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(54) Title: SOLVENT-BASED FLUOROPOLYMER ADDITIVES AND THEIR USE IN COATING COMPOSITIONS

(57) Abstract: This invention relates to a composition comprising a solvent-based fluoropolymer and its use as a coating additive, and a coating composition comprising the fluoropolymer. The coating composition comprising the solvent-based fluoropolymer provides desirable properties including uniform spreading, and cleanability and increased contact angle to a coated substrate. There is further provided a method of treating a substrate using the coating composition.



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TITLE

SOLVENT-BASED FLUOROPOLYMER ADDITIVES AND THEIR USE IN COATING COMPOSITIONS

FIELD OF THE INVENTION

5 This invention relates to a composition comprising a fluoropolymer and its use as an additive to coating compositions such as alkyd paints or polymeric resins, to provide durable surface effects.

BACKGROUND OF THE INVENTION

10 Fluoroalkyl (meth)acrylate copolymers have been used in aqueous emulsions as in textile fabric treatment processes to provide coatings which impart desirable properties such as high levels of water-, alcohol-, and oil repellency to the fabrics. Aqueous emulsions of such fluoroalkyl (meth)acrylates copolymers, as disclosed in U.S. Patent 5,344,903 are require an additional heat-cure step after application in order to impart the
15 desired repellency traits to the fibers.

 Fluorinated polymer compositions are used in the preparation of a wide variety of surface treatment materials to provide surface effects to substrates. Many such compositions are fluorinated acrylate polymers or copolymers which contain predominantly eight or more carbons in the
20 perfluoroalkyl chain to provide the desired properties. Honda, et al., in Macromolecules, 2005, 38, 5699-5705 teach that for perfluoroalkyl chains of greater than 8 carbons, orientation of the perfluoroalkyl groups, designated R_f groups, is maintained in a parallel configuration while for such chains having 6 or less carbons, reorientation occurs. This
25 reorientation is recited to decrease surface properties such as contact angle. Thus, polymers containing shorter perfluoroalkyl chains have traditionally not been commercially successful.

 Alternatively, solvent-based polymer systems, particularly for alkyd coating and urethane coating compositions, do not require such a heat-

cure step after application. However, alkyd and urethane coatings produced using solvent-based polymer systems have a tendency to be non-uniform and uneven after drying (air-cure), have low oil-contact angles, and poor cleanability ratings. Attempts have been made to overcome the problem of lack of evenness/uniformity, and to increase the cleanability and oil- and water-repellency of these types of coatings by the addition of a variety of surfactants and other compounds.

The present invention addresses the issues described above by introducing compositions comprised of solvent-based fluoroalkyl (meth)acrylate copolymers with short perfluoroalkyl groups of 6 or less carbons. They are utilized as coating additives and impart unexpectedly desirable surface effects such as: uniform spreading, increased water and oil contact angles, enhanced cleanability to the coated film and air-cured coated surface.

SUMMARY OF THE INVENTION

The present invention provides a fluoropolymer composition that is useful as a coating additive comprising a fluoropolymer and a solvent, wherein the fluoropolymer comprises repeating units in any sequence of the following:

- I: $[R_f-X-Y-C(O)-CZ-CH_2]_a-$
 II: $[R_f-X-Y-C(O)-CH-CH_2]_b-$
 III: $[R^1-O-C(O)-C(CH_3)-CH_2]_c-$
 IV: $[R^1-O-C(O)-CH-CH_2]_d-$
 V: $[R^2-O-C(O)-CH-CH_2]_e-$
 VI: $[R^2-O-C(O)-C(CH_3)-CH_2]_g-$
 VII: $[R^3-Y-C(O)-CT-CH_2]_h-$

wherein

R_f is a straight or branched perfluoroalkyl group having 2-6 carbon atoms, which is optionally interrupted by at least one oxygen atom, or a mixture thereof of two or more thereof;

X is an organic divalent linking group having from about 1 to about 20 carbon atoms, optionally containing a triazole, oxygen, nitrogen, or sulfur, or a combination thereof;

Y is O, S or N(R) wherein R is H or C_1 to C_{20} alkyl;

Z is a straight or branched alkyl group having from about 1 to about 4 carbon atoms, or halide;

R^1 is a straight or branched alkyl group having from 12 to 22 carbon atoms;

R^2 is an alkyl group having a chain length of from 1 to 6 carbon atoms, which carbon chain may be branched;

a is a positive integer;

b is zero or a positive integer;

c is a positive integer;

d is zero or a positive integer;

e is zero or a positive integer;

g is a positive integer;

h is zero or a positive integer;

T is H, a straight, branched or cyclic alkyl group having from about 1 to about 10 carbon atoms, or halide;

R^3 is H, C_nH_{2n+1} , C_nH_{2n-1} , $C_mH_{2m}-CH(O)CH_2$, $[CH_2CH_2O]_iR^4$, $[CH_2CH(CH_3)O]_iR^4$, $[C_mH_{2m}]N(R^4)_2$;

n is 8 to about 40;

m is 1 to about 40;

each R^4 is independently H, CH_2OH or C_jH_{2j+1} ;

i is 1 to about 200; and

j is 0 to about 40;

provided that

5 1) the repeating unit I, $[R_f-X-Y-C(O)-CZ-CH_2]_a-$, is present at a minimum of about 25% by weight of the polymer;

2) repeating units I and II ($[\text{R}_f\text{—X—Y—C(O)—CZ—CH}_2]_a$ and $[\text{R}_f\text{—X—Y—C(O)—CH—CH}_2]_b$) are present at a minimum combined total of about 30% by weight of the polymer; and

10 3) the total of all repeating units, I – VII plus any optional monomers equals 100% by weight of the polymer.

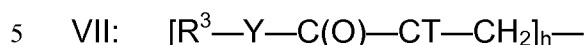
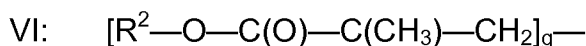
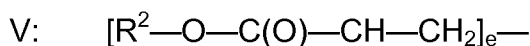
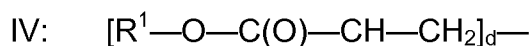
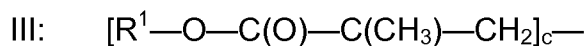
The invention further provides a coating composition comprising the fluoropolymer composition and a method for treating a substrate comprising contacting the substrate with the coating composition.

15 DETAILED DESCRIPTION

All trademarks are denoted herein by capitalization. In all instances herein, the term “(meth)acrylate” is used to denote either or both acrylate or methacrylate.

