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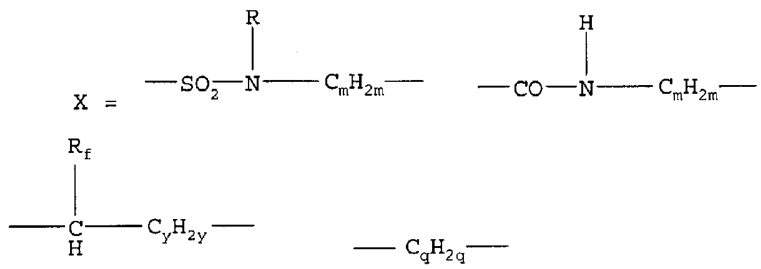
(54) Title: FLUOROACRYLATE-MERCAPTOFUNCTIONAL COPOLYMERS



(I)

(57) Abstract: A copolymer comprises repeating units derived from at least one co-reactant comprising two or more mercapto functional groups, and repeating units derived from a fluoroacrylate comprising the reaction product of: (a) at least one fluorochemical alcohol represented by the formula: C_4F_9-X-OH wherein: formula (I), R = hydrogen or an alkyl group of 1 to 4 carbon atoms, m = 2 to 8, R_fF_{2n+1}, n = 1 to 5, y = 0 to 6, and q = 1 to 8; (b) at least one unbranched symmetric diisocyanate; and at least one hydroxy-terminated alkyl (meth)acrylate or 2-fluoroacrylate monomer having 2 to about 30 carbon atoms in its alkylene portion.

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FLUOROACRYLATE-MERCAPTOFUNCTIONAL COPOLYMERS

FIELD

This invention relates to fluoroacrylate-mercaptofunctional copolymers.

BACKGROUND

Various fluorinated acrylic resins containing urethane linkages are known to have oil and water repellency properties (see, for example, U.S. Patent Nos. 4,321,404 (Williams et al.), 4,778,915 (Lina et al.), 4,920,190 (Lina et al.), 5,144,056 (Anton et al.), and 5,446,118 (Shen et al.)). These resins can be polymerized and applied as coatings to substrates such as, for example, textiles, carpets, wall coverings, leather, and the like to impart water- and oil repellency.

Typically, these resins comprise long chain pendant perfluorinated groups (for example, 8 carbon atoms or greater) because long chains readily align parallel to adjacent pendant groups attached to acrylic backbone units, and thus maximize water- and oil-repellency. However, long chain perfluorinated group-containing compounds such as, for example, perfluorooctyl containing compounds may bioaccumulate in living organisms (see, for example, U.S. Patent No. 5,688,884 (Baker et al.)).

SUMMARY

In view of the foregoing, we recognize that there is a need for water- and oil-repellent acrylic polymers that are less bioaccumulative. In addition, we recognize that for some applications the flexibility provided by graft and block copolymers can be an advantage.

Briefly, in one aspect, the present invention provides water- and oil-repellent fluoroacrylate-mercaptofunctional copolymers that have four carbon chain perfluorinated groups, which are believed to be less toxic and less bioaccumulative than longer chain perfluorinated groups (see, for example, WO 01/30873). The copolymers of the invention comprise repeating units derived from at least one co-reactant comprising two or more mercapto functional groups, and repeating units derived from a fluoroacrylate comprising the reaction product of:

(a) at least one fluorochemical alcohol represented by the formula:

$$C_4F_9\text{-}X\text{-}OH$$

wherein:

$$X = -SO_2-\underset{\displaystyle |}{\overset{\displaystyle R}{N}}-C_mH_{2m}- \;,\quad -CO-\overset{\displaystyle H}{N}-C_mH_{2m}- \;,$$

$$-\underset{\displaystyle H}{\overset{\displaystyle R_f}{C}}-C_yH_{2y}- \;,\ \text{or}\ -C_qH_{2q}- \;,$$

R = hydrogen or an alkyl group of 1 to 4 carbon atoms,

m = 2 to 8,

$R_f = C_nF_{2n+1}$,

n = 1 to 5,

y = 0 to 6, and

q = 1 to 8;

(b) at least one unbranched symmetric diisocyanate; and

(c) at least one hydroxy-terminated alkyl (meth)acrylate or 2-fluoroacrylate monomer having 2 to about 30 carbon atoms in its alkylene portion.

