ou

(b) un véhicule qui n'est pas dangereux pour le cuir, les colorants qui ont été appliqués sur le cuir, les textiles ou les matières cellulosiques.

35

10. Composition selon la revendication 9, dans lequel le véhicule comprend au moins un solvant organique du composé.

11. Composition selon la revendication 10, dans laquelle le véhicule comprend en outre un propulseur.

40

12. Composition selon la revendication 10, dans laquelle le véhicule comprend en outre un agent de gélification.

13. Composition selon la revendication 12, qui contient en outre de l'eau.

45

14. Composition selon la revendication 13, qui contient en outre un émulsifiant.

50

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