The present invention provides a fluoropolymer composition comprising a fluoropolymer and a solvent wherein the fluoropolymer is a fluoroalkyl (meth)acrylate copolymer. The fluoropolymer comprises repeating units I – VII as set forth herein, in any sequence. The fluoropolymer may be a random copolymer, statistical copolymer, block copolymer, multiblock copolymer, gradient copolymer, or alternating copolymer. The fluoropolymer comprises repeating units in any sequence of the following:

$$\text{I: } [\text{R}_f\text{—X—Y—C(O)—CZ—CH}_2]_a\text{—}$$
$$\text{II: } [\text{R}_f\text{---X---Y---C(O)---CH---CH}_2]_b\text{---}$$



wherein

R_f is a straight or branched perfluoroalkyl group having 2-6 carbon atoms, which is optionally interrupted by at least one oxygen atom, or a mixture thereof of two or more thereof;

10 X is an organic divalent linking group having from about 1 to about 20 carbon atoms, optionally containing a triazole, oxygen, nitrogen, or sulfur, or a combination thereof;

Y is O, S or N(R) wherein R is H or C_1 to C_{20} alkyl;

15 Z is a straight or branched alkyl group having from about 1 to about 4 carbon atoms, or halide;

R^1 is a straight or branched alkyl group having from 12 to 22 carbon atoms;

R^2 is an alkyl group having a chain length of from 1 to 6 carbon atoms, which carbon chain may branched;

20 a is a positive integer;

b is zero or a positive integer;

c is a positive integer;

d is zero or a positive integer;

e is zero or a positive integer;

25 g is a positive integer;

h is zero or a positive integer;

T is H, a straight, branched or cyclic alkyl group having from about 1 to about 10 carbon atoms, or halide;

R^3 is H, C_nH_{2n+1} , C_nH_{2n-1} , $C_mH_{2m}-CH(O)CH_2$, $[CH_2CH_2O]_iR^4$, $[CH_2CH(CH_3)O]_iR^4$, $[C_mH_{2m}]N(R^4)_2$;

5 n is 8 to about 40;

m is 1 to about 40;

each R^4 is independently H, CH_2OH or C_jH_{2j+1} ;

i is 1 to about 200; and

j is 0 to about 40;

10 provided that

1) the repeating unit I, $[R_f-X-Y-C(O)-CZ-CH_2]_a-$, is present at a minimum of about 25% by weight of the polymer;

2) repeating units I and II ($[R_f-X-Y-C(O)-CZ-CH_2]_a$ and $[R_f-X-Y-C(O)-CH-CH_2]_b$) are present at a minimum combined total of
15 about 30% by weight of the polymer; and

3) the total of all repeating units, I – VII plus any optional monomers equals 100% by weight of the polymer.

In units I and II, R_f is a straight or branched perfluoroalkyl group having 2-6 carbon atoms, which is optionally interrupted by at least one
20 oxygen atom, or a mixture of two or more thereof. Preferably R_f is $C_6F_{13}-$ and is a straight or branched alkyl, or a combination thereof.

The subscripts a, c, and g are each independently a positive integer, preferably from 1 to about 10,000, more preferably from about 5 to about 2000. The subscripts b, d, e and h are each independently zero or
25 a positive integer, preferably from 0 to about 10,000, more preferably from about 0 to about 2000.

Examples of suitable linking groups X in units I and II, include straight chain, branched chain or cyclic structures of alkylene, arylene, aralkylene, sulfonyl, sulfoxy, sulfonamido, carbonamido, carbonyloxy, urethanylene, ureylene, and combinations of such linking groups such as
5 sulfonamidoalkylene.

Examples of groups Y in units I, II and VII are O, S or N(R) wherein R is H or C₁ to C₂₀ alkyl. Preferably R is H or C₁ to C₄ alkyl.

Z is a straight or branched chain alkyl group having from 1 to 4 carbon atoms or Z is a halide. Useful halides or fluoride, chloride and
10 iodide.

Fluorinated (meth)acrylate monomers suitable for use in this invention to provide unit I have the general formula $R_f-X-Y-C(O)-C(Z)=CH_2$, wherein R_f, X, Y and Z are defined herein. Similarly, fluorinated (meth)acrylate monomers suitable for use in this invention to
15 provide unit II have the general formula $R_f-X-Y-C(O)-CH=CH_2$, wherein R_f, X, and Y are defined herein.

R¹ is a straight or branched alkyl group having from 12 to 22 carbon atoms. Preferably R¹ is stearyl (octadecyl), CH₃(CH₂)₁₇. Specific alkyl (meth)acrylate monomers useful to provide units III and IV include
20 stearyl (meth)acrylate, tridecyl (meth)acrylate, and lauryl (meth)acrylate, wherein stearyl (meth)acrylate is preferred.

R² is an alkyl group having a chain length of from 1 to 6 carbon atoms, which carbon chain may be branched. Preferably R² is 2-ethylhexyl, CH₃(CH₂)₃CH(C₂H₅)CH₂. Specific alkyl (meth)acrylate monomers useful
25 to provide units V and VI include 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate and hexyl (meth)acrylate, preferably 2-ethylhexyl (meth)acrylate.

Nonfluorinated (meth)acrylate monomers suitable for the use in the present invention to provide unit VII include one or more alkyl

(meth)acrylates wherein the alkyl group, R^3 , for each alkyl (meth)acrylate is independently a straight or branched chain containing 8 to 40 carbon atoms. Two or more alkyl (meth)acrylates can be used. Preferably the alkyl group in the alkyl (meth)acrylate contains 8 to 20 carbon atoms. The
5 alkyl (meth)acrylate can be linear or branched. Examples of suitable alkyl (meth)acrylates include, but are not limited to, alkyl(meth)acrylates wherein the alkyl group is octyl, 2-ethylhexyl, decyl, isodecyl, lauryl, cetyl, or stearyl. Preferred alkyl (meth)acrylates to provide unit VII are 2-ethylhexyl acrylate, lauryl acrylate and stearyl acrylate.

10 Other nonfluorinated (meth)acrylate monomers suitable for the use in the present invention to provide unit VII include one or more of the following: N-methylol (meth)acrylates, hydroxyalkyl (meth)acrylates, alkyloxy(meth)acrylates, glycidyl (meth)acrylates, stearyl acrylate, aminoalkyl methacrylate hydrochloride, acrylamide, and alkyl acrylamide.
15 N-Methylol monomers include, but are not limited to N-methylolacrylamide and N-methylolmethacrylamide. Suitable hydroxyalkyl (meth)acrylates have alkyl chain lengths of 2 to 4 carbon atoms, and include 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate. Suitable alkyloxy(meth)acrylates have alkyl chain lengths of 2 to 4 carbon atoms,
20 and contain between 1 and 12 oxyalkylene units per molecule, preferably between 4 and 10 oxyalkylene units per molecule, and most preferably between 6 and 8 oxyalkylene units per molecule.