As used herein, a "co-reactant comprising two or more mercapto functional groups" refers to multithiols (for, example, dithiols, trithiols, etc.), or organic compounds resembling polyols but having the oxygens of the hydroxyl groups replaced by sulfurs. The term "(meth)acrylate" refers to both acrylates and methacrylates.

It has been discovered that the copolymers of the invention exhibit good water- and oil-repellency properties. In light of the prior art, one would expect that copolymers comprising fluoroacrylates derived from shorter perfluorinated chains would not be as effective at imparting water- and oil-repellency as those derived from longer perfluorinated chains (see, for example, U.S. Patent Nos. 2,803,615 (Ahlbrecht et al.) and 3,787,351 (Olson)). Surprisingly, however, the fluoroacrylate-mercaptofunctional copolymers of the invention exhibit water- and oil-repellency comparable to fluoroacrylates with longer perfluorinated chains.

The fluoroacrylate-mercaptofunctional copolymers of the invention therefore meet the need in the art for polymerizable water- and oil-repellent acrylic resins that are less bioaccumulative.

In addition, the fluoroacrylate-mercaptofunctional copolymers of the invention provide the flexibility of block and graft copolymers, which combine the properties of two dissimilar polymers. Such copolymers find use in applications that require a combination of the unique properties of the fluoroacrylate with those of various mercaptofunctional polymers.

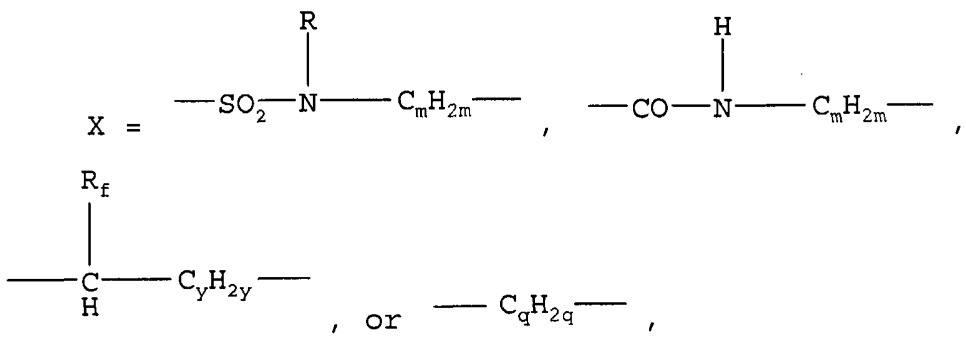
DETAILED DESCRIPTION

Fluoroacrylates useful in the invention are the reaction product of a fluorochemical alcohol, at least one unbranched symmetric diisocyanate, and at least one hydroxy-terminated alkyl (meth)acrylate or 2-fluoroacrylate monomer.

Useful fluorochemical alcohols can be represented by the formula:

$$C_4F_9\text{-}X\text{-}OH$$

wherein:



R = hydrogen or an alkyl group of 1 to 4 carbon atoms,

m = 2 to 8,

$R_f = C_nF_{2n+1}$,

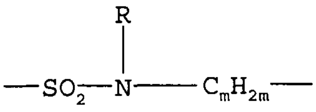
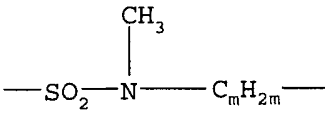
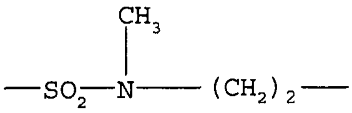
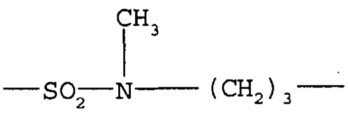
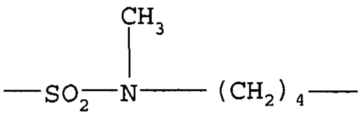
n = 1 to 5,

y = 0 to 6, and

q = 1 to 8.

Representative examples of suitable alcohols include $C_4F_9SO_2NH(CH_2)_2OH$, $C_4F_9SO_2NCH_3(CH_2)_2OH$, $C_4F_9SO_2NCH_3(CH_2)_4OH$, $C_4F_9SO_2NC_2H_5(CH_2)_6OH$, $C_4F_9(CH_2)_4OH$, $C_4F_9CONH(CH_2)_4OH$, $C_4F_9SO_2NCH_3(CH_2)_3OH$, $C_4F_9SO_2NH(CH_2)_6OH$, $C_4F_9CH_2OH$, $C_4F_9CONH(CH_2)_8OH$, $C_4F_9(CH_2)_2OH$, $C_4F_9SO_2NCH_3(CH_2)_2OH$, $C_4F_9CONH(CH_2)_2OH$, $C_4F_9SO_2NCH_3(CH_2)_6OH$, $C_4F_9SO_2NH(CH_2)_7OH$, $C_4F_9SO_2NC_3H_7(CH_2)_2OH$, $C_4F_9SO_2NC_4H_9(CH_2)_2OH$, $C_4F_9CONH(CH_2)_2OH$, and $C_4F_9(CH_2)_4OH$.

Preferably, m is 2 to 4. Preferably, q is 2.

Preferably, X is  . More preferably, X is  . Most preferably, X is selected from the group consisting of  ,  , and  .

Preferred fluorochemical alcohols include, for example, $C_4F_9SO_2NCH_3(CH_2)_2OH$, $C_4F_9SO_2NCH_3(CH_2)_4OH$, and $C_4F_9(CH_2)_2OH$. A more preferred fluorochemical alcohol is $C_4F_9SO_2NCH_3(CH_2)_2OH$.

Symmetric diisocyanates are diisocyanates that meet the three elements of symmetry as defined by Hawley's Condensed Chemical Dictionary 1067 (1997). First, they have a center of symmetry, around which the constituent atoms are located in an ordered arrangement. There is only one such center in the molecule, which may or may not be an atom. Second, they have a plane of symmetry, which divides the molecule into mirror-image segments. Third, they have axes of symmetry, which can be represented by lines passing through the center of symmetry. If the molecule is rotated, it will have the same position in space more than once in a complete 360° turn.

As used herein, the term "unbranched" means that the symmetric diisocyanate does not contain any subordinate chains of one or more carbon atoms.

Representative examples of unbranched symmetric diisocyanates include 4,4'-diphenylmethane diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI), 1,4-phenylene diisocyanate (PDI), 1,4-butane diisocyanate (BDI), 1,8-

octane diisocyanate (ODI), 1,12-dodecane diisocyanate, and 1,4-xylylene diisocyanate (XDI). Preferably, unbranched symmetric diisocyanates are aromatic.

Preferred unbranched symmetric diisocyanates include, for example, MDI, HDI, and PDI. A more preferred unbranched symmetric diisocyanate is MDI. In its pure form, MDI is commercially available as Isonate™ 125M from Dow Chemical Company (Midland, MI), and as Mondur™ from Bayer Polymers (Pittsburgh, PA).

Hydroxy-terminated alkyl (meth)acrylate and 2-fluoroacrylate monomers that are useful in the fluoroacrylates of the invention can have from 2 to about 30 carbon atoms (preferably, from 2 to about 12 carbon atoms) in their alkylene portion.

Preferably, the hydroxy-terminated alkyl (meth)acrylate monomer is a hydroxy-terminated alkyl acrylate. Preferred hydroxy-terminated alkyl acrylates include, for example, hydroxy ethyl acrylate, hydroxy butyl acrylate, hydroxy hexyl acrylate, hydroxy decyl acrylate, hydroxy dodecyl acrylate, and mixtures thereof.

The fluoroacrylates useful in the invention can be prepared, for example, by first combining the fluorochemical alcohol and unbranched symmetric diisocyanate in a solvent, and then adding the hydroxy-terminated alkyl (meth)acrylate. Useful solvents include esters (for example, ethyl acetate), ketones (for example, methyl ethyl ketone), ethers (for example, methyl-tert-butyl ether), and aromatic solvents (for example, toluene).

Preferably, the reaction mixture is agitated. The reaction can generally be carried out at a temperature between room temperature and about 120°C (preferably, between about 50°C and about 70°C).