Suitable optional monomers for use in the preparation of the fluoropolymer described herein include vinyl acetate, vinyl stearate, alkyl
25 vinyl sulfone, styrene, vinyl benzoic acid, alkyl vinyl ether, maleic anhydride, vinyl chloride, and olefins.

The fluoropolymers in the present invention are prepared by polymerization of the fluorinated and nonfluorinated (meth)acrylate monomers. The polymerization process comprises contacting the
30 fluorinated and non-fluorinated (meth)acrylate monomers as defined

hereinabove in an organic solvent in the presence of a free radical initiator and optionally other monomers in an inert atmosphere. For example, the monomers can be mixed in a suitable reaction vessel equipped with an agitation device. A heating source and a cooling source are provided as
5 necessary. In a typical process, the fluorinated and nonfluorinated monomers are combined with the solvent to provide a reaction mixture and the reaction mixture is heated to an appropriate temperature, e.g. 70°C. Temperatures in the range of 20-90°C may be suitable, depending, for example, on the choice of organic solvent and the choice of free radical
10 initiator. The free radical initiator is typically added after the reaction mixture has reached the appropriate temperature.

Suitable free radical initiators include organic peroxides and azo compounds. Examples of particularly useful organic peroxides are benzoyl peroxide, *t*-butyl peroxide, acetyl peroxide, and lauryl peroxide.
15 Examples of particularly useful azo compounds include 2,2'-azobis(2-amidinopropane dihydrochloride, 2,2'-azobis(isobutyramidine) dihydrochloride, and azodiisobutyronitrile. Azo initiators are commercially available from E. I. du Pont de Nemours and Company, Wilmington, DE, under the name of "VAZO".

20 The free radical initiator is generally added over a period of time after the reaction monomers have dissolved in the solvent and/or after the reaction mixture is at the desired temperature. The radical initiator is added in an effective amount. By an "effective amount" of a radical initiator is meant an amount sufficient to initiate the reaction between the
25 monomers and preferably to sustain the reaction for a sufficient period of time to maximize yield of the polymer product. An effective amount of initiator will vary with the exact composition and reaction conditions used. An effective amount of initiator for a given set of conditions is easily determined experimentally by one skilled in the art.

30 The process to prepare the fluoropolymer may further comprise adding a polymerization regulator (also referred to as a chain transfer

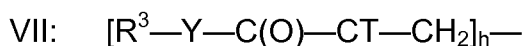
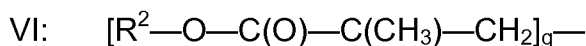
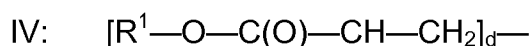
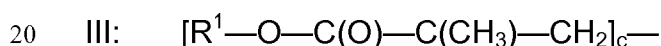
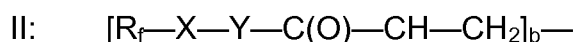
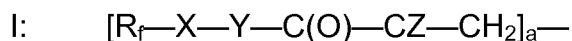
agent) to the reaction mixture. The polymerization regulator may be incorporated into the fluoropolymer. A polymerization regulator may be added for the purpose of limiting the molecular weight of the fluoropolymer. Examples of suitable polymerization regulators include

5 acetic acid, acetone, n-butyl alcohol, chloroform, di-n-butyl disulfide, carbon tetrachloride, carbon tetrabromide, triethylamine, n-butyl mercaptan, dodecylmercaptan. Preferably, when a polymerization regulator is used, the polymerization regulator is dodecylmercaptan.

Suitable organic solvents useful in the preparation of the

10 fluoropolymer include methyl isobutyl ketone, butyl acetate, tetrahydrofuran, acetone, isopropanol, ethyl acetate, methylene chloride, chloroform, carbon tetrachloride, cyclohexane, hexane, dioxane, hexafluoroisopropanol, and mixtures of two or more thereof. Cyclohexane or methyl isobutyl ketone is preferred.

15 The product of the polymerization process is a fluoropolymer in an organic solvent, more particularly a fluorinated (meth)acrylate copolymer comprising repeating units in any sequence of the following:



25 wherein

R_f is a straight or branched perfluoroalkyl group having 2-6 carbon atoms, which is optionally interrupted by at least one oxygen atom, or a mixture of two or more thereof;

X is an organic divalent linking group having from about 1 to about 20 carbon atoms, optionally containing a triazole, oxygen, nitrogen, or sulfur, or a combination thereof;

Y is O, S or N(R) wherein R is H or C₁ to C₂₀ alkyl;

5 Z is a straight or branched alkyl group having from about 1 to about 4 carbon atoms, or halide;

R¹ is a straight or branched alkyl group having from 12 to 22 carbon atoms;

10 R² is an alkyl group having a chain length of from 1 to 6 carbon atoms, which carbon chain may branched;

a is a positive integer;

b is zero or a positive integer;

c is a positive integer;

d is zero or a positive integer;

15 e is zero or a positive integer;

g is a positive integer;

h is zero or a positive integer;

T is H, a straight, branched or cyclic alkyl group having from about 1 to about 10 carbon atoms, or halide;

20 R³ is H, C_nH_{2n+1}, C_nH_{2n-1}, C_mH_{2m}—CH(O)CH₂, [CH₂CH₂O]_iR⁴, [CH₂CH(CH₃)O]_iR⁴, [C_mH_{2m}]N(R⁴)₂;

n is 8 to about 40;

m is 1 to about 40;

each R⁴ is independently H, CH₂OH or C_jH_{2j+1};

25 i is 1 to about 200; and

j is 0 to about 40;

provided that

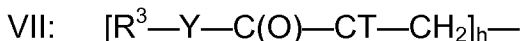
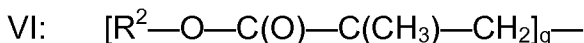
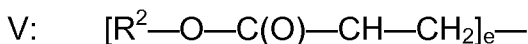
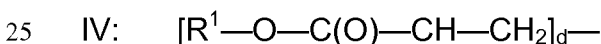
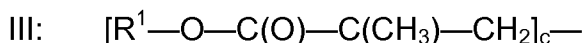
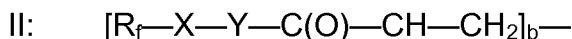
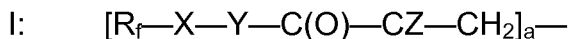
1) the repeating unit I, $[R_f-X-Y-C(O)-CZ-CH_2]_a-$, is present at a minimum of about 25% by weight of the polymer;

2) repeating units I and II ($[R_f-X-Y-C(O)-CZ-CH_2]_a$ and $[R_f-X-Y-C(O)-CH-CH_2]_b$) are present at a minimum combined total of about 30% by weight of the polymer; and

3) the total of all repeating units, I – VII plus any optional monomers equals 100% by weight of the polymer.

The fluoropolymer composition produced as described above may be used directly in a coating composition or added solvent (the “application solvent”) may be added to achieve a desirable solids content. recovered, e.g., by filtering and distilling off the solvent. The application solvent is typically a solvent selected from the group consisting of alcohols and ketones.

The fluoropolymer composition is useful as a coating additive, wherein the fluoropolymer composition can be added to a coating base, which is applied to a substrate. Thus, the present invention provides a coating composition comprising a fluoropolymer, an organic solvent and a coating base, optionally further comprising one or more of an application solvent, wherein the fluoropolymer comprises repeating units in any sequence of the following:



wherein

R_f is a straight or branched perfluoroalkyl group having 2-6 carbon atoms, which is optionally interrupted by at least one oxygen atom, or a mixture of two or more thereof;

5 X is an organic divalent linking group having from about 1 to about 20 carbon atoms, optionally containing a triazole, oxygen, nitrogen, or sulfur, or a combination thereof;

Y is O, S or N(R) wherein R is H or C_1 to C_{20} alkyl;

10 Z is a straight or branched alkyl group having from about 1 to about 4 carbon atoms, or halide;

R^1 is a straight or branched alkyl group having from 12 to 22 carbon atoms;

R^2 is an alkyl group having a chain length of from 1 to 6 carbon atoms, which carbon chain may be branched;

15 a is a positive integer;

b is zero or a positive integer;

c is a positive integer;

d is zero or a positive integer;

e is zero or a positive integer;

20 g is a positive integer;

h is zero or a positive integer;

T is H, a straight, branched or cyclic alkyl group having from about 1 to about 10 carbon atoms, or halide;

25 R^3 is H, C_nH_{2n+1} , C_nH_{2n-1} , $C_mH_{2m}-CH(O)CH_2$, $[CH_2CH_2O]_iR^4$, $[CH_2CH(CH_3)O]_iR^4$, $[C_mH_{2m}]N(R^4)_2$;

n is 8 to about 40;

m is 1 to about 40;

each R^4 is independently H, CH_2OH or C_jH_{2j+1} ;

i is 1 to about 200; and

j is 0 to about 40;

5 provided that

1) the repeating unit I, $[R_f-X-Y-C(O)-CZ-CH_2]_a-$, is present at a minimum of about 25% by weight of the polymer;

2) repeating units I and II ($[R_f-X-Y-C(O)-CZ-CH_2]_a$ and $[R_f-X-Y-C(O)-CH-CH_2]_b$) are present at a minimum combined total of
10 about 30% by weight of the polymer; and

3) the total of all repeating units, I – VII plus any optional monomers equals 100% by weight of the polymer.

As used herein, the term “coating base” is a composition, typically a solvent-based paint that is applied to a substrate for the purpose of
15 creating a lasting film on the substrate surface. The coating base may be selected from the group consisting of an alkyd coating, a Type I urethane coating, and an unsaturated polyester coating. These coating bases include paints, stains, and similar coatings.

The coating compositions of the present invention are useful for
20 providing a protective and/or decorative coating to a wide variety of substrates. Such substrates include primarily construction materials and hard surfaces. The substrate is preferably selected from the group consisting of wood, metal, wallboard, masonry, concrete, fiberboard, and paper. Other materials may also be used as the substrate.

25 The present invention further provides a method for treating a substrate comprising contacting the substrate with a coating composition comprising a fluoropolymer composition, which comprises a fluoropolymer and an organic solvent, and a coating base wherein the fluoropolymer,

organic solvent and coating base are described hereinabove and wherein the method comprises contacting the substrate with the coating composition and drying or curing the coating composition on the substrate. The method of this invention imparts improved oil repellency, water
5 repellency, cleanability to the substrate. Any method of contacting a coating composition with a substrate can be used. Such methods are well known to a person skilled in the art, such as by brush, spray, roller, doctor blade, wipe, dip, foam, liquid injection, immersion or casting.

By the term "alkyd coating" as used herein is meant a liquid coating
10 based on alkyd resins, typically a paint, clear coating, or stain. The alkyd resins are complex branched and cross-linked polyesters containing unsaturated aliphatic acid residues. Alkyd coatings use, as the binder or film-forming component, a curing or drying alkyd resin. Alkyd resins contain unsaturated aliphatic acid residues derived from drying oils.
15 These resins spontaneously polymerize in the presence of oxygen or air to yield a solid protective film. The polymerization is termed "drying" or "curing" and occurs as a result of autoxidation of the unsaturated carbon-carbon bonds in the aliphatic acid component by atmospheric oxygen. When applied to a surface as a thin liquid layer of a formulated alkyd
20 coating, the cured films that form are relatively hard, non-melting, and substantially insoluble in many organic solvents that act as solvents or thinners for the unoxidized alkyd resin or drying oil.

By the term "urethane coating" as used hereinafter is meant a liquid coating based on Type I urethane resins, typically a paint, clear coating, or
25 stain. Urethane coatings typically contain the reaction product of a polyisocyanate, usually toluene diisocyanate, and a polyhydric alcohol ester of drying oil acids. Urethane coatings are classified by ASTM D-1 into five categories. Type I urethane coatings contain a pre-reacted autoxidizable binder. These are also known as uralkyds, urethane-
30 modified alkyds, oil-modified urethanes, urethane oils, or urethane alkyds. Type I urethane coatings are the largest volume category of polyurethane

coatings and include paints, clear coatings, or stains. The cured coating for a Type I urethane coating is formed by air oxidation and polymerization of the unsaturated drying oil residue in the binder.