Typically the reaction is carried out in the presence of a catalyst. Useful catalysts include bases (for example, tertiary amines, alkoxides, and carboxylates), metal salts and chelates, organometallic compounds, acids and urethanes. Preferably, the catalyst is an organotin compound (for example, dibutyltin dilaurate (DBTDL) or a tertiary amine (for example, diazobicyclo[2.2.2]octane (DABCO)), or a combination thereof. More preferably, the catalyst is DBTDL.

When fluorochemical alcohols represented by the formula $C_4F_9SO_2NCH_3(CH_2)_mOH$, wherein m = 2 to 4, are reacted with MDI, the process described in U.S. Patent Application Serial No. 10/751142, entitled "Process For Preparing Fluorochemical Monoisocyanates," filed on December 31, 2003, can be used.

Fluoroacrylates useful in the compositions of the invention can be represented by the following general formula:

$$C_4F_9\text{-}X\text{-}OC(O)NH\text{-}A\text{-}HNC(O)O\text{-}(C_pH_{2p})(O)COC(R')=CH_2$$

wherein:

X = $-SO_2-N(R)-C_mH_{2m}-$, $-CO-N(H)-C_mH_{2m}-$,

$-CH(R_f)-C_yH_{2y}-$, or $-C_qH_{2q}-$,

R = H or an alkyl group of 1 to 4 carbon atoms,

m = 2 to 8,

$R_f = C_nF_{2n+1}$,

n = 1 to 5,

y = 0 to 6,

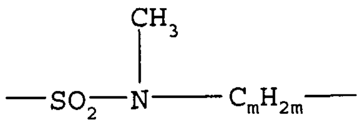
q = 1 to 8,

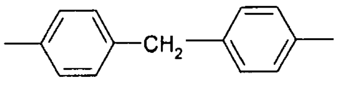
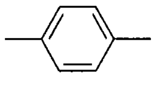
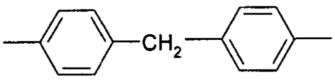
A = an unbranched symmetric alkylene group, arylene group, or aralkylene group,

p = 2 to 30, and

R′ = H, CH_3, or F.

Preferably, q is 2.

Preferably, X is  and m is 2 to 4.

Preferably, A is selected from the group consisting of C_6H_{12}, , and ; more preferably, A is .

Preferably, p is 2 to 12; more preferably, p is selected from the group consisting of 2, 4, 6, 10, and 12; most preferably, p is 2.

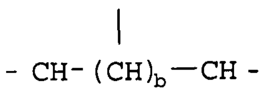
Preferably, R′ is H.

The fluoroacrylates described above can be reacted with co-reactants comprising two or more mercapto functional groups to form the water- and oil-repellent fluoroacrylate-mercaptofunctional copolymers of the invention.

Suitable co-reactants include, for example, multimercaptans represented by the formula:

$$(B)_n(Q\text{-}SH)_k$$

wherein:

B = a multivalent segment selected from the group consisting of , $-(CH_2)_b-$, $-(CH_2CH_2O)_b-$, $-(CHCH_3CH_2O)_b-$, $-(CH_2CH_2O)_b-(CHCH_3CH_2O)_b$, $-C_4H_8(OC_4H_8)_b-$, $-C_2H_4OC_2H_4OC_2H_4-$, $C_6H_5CR''_2C_6H_5-$, and $-(C_2H_4O)_bC_6H_5CR''_2C_6H_5(OC_2H_4)_b-$;

b = 1 to 100;

R″ = CH_3, CF_3, or H;

Q = $-(CH_2)_b-$, $-C(O)(CH_2)_a-$, or $-OC(O)(CH_2)_a-$;

a = 1 to 10;

n = 1 or greater; and

k = 2 or greater.

Other suitable co-reactants include, for example, dimercaptans represented by the formula:

$$HS(Q'-(B')_n-Q'S)_bH$$

wherein:

B′ = a multivalent segment selected from the group consisting of $-(CH_2)_b-$, $-(CH_2CH_2O)_b-$, $-(CHCH_3CH_2O)_b-$, $-(CH_2CH_2O)_b-(CHCH_3CH_2O)_b$, $-C_4H_8(OC_4H_8)_b-$, $-C_2H_4OC_2H_4OC_2H_4-$, $C_6H_5CR''_2C_6H_5-$, and $-(C_2H_4O)_bC_6H_5CR''_2C_6H_5(OC_2H_4)_b-$;

b = 1 to 100;

R″ = CH_3, CF_3, or H;

n = 1 or greater; and

Q′ = $-OC(O)CH_2CH_2-$ or $-C(O)CH_2CH_2-$.

These dimercaptans can be prepared, for example, by reacting di(meth)acrylates with disulfhydryl group-containing reactants (for example, hydrogen sulfide, 1,4-butanedithiol, 2-hydroxy-propane-1,3-dithiol, 2,2-dithiol-diethyl ether, 3,3-dimercaptodipropyl sulfone, diethylene glycol-bis-thioglycolate, and the like) as described in U.S. Patent No. 3,278,352 (Erickson et al.).

Still other suitable co-reactants include, for example, fluorinated dimercaptans represented by the formula:

$$(R_{f'})_n(Q''-SH)_k$$

wherein:

$R_{f'}$ = a multivalent segment comprising a fluorinated alkyl or alkylene group (for example, $-C_2H_4N(SO_2C_4F_9)C_2H_4-$, $-(CF_2)_d-$, $-(CF_2CF_2O)_e(CF_2O)_fCF_2-$);

d = 2 to 10;

e = 2 to 30;

f = 1 to 30;

Q″ = $-C(O)NH(CH_2)_b-$ or $-OC(O)(CH_2)_b-$;

b = 2 to 12;

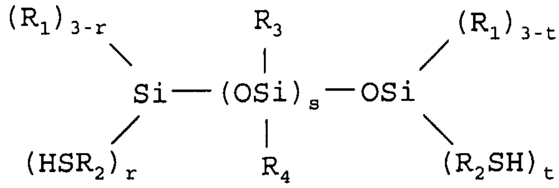
n = 1 or greater; and

k = 2 or greater.

Preferred fluorinated dimercaptans include, for example, $C_4F_9SO_2N(C_2H_4OC(O)CH_2SH)_2$, $HSC_2H_4NHC(O)(CF_2)_4C(O)NHC_2H_4SH$, and $HSC_2H_4NHC(O)CF_2(OC_2F_4)e(OCF_2)_fC(O)NHC_2H_4SH$.

These fluorinated dimercaptans can be prepared, for example, from the corresponding fluorinated diols and $HS(CH_2)_bCO_2H$ as described in GB 1120304, or from a fluorinated dimethyl ester and $NH_2C_2H_4SH$.

Still more suitable co-reactants include, for example, mercapto functional silicone compounds such as those represented by the following formula:



wherein:

R_1 = monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, hydroxyl, hydrogen, and fluoroalkyl;

R_2 = divalent linking groups which can independently be the same or different;

R_3 = monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, hydroxyl, hydrogen, fluoroalkyl, and -ZSH;

R_4 = monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, hydroxyl, hydrogen, fluoroalkyl, and -ZSH;

wherein:

Z = a divalent linking group;

r = 0 to 3;

s = 10 or greater; and

t = 0 to 3;

wherein at least two of the following are true:

t = at least 1

r = at least 1

R_3 comprises at least one -ZSH moiety; and

R_4 comprises at least one -ZSH moiety.

Mercapto functional silicone compounds such as those described above can be prepared, for example, as described in U.S. Patent No. 5,032,460 (Kantner et al.).

A preferred mercapto functional silicone compound is the mercapto functional dimethyl siloxane available as KF-2001 from Shin-Etsu, Japan.

Many useful co-reactants are commercially available. Commercially available co-reactants include, for example, 2,2'-oxydiethanethiol, 1,2-ethanethiol, 2-mercaptoethane sulfide, 3,7-dithia-1,9-nonanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, 1,5-pentanedithiol, 1,6-hexanedithiol, 1,7-heptanedithiol, 1,8-octanedithiol, 1,9- nonanedithiol, 3,6-dioxa-1,8-octanedithiol, 1,10-decanedithiol, 1,12-dimercaptododecane, ethylene glycol bis(3-mercaptopropionate), 1,4- butanediol bis(3-mercaptopropionate), 1,1,1-trimethylolpropane tris-(3-mercaptopropionate), pentaerythritol tetra(3-mercaptopropionate), trimethylolpropane tris(3-

mercaptopropionate), and tris[2-(3-mercaptopropionyloxy)ethyl] isocyanurate.