By the term "unsaturated polyester coating" as used hereinafter is meant a liquid coating based on unsaturated polyester resins, dissolved in monomers and containing initiators and catalysts as needed, typically as a paint, clear coating, or gel coat formulation. Unsaturated polyester resins contain as the unsaturated prepolymer, the product obtained from the condensation polymerization of a glycol such as 1,2-propylene glycol or 1,3-butylene glycol with an unsaturated acid such as maleic acid in the acid or anhydride form or a saturated acid such as phthalic acid in the acid or anhydride form. The unsaturated prepolymer is a linear polymer containing unsaturation in the chain. This is dissolved in a suitable monomer, for instance styrene, to produce the final resin. The film is produced by copolymerization of the linear polymer and monomer by means of a free radical mechanism. The free radicals can be generated by heat, or more usually by addition of a peroxide, such as benzoyl peroxide, separately packaged and added before use. Such coating compositions are frequently termed "gel coat" finishes. For curing coatings at room temperature, the decomposition of peroxides into free radicals is catalyzed by certain metal ions, usually cobalt. The solutions of peroxide and cobalt compound are added separately to the mix and well stirred before application. The unsaturated polyester resins that cure by a free radical mechanism are also suited to irradiation curing using, for instance, ultraviolet light. This form of cure, in which no heat is produced, is particularly suited to films on wood or board. Other radiation sources, for instance electron-beam curing, may also be used.

The present invention further provides a coated substrate wherein the substrate comprises a dried coating produced from the coating composition of the invention. By the term "dried coating" as used herein is meant the final decorative and/or protective film obtained after the coating

composition has dried, set or cured. Such a final film can be achieved by, for example, air curing, polymerizing, or energy curing.

When used as an additive to a coating base, the fluoropolymer composition as described herein is effectively introduced to the coating base by thoroughly contacting, e.g., by mixing the fluoropolymer composition with the coating base. The contacting of fluoropolymer and coating base can be performed, for example and conveniently, at ambient temperature. More elaborate contacting or mixing methods can be employed such as using a mechanical shaker or providing heat. Such methods are generally not necessary and generally do not substantially improve the final coating composition.

When used as an additive to a coating base, which is a solvent-based paint, the fluoropolymer composition of the invention is generally added at about 0.001 weight % to about 1 weight % on a dry weight basis of the fluoropolymer to the weight of the wet paint. Preferably about from about 0.01 weight % to about 0.5 weight %, and more preferably from about 0.05 weight % to about 0.25 weight % of the fluoropolymer is added to the paint.

In methods of the present invention, the fluoropolymer compositions of this invention have been used as coating additives and applied to substrates to provide superior surface effects such as desirably uniform spreading of the coating composition comprising the fluoropolymer, cleanability of the coated substrate, and increased contact angle of the coated substrate. The uniform spread characteristics reduce the amount of fluoropolymer needed to coat the treated substrate surface with a very thin coating film.

Furthermore, the fluoropolymer as described herein, which contains short perfluoroalkyl chains, has a relatively low molecular weight, that is, a weight-average molar mass (M_w) of between 3,000 and 100,000, in contrast to the molar mass of copolymers derived from longer

perfluoroalkyl chains which provide cleanability effects. Therefore, the amount by weight percent of the fluoropolymer of this invention that is needed for desired effects is less than the amount needed for similar effects provided by fluoropolymers having longer perfluoroalkyl chains, when both are used as the coating additives. Since perfluoroalkyl materials are expensive, reducing the fluorine content can reduce the cost. Reduction of the fluorine content with delivery of the same or higher performance is therefore achieved in the present invention. The composition of the present invention is particularly suitable for use as additives to exterior coating and paints.

EXAMPLES

TEST METHODS

Method 1 - Contact Angle Measurement

Contact angles are measured by the Sessile Drop Method, which is described by A. W. Adamson in *The Physical Chemistry of Surfaces*, Fifth Edition, Wiley & Sons, New York, NY, 1990. Additional information on the equipment and procedure for measuring contact angles is provided by R. H. Dettre et al. in "Wettability", Ed. by J. C. Berg, Marcel Dekker, New York, NY, 1993.

In the Sessile Drop Method, a Ramè-Hart optical bench (available from Ramè-Hart Inc., 43 Bloomfield Ave., Mountain Lakes, NJ) is used to hold the substrate in the horizontal position. The contact angle is measured at a prescribed temperature with a telescoping goniometer from the same manufacturer. A drop of test liquid is placed on a surface and the tangent is precisely determined at the point of contact between the drop and the surface. An advancing angle is determined by increasing the size of the drop of liquid and a receding angle is determined by decreasing the size of the drop of liquid. The data are presented typically as advancing and receding contact angles.

Method 2 - Leneta Oil Stain Test

The test method described herein is a modification of ASTM 3450 - 00 — Standard Test Method for Washability Properties of Interior Architectural Coatings, which is hereby specifically incorporated by
5 reference.

Drawdowns were prepared by applying a coat of coating composition on Leneta Black MYLAR cards (The Leneta Company, Mahwah, NJ) using a BYK-Gardner automatic drawdown machine (BYK-Gardner, Silver Spring, MD) and a 5 mil (0.127 mm) Bird applicator
10 drawdown blade (BYK-Gardner, Silver Spring, MD). The drawdown speed was set to be slow enough to prevent pinholes or holidays in the resulting coating. Several drawdowns were prepared for each paint and additive combination. The coated cards were allowed to dry for seven days for testing for cleanability.

15 Staining media were prepared using VASELINE NURSERY petroleum jelly (Marietta Corporation, Cortland, NY) and Leneta Carbon Black Dispersion in Mineral Oil (ST-1) (The Leneta Company, Mahwah, NJ). The petroleum jelly was melted in a clean glass container for 30 minutes in an oven set at 70°C. Then the petroleum jelly was mixed with
20 5% of its weight of Leneta Carbon Black. For instance, 95 g of petroleum jelly was mixed with 5 g of Leneta Carbon Black to produce 100 g of staining media. The mixed staining media was cooled for several hours in a refrigerator at 4°C.

Cleaning media were prepared using a JOY ULTRA
25 CONCENTRATED COUNTRY LEMON dishwashing liquid (The Procter & Gamble Company, Cincinnati, OH). Dishwashing liquid was mixed with deionized water at a ratio of 1 g of dishwashing liquid for every 99 g of water.

Each drawdown was stained in the same manner. A staining
30 template was prepared from a MYLAR Leneta card by cutting out a 3" by

1" (7.6 cm by 2.5 cm) strip from the interior of the card. The template was placed over a coated drawdown card to be stained. Staining media was spread over the drawdown card and the template using a spatula so that none of the drawdown card remained visible. Excess stain was removed
5 with a spatula. Stained cards were allowed to set and dry for 60 minutes.