The fluoroacrylate-mercaptofunctional copolymers of the invention can be prepared, for example, by combining the fluoroacrylates and the co-reactants comprising two or more mercapto functional groups in a solvent. Useful reaction solvents include esters (for example, ethyl acetate), ketones (for example, methyl ethyl ketone), ethers (for example, methyl-tert-butyl ether), amides (for example, dimethyl formamide), and alcohols.

Preferably, the reaction mixture is agitated. The reaction can generally be carried out at a temperature between about room temperature and about 120°C (preferably, between about 50°C and about 70°C).

The reaction is carried out using an initiator. Useful initiators include, for example, substituted azonitrile compounds, peroxides, peracids, and peresters. Specific examples of useful initiators include 2,2-azo-bis-(isobutyronitrile), dimethyl 2,2'-azo-bis-isobutyrate, azo-bis-(diphenylmethane), 4-4'-azo-bis(4-cyanopentanoic) acid, 1,1'azo-bis-(cyclohexane carbonitrile), 2,2'-azo-bis-(2-methyl butyronitrile), 2,2'-azo-bis-(2,4-dimethyl valeronitrile), azo-bis-dimethyl valeronitrile,4,4'-azo-bis-(4-cyanovaleric acid), benzoyl peroxide, cumyl peroxide, tert-butyl peroxide, cyclohexanone peroxide, glutaric acid peroxide, lauroyl peroxide, methyl ethyl ketone peroxide, hydrogen peroxide, hydroperoxides such as tert butyl hydroperoxide and cumene hydroperoxide, peracetic acid, perbenzoic acid, diisopropyl percarbonate, and the like.

The copolymers of the invention can include repeating units derived from one or more comonomers or functionalized comonomers in order to modify their properties and performance for different applications.

Comonomers such as, for example, alkyl acrylates can improve durability and film-forming properties. Representative examples of useful comonomers include methyl (meth)acrylate, butyl acrylate, isobutyl (meth)acrylate, hexyl acrylate, dodecyl acrylate, and octadecyl acrylate.

Other comonomers can modify properties such as, for example, adhesion, hydrophilicity, reactivity, or glass transition temperature. Groups that are useful in comonomers include, for example, hydroxy, carboxy, quaternary ammonium, acetate, pyrrolidine, polyethylene glycol, sulfonic acid, trialkoxysilane, and silicone. Useful comonomers include, for example, hydroxy ethyl acrylate, hydroxy butyl acrylate, hydroxy hexyl acrylate, hydroxy decyl acrylate, hydroxy dodecyl acrylate, acrylic acid, methacrylic acid, N-vinyl 2-pyrrolidinone, hydroxypropyl acrylic acid, diacetone acrylamide, poly(ethylene glycol) methylethyl ether, ethylene glycol methacrylate phosphate, 2-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltrimethoxysilane, 3-methacryloxypropyltrichlorosilane, glycidyl methacrylate, glycidyl acrylate, N-methylol methacrylamide, and N-methylol acrylamide.

Copolymers of the invention can be used in coating compositions to impart water- and oil-repellency to a wide variety of substrates. The coating compositions comprise a copolymer of the invention and a solvent (for example, water and/or an organic solvent). When the solvent is water, the coating composition typically further comprises a surfactant.

The fluoroacrylate-mercaptofunctional copolymers of the invention can be dissolved, suspended, or dispersed in a wide variety of solvents to form coating compositions suitable for coating onto a substrate. The coating compositions can generally contain from about 0.1 about 10 percent fluoroacrylate-mercaptofunctional copolymer (preferably about 1 to about 5 percent), based on the weight of the coating composition.

The coating compositions can be applied to a wide variety of substrates such as, for example, fibrous substrates and hard substrates. Fibrous substrates include, for example, woven, knit, and non-woven fabrics, textiles, carpets, leather, and paper. Hard substrates include, for example, glass, ceramic, masonry, concrete, natural stone, man-made stone, grout, metals, wood, plastics, and painted surfaces.

The coating compositions can be applied to a substrate (or articles comprising a substrate) by standard methods such as, for example, spraying, padding, dipping, roll coating, brushing, or exhaustion. Optionally, the composition can be dried to remove any remaining water or solvent.

Fluoroacrylate-mercaptofunctional copolymers of the invention can be used in release coatings. Comonomers that are useful in release coatings include, for example, octadecyl acrylate, N-vinyl 2-pyrollidinone, methacryloxy propyl dimethyl siloxane, acrylic acid, methacrylic acid, acrylonitrile and methyl acrylate. The release coating compositions may or may not require a curing step after coating on a substrate.

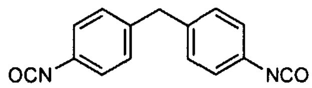
Coating compositions useful for release coatings can be applied to surfaces requiring release properties from adhesives. Substrates suitable for release coatings include, for example, paper, metal sheets, foils, non-woven fabrics, and films of thermoplastic resins such as polyesters, polyamides, polyolefins, polycarbonates, and polyvinyl chloride.

Release coating compositions can be applied to suitable substrates by conventional coating techniques such as, for example, wire-wound rod, direct gravure, offset gravure, reverse roll, air-knife, and trailing blade coating. The resulting release coating compositions can provide effective release for a wide variety of pressure sensitive adhesives such as, for example, natural rubber based adhesives, silicone based adhesives, acrylic adhesives, and other synthetic film-forming elastomeric adhesives.

EXAMPLES

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

Designator	Name, Formula and/or Structure	Availability
PEG-900	Polyethylene glycol $HO(C_2H_4O)_nH$, Mn ca. 900	Sigma Aldrich, Milwaukee, WI
Carbowax-1450	Polyethylene glycol $HO(C_2H_4O)_nH$, Mn ca. 1450	Acros Organics USA Morris Plains, NJ
MCAA	Mercaptoacetic acid $HSCH_2CO_2H$	Sigma Aldrich,
TFMSA	Trifluoromethanesulfonic Acid CF_3SO_3H	Sigma Aldrich,
HEMAPA	2-(Methacryloyloxy)ethyl phosphate $CH_2{=}CMeCO_2CH_2CH_2OP(O)(OH)_2$	Sigma Aldrich,
DOODS	3,6-dioxa-1,8-octanedithiol $HSC_2H_4OC_2H_4OC_2H_4SH$	Sigma Aldrich,
C10DO	1,10-Decanediol $HO(CH_2)_{10}OH$	Sigma Aldrich,
KF-2001	Copolymer of	Shin-Etsu

Designator	Name, Formula and/or Structure	Availability
	(mercaptopropyl)methylsiloxane and dimethylsiloxane (MW ~ 8,000/4-SH) $-[SiMe_2O]_x-[SiMe(C_3H_6SH)O]_y-$	Japan
AA	Acrylic acid	Sigma Aldrich
VAZO-67	2,2'-azobis(2-cyanopentane)	DuPont, Wilmington,DE
MDI	4,4'-methylenebis(phenyl isocyanate); 	Sigma-Aldrich
EtOAc	Ethyl acetate $CH_3CO_2CH_2CH_3$	Sigma-Aldrich
HEA	2-Hydroxyethyl acrylate; $HOCH_2CH_2OC(O)CH=CH_2$	Sigma-Aldrich
DMF	N,N-Dimethylformamide $HC(O)NMe_2$	Sigma-Aldrich
EGDS	Ethylene Glycol Bisthioglycolate $HSCH_2CO_2CH_2CH_2OC(O)CH_2SH$	Sigma Aldrich,
LTMDME	Perfluoropolyether dimethyl ester $CH_3OC(O)CF_2(OC_2F_4)_n(OCF_2)_mCO_2CH_3$	Solvay Solexis, Inc. Italy
CSA	Cysteamine $NH_2CH_2CH_2SH$	Fluka Chemical Milwaukee, WI
ODA	Octadecyl acrylate $CH_2=CHCO_2(CH_2)_{17}CH_3$	Sigma Aldrich
MeOPEGA	Methoxy-polyethylene glycol monoacrylate (MW 454) $CH_3O-(CH_2CH_2O)_n-C(O)CH=CH_2$	Sigma-Aldrich

Test Method:

Dynamic Contact Angle Measurement

A test solution, emulsion, or suspension (typically at about 3% solids) was applied to nylon 66 film (available from DuPont) by dip-coating strips of the film. Prior to coating the film was cleaned with methyl alcohol. Using a small binder clip to hold one end of the nylon film, the strip was immersed in the treating solution, and then withdrawn slowly and smoothly from the solution. The coated strip was allowed to air dry in a protected location for a minimum of 30 minutes and then was cured for 10 minutes at 150°C.