In preparation for cleaning, scrap MYLAR was used to gently scrape the excess dried stain from the stained section of the card, both the washed and unwashed sections. Similarly a v-folded clean paper towel was used to remove unset stain from the entire card, both the washed and
10 unwashed sections. The card was then securely attached to a BYK-Gardner Abrasion tester (BYK-Gardner, Silver Spring, MD) or other method. A piece of cheesecloth (VWR International, San Diego, CA) was attached to the cleaning block on the abrasion tester. The cheesecloth was folded and attached so that the contacting surface was 8 layers thick.
15 10 mL of cleaning solution prepared as specified above was applied to the contacting surface of the cheesecloth. The abrasion tester was run through 5 cycles (10 wipes) over a stained section of the drawdown card that is henceforth designated as stained and cleaned. Excess cleaning solution was rinsed away with deionized water for a few seconds and then
20 allowed to dry for 2 hours or until completely dry by visible inspection. One section of each stained drawdown card was cleaned in this manner.

Cleanability was determined by evaluating the stained and washed painted portion of the drawdown card in comparison to both the unstained and painted portion of the card and the stained and unwashed painted
25 portion of the card. A HunterLab ULTRASCAN Pro colorimeter (Hunter Associates Laboratory, Inc, Reston, VA) was used to take three different measurements for each designated painted portion of the drawdown card: stained and washed, unstained, and stained and unwashed. The measurements were averaged to obtain a mean value for that section that
30 is used to evaluate the cleanability rating for that card as described below.

The colorimeter was set to read the L* function and the aperture was no larger than ¾ of an inch (1.9 cm).

A cleanability score was calculated ranging from 0-10 wherein 0 is uncleanable, and 10 is completely cleanable. Values 1 – 9 were
5 established in numerical order equidistant from 0, 10, and one another on a linear slope. The above description fits the following equation: [(mean L* value of stained and washed painted section) – (mean L* value of stained and unwashed painted section)]/[(mean L* value of unstained painted section) – (mean L* value of stained and unwashed painted section)] * 10
10 = cleanability rating.

Example 1

4-methyl-2-pentanone ("MIBK", 90 g), 2-propenoic acid, 2-methyl-, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl ester (18.36 g), poly(oxy-1,2-ethanediyl), α-(2-methyl-1-oxo-2-propenyl)-ω-hydroxy- (0.51 g), 2-
15 propenoic acid, 2-methyl-, octadecyl ester (4.09 g), 2-propenamide, N-(hydroxymethyl)- (1.4 g), 2-propenoic acid, 2-methyl-, 2-hydroxyethyl ester (0.17 g), 2-methyl-2-propenoic acid, 2-ethylhexyl ester (25.81 g) and 1-dodecanethiol (0.18 g) were charged to a 250-mL, 4-neck round-bottom flask equipped with a condenser, overhead stirrer and nitrogen sparge.
20 The mixture was sparged with nitrogen while being heated to 70°C. After the reaction mixture reached 70°C, nitrogen sparging was ceased and a nitrogen blanket was introduced. A solution of 2,2'-azobis(2-methylbutyronitrile) (VAZO 67) in MIBK was then added (0.145 g VAZO 67 in 1.00 g MIBK), followed by a second addition (0.097 g of VAZO 67 in
25 1.00 g of MIBK) after 1 hour and a final addition after 3 hours (0.097g Vazo 67 in 1.00 g MIBK). The solution was then allowed to stir at 70°C for an additional 12 hours, producing a fluoropolymer mixture. After cooling to room temperature, the fluoropolymer mixture was filtered through a milk filter and percent solids were measured (crude solids = 35 %). The final
30 product was diluted to 30 % solids with MIBK.

Example 2

The product of Example 1 (Additive A) was dosed into a commercially available semi-gloss alkyd paint at about 0.05% active ingredient by weight of the wet paint and evaluated for the contact angle performance based on Method 1. A blank paint (un-dosed) was evaluated as a control sample. The curing time of the applied paint was 10 days at ambient temperature. The resulted wet paint film thickness was about 100-150 micron, and cured and dry film thickness was about 50-60 micron. Results are provided in Table 1.

10

Table 1. Water and Oil Contact Angle Data on Semi-gloss Alkyd Paint

Additive	Advancing Water	Advancing Oil
	Avg. of 3-6 trials	Avg. of 3-6 trials
Blank (Control)	78.4	0.0
0.05% Additive A	106.5	64.9

Example 3

The product of Example 1 (Additive A) was dosed into a commercially available alkyd satin paint at about 0.05% active ingredient by weight of the wet paint and evaluated for the contact angle performance based on Method 1. A blank paint (un-dosed) was evaluated as a control sample. The curing time of the applied paint was 10 days at ambient temperature. The resulted wet paint film thickness was about 100-150 micron, and cured and dry film thickness was about 50-60 micron. Results are provided in Table 2.

Table 2. Water and Oil Contact Angle Data on Alkyd Satin Paint

Additive	Advancing Water	Advancing Oil
	Avg. of 3-6 trials	Avg. of 3-6 trials
Blank (Control)	89.2	11.7
0.05% Additive A	111.4	64.3

Example 4

The product of Example 1 (Additive A) was dosed into a commercially available high-gloss alkyd paint at about 0.025% active ingredient by weight of the wet paint and evaluated for the contact angle performance according to the Method 1. A blank paint (un-dosed) was evaluated as a control sample. In another sample, in addition to the Additive A, a non-fluorinated paint additive (Additive B) was dosed into the high-gloss alkyd paint at about 0.6% active ingredient. The curing time of the applied paint was 10 days at ambient temperature. The resulted wet paint film thickness was about 120-150 micron, and cured and dry film thickness was about 50-70 micron. Results are provided in Table 3.

Table 3. Water and Oil Contact Angle Data on High-gloss Alkyd Paint

Additive	Advancing Water	Advancing Oil
Blank (Control)	95	32
0.025% Additive A	98	40
0.025% Additive A +0.6% Additive B	99	39

The above samples were also evaluated for the Leneta Oil Stain Test according to Method 2. Results are provided in Table 4.

Table 4. Leneta Oil Stain Test on High-gloss Alkyd Paint

Additive	Rating	Visual
Blank Control	7.1	9.0
0.025% Additive A	8.1	10.0
0.025% Additive A +0.6% Additive B	8.9	10.0

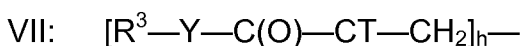
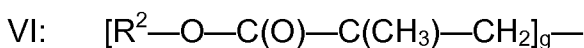
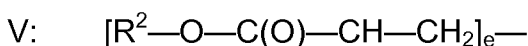
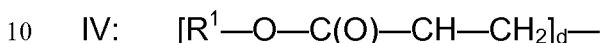
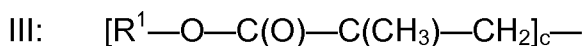
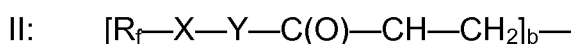
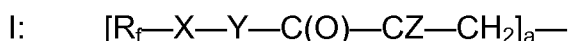
As can be seen from the contact angle data provided in Tables 1-3, the surfaces coated with the fluoropolymer and coating compositions of the invention illustrated significantly improved oil contact angle for both high gloss, satin and semi-gloss alkyd paints at very low use rate (0.025% to 0.05%).

In addition, the Leneta cleanability data, as provided in Table 4, illustrated surfaces coated with the fluoropolymer and coating compositions of the invention have improved cleanability against oily stains which simulates organic soil and dirty finger prints.

CLAIMS

What is claimed is:

1. A coating composition comprising a fluoropolymer composition and a coating base, wherein the fluoropolymer composition comprises a fluoropolymer and an organic solvent and further wherein the fluoropolymer comprises repeating units in any sequence of polymer units:



wherein

- 15 R_f is a straight or branched perfluoroalkyl group having 2-6 carbon atoms, which is optionally interrupted by at least one oxygen atom, or a mixture of two or more thereof;

X is an organic divalent linking group having from about 1 to about 20 carbon atoms, optionally containing a triazole, oxygen, nitrogen, or sulfur, or a combination thereof;

Y is O, S or N(R) wherein R is H or C₁ to C₂₀ alkyl;

Z is a straight or branched alkyl group having from about 1 to about 4 carbon atoms, or halide;

25 R^1 is a straight or branched alkyl group having from 12 to 22 carbon atoms;

R^2 is an alkyl group having a chain length of from 1 to 6 carbon atoms, which carbon chain may be branched;

a is a positive integer;

b is zero or a positive integer;

c is a positive integer;

d is zero or a positive integer;

5 e is zero or a positive integer;

g is a positive integer;

h is zero or a positive integer;

T is H, a straight, branched or cyclic alkyl group having from about 1 to about 10 carbon atoms, or halide;

10 R^3 is H, C_nH_{2n+1} , C_nH_{2n-1} , $C_mH_{2m}-CH(O)CH_2$, $[CH_2CH_2O]_iR^4$, $[CH_2CH(CH_3)O]_iR^4$, $[C_mH_{2m}]N(R^4)_2$;

n is 8 to about 40;

m is 1 to about 40;

each R^4 is independently H, CH_2OH or C_jH_{2j+1} ;

15 i is 1 to about 200; and

j is 0 to about 40;

provided that

1) the repeating unit I, $[R_f-X-Y-C(O)-CZ-CH_2]_a-$, is present at a minimum of about 25% by weight of the polymer;

20 2) repeating units I and II ($[R_f-X-Y-C(O)-CZ-CH_2]_a$ and $[R_f-X-Y-C(O)-CH-CH_2]_b$) are present at a minimum combined total of about 30% by weight of the polymer; and

3) the total of all repeating units, I – VII plus any optional monomers equals 100% by weight of the polymer.

25

2. The coating composition according to claim 1 wherein R_f is C_6F_{13} —, and is a straight or branched alkyl, or a combination thereof.
3. The coating composition according to claim 1 wherein the
5 fluoropolymer has a weight-average molar mass (M_w) of between 3,000 and 100,000.
4. The coating composition according to claim 1 wherein R^1 is stearyl (octadecyl), $CH_3(CH_2)_{17}$ and R^2 is 2-ethylhexyl, $CH_3(CH_2)_3CH(C_2H_5)CH_2$.
10
5. The coating composition according to claim 1 wherein the organic solvent is methyl isobutyl ketone, butyl acetate, tetrahydrofuran, acetone, isopropanol, ethyl acetate, methylene chloride, chloroform, carbon tetrachloride, cyclohexane, hexane, dioxane, hexafluoroisopropanol, or a
15 mixture of two or more thereof.
6. The coating composition according to claim 1 wherein the organic solvent is cyclohexane or methyl isobutyl ketone.
7. The composition of claim 1 further comprising an application
20 solvent, which is selected from the group consisting of alcohols and ketones.
8. The coating composition according to claim 1 wherein the coating
25 base is selected from the group consisting of an alkyd coating, a Type I urethane coating, and an unsaturated polyester coating.

9. The coating composition according to claim 1 wherein the coating base is a solvent-based paint and the fluoropolymer composition is added to the paint in an amount of 0.001 weight % to about 1 weight % on a dry weight basis of the fluoropolymer to the weight of the wet paint.

5

10. The coating composition according to claim 9 wherein the fluoropolymer composition is added to the paint in an amount of 0.01 weight % to about 0.5 weight % on a dry weight basis of the fluoropolymer to the weight of the wet paint.

10

11. The coating composition according to claim 9 wherein the fluoropolymer composition is added to the paint in an amount of 0.05 weight % to about 0.25 weight % on a dry weight basis of the fluoropolymer to the weight of the wet paint.

15

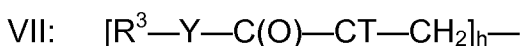
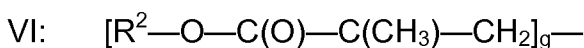
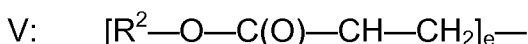
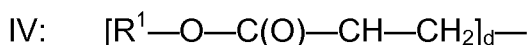
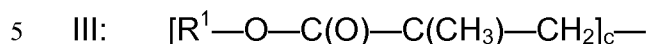
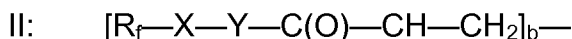
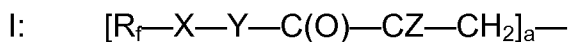
12. The coating composition of claim 1 wherein R_f is $C_6F_{13}-$, and is a straight or branched alkyl, or a combination thereof; R^1 is stearyl (octadecyl), $CH_3(CH_2)_{17}$; R^2 is 2-ethylhexyl, $CH_3(CH_2)_3CH(C_2H_5)CH_2$; R^3 is an alkyl group containing 8 to 20 carbon atoms; the organic solvent is cyclohexane or methyl isobutyl ketone and the coating base is selected from the group consisting of an alkyd coating, a Type I urethane coating, and an unsaturated polyester coating.

20

13. A method for treating a substrate with a coating composition comprising contacting the substrate with the coating composition and drying or curing the coating composition on the substrate, wherein the coating composition comprises a fluoropolymer composition and a coating base, wherein the fluoropolymer composition comprises a fluoropolymer

25

and an organic solvent and further wherein the fluoropolymer comprises repeating units in any sequence of polymer units:



10 wherein

R_f is a straight or branched perfluoroalkyl group having 2-6 carbon atoms, which is optionally interrupted by at least one oxygen atom, or a mixture of two or more thereof;

15 X is an organic divalent linking group having from about 1 to about 20 carbon atoms, optionally containing a triazole, oxygen, nitrogen, or sulfur, or a combination thereof;

Y is O, S or N(R) wherein R is H or C_1 to C_{20} alkyl;

Z is a straight or branched alkyl group having from about 1 to about 4 carbon atoms, or halide;

20 R^1 is a straight or branched alkyl group having from 12 to 22 carbon atoms;

R^2 is an alkyl group having a chain length of from 1 to 6 carbon atoms, which carbon chain may branched;

a is a positive integer;

25 b is zero or a positive integer;

c is a positive integer;

d is zero or a positive integer;

e is zero or a positive integer;

g is a positive integer;

h is zero or a positive integer;

- 5 T is H, a straight, branched or cyclic alkyl group having from about 1 to about 10 carbon atoms, or halide;

R^3 is H, C_nH_{2n+1} , C_nH_{2n-1} , $C_mH_{2m}-CH(O)CH_2$, $[CH_2CH_2O]_iR^4$, $[CH_2CH(CH_3)O]_iR^4$, $[C_mH_{2m}]N(R^4)_2$;

n is 8 to about 40;

- 10 m is 1 to about 40;

each R^4 is independently H, CH_2OH or C_jH_{2j+1} ;

i is 1 to about 200; and

j is 0 to about 40;

provided that

- 15 1) the repeating unit I, $[R_f-X-Y-C(O)-CZ-CH_2]_a-$, is present at a minimum of about 25% by weight of the polymer;

2) repeating units I and II ($[R_f-X-Y-C(O)-CZ-CH_2]_a$ and $[R_f-X-Y-C(O)-CH-CH_2]_b$) are present at a minimum combined total of about 30% by weight of the polymer; and

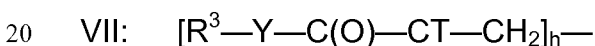
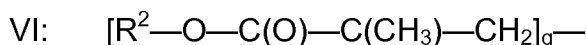
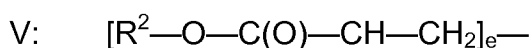
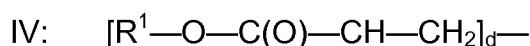
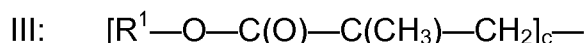
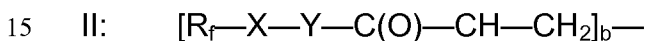
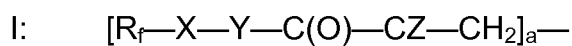
- 20 3) the total of all repeating units, I – VII plus any optional monomers equals 100% by weight of the polymer.

14. The method according to claim 13 wherein the coating base is selected from the group consisting of an alkyd coating, a Type I urethane
25 coating, and an unsaturated polyester coating.

15. The method according to claim 13 wherein the contacting step by brush, spray, roller, doctor blade, wipe, dip, foam, liquid injection, immersion or casting.

5 16. The method according to claim 14 wherein drying or curing step is performed by air curing, polymerizing, or energy curing.

17. A coated substrate wherein the substrate comprises a dried coating produced from the coating composition of the invention, wherein the
10 coating composition comprises comprising a fluoropolymer composition and a coating base, wherein the fluoropolymer composition comprises a fluoropolymer and an organic solvent and further wherein the fluoropolymer comprises repeating units in any sequence of polymer units:



wherein

R_f is a straight or branched perfluoroalkyl group having 2-6 carbon atoms, which is optionally interrupted by at least one oxygen atom, or a mixture of two or more thereof;

25 X is an organic divalent linking group having from about 1 to about 20 carbon atoms, optionally containing a triazole, oxygen, nitrogen, or sulfur, or a combination thereof;

Y is O, S or N(R) wherein R is H or C₁ to C₂₀ alkyl;

Z is a straight or branched alkyl group having from about 1 to about 4 carbon atoms, or halide;

R¹ is a straight or branched alkyl group having from 12 to 22 carbon atoms;

R² is an alkyl group having a chain length of from 1 to 6 carbon atoms, which carbon chain may branched;

a is a positive integer;

b is zero or a positive integer;

c is a positive integer;

d is zero or a positive integer;

e is zero or a positive integer;

g is a positive integer;

h is zero or a positive integer;

T is H, a straight, branched or cyclic alkyl group having from about 1 to about 10 carbon atoms, or halide;

R³ is H, C_nH_{2n+1}, C_nH_{2n-1}, C_mH_{2m}—CH(O)CH₂, [CH₂CH₂O]_iR⁴, [CH₂CH(CH₃)O]_iR⁴, [C_mH_{2m}]N(R⁴)₂;

n is 8 to about 40;

m is 1 to about 40;

each R⁴ is independently H, CH₂OH or C_jH_{2j+1};

i is 1 to about 200; and

j is 0 to about 40;

provided that

1) the repeating unit I, [R_f—X—Y—C(O)—CZ—CH₂]_a—, is present at a minimum of about 25% by weight of the polymer;

2) repeating units I and II ($[R_f-X-Y-C(O)-CZ-CH_2]_a$ and $[R_f-X-Y-C(O)-CH-CH_2]_b$) are present at a minimum combined total of about 30% by weight of the polymer; and

3) the total of all repeating units, I – VII plus any optional monomers
5 equals 100% by weight of the polymer.

18. The substrate of claim 17 wherein the substrate is selected from the group consisting of wood, metal, wallboard, masonry, concrete, fiberboard, and paper.

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19. The substrate of claim 18 wherein in the fluoropolymer, R_f is $C_6F_{13}-$, and is a straight or branched alkyl, or a combination thereof; R^1 is stearyl (octadecyl), $CH_3(CH_2)_{17}$; R^2 is 2-ethylhexyl, $CH_3(CH_2)_3CH(C_2H_5)CH_2$; R^3 is an alkyl group containing 8 to 20 carbon
15 atoms; and wherein the organic solvent is cyclohexane or methyl isobutyl ketone and wherein the coating base is selected from the group consisting of an alkyd coating, a Type I urethane coating, and an unsaturated polyester coating.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/038034

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D133/16
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2004 114620 A (NOF CORP) 15 April 2004 (2004-04-15) Working example 3 Working examples 6-25 -----	1-19
A	WO 00/53676 A1 (DU PONT [US]) 14 September 2000 (2000-09-14) examples -----	1-19

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Further documents are listed in the continuation of Box C.

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See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

29 August 2011

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/038034

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2004114620	A	15-04-2004	NONE

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