Advancing and receding contact angles on the coated film were measured using a CAHN Dynamic Contact Angle Analyzer, Model DCA 322 (a Wilhelmy balance apparatus equipped with a computer for control and data processing, commercially available from ATI, Madison, WI). Water and hexadecane were used as probe liquids. Values for both water and hexadecane are reported.

Preparation of $C_4F_9SO_2N(CH_3)CH_2CH_2OH$ (MeFBSE)

MeFBSE was prepared by essentially following the procedure described in U.S. Patent No. 6,664,354 (Savu et al.), Example 2, Part A.

Preparation of $C_4F_9SO_2N(CH_3)C_2H_4OC(O)NHC_6H_4CH_2C_6H_4NCO$ (MeFBSE-MDI)

A one liter, three-necked round bottom flask, fitted with a heater, nitrogen inlet, reflux condenser and thermocouple was charged with MeFBSE (357.0 g; 1.0 mole) and MEK (600 mL) and heated to reflux, while distilling out 30 mL of MEK. The mixture was then cooled to 30°C and treated with MDI (750 g; 3.0 mole). The temperature of the mixture was then increased to about 40°C for 4 hours, filtered and added to 4 liters of toluene. The resulting off white precipitate was collected by filtration, and re-crystallized from toluene (white solid; 689.4 g; 57% yield). Structure was confirmed using liquid chromatography/mass spectroscopy (LC/MS) and LC/UV analysis.

Preparation of $C_4F_9SO_2N(CH_3)C_2H_4OC(O)NHC_6H_4CH_2C_6H_4NHCOOCH_2CH_2OC(O)CH=CH_2$ (MeFBSE-MDI-HEA or C4MH)

A one liter flask containing 500ml ethyl acetate was heated to reflux under N_2, and 100 mL of ethyl acetate (EtOAc) was distilled out. The remaining solvent was cooled under dry air and treated with 151.9g MeFBSE-MDI, 29.1g 2-hydroxyethyl acrylate, 2 drops DBTDL, and 7mg phenothiazine. After 5 hr at 50°C, infrared spectroscopy indicated complete conversion of the isocyanate. The cloudy solution was filtered through 40g diatomaceous earth and rinsed with hot ethyl acetate to give 473.5g clear solution, (29.6% solids, yield as MeFBSE-MDI-HEA, 77%).

Preparation of $C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$ (MeFBSEA)

MeFBSEA was prepared by essentially following the procedure described in U.S. Patent No. 6,664,354 (Savu et al.) Example 2, Part A & B.

Preparation of PEGDS-1048

A 250ml three necked round-bottom flask was charged 30g PEG-900 (MW=900, 33.33 mmol), 6.13g mercaptoacetic acid (MW=92, 66.66 mmol), 150g toluene, and three drops CF_3SO_3H. The mixture was heated to reflux with mechanical stirring under N_2. Water formed as a byproduct was captured by an azeotropic condensation trap. The mixture was allowed to reflux for 6 hours, and 1.20g water was isolated. Toluene was removed by roto-evaporation and 32.56g or product was recovered.

Preparation of PEGDS-1598

A 250ml three necked round-bottom flask was charged with melted Carbowax-1450 45.4g (MW=1450, 31.31 mmol), 5.76g mercaptoacetic acid (MW=92, 62.62 mmol), 150g toluene, and three drops CF_3SO_3H. The mixture was heated to reflux with mechanical stirring under N_2. Water formed as a byproduct was captured by an azeotropic condensation trap. The mixture was allowed to reflux for 4 hours, and 1.13g water was isolated. Toluene was removed by roto-evaporation 51.46g of product was recovered.

Preparation of $HSCH_2C(O)\text{-}O\text{-}(CH_2)_{10}\text{-}O\text{-}C(O)CH_2SH$ (C10DS)

A 250ml three necked round-bottom flask was charged with 34.86g melted 1,10-decanediol (MW=174.28, 200 mmol), 36.80g mercaptoacetic acid (MW=92, 400 mmol), 150g toluene, and three drops CF_3SO_3H. The mixture was heated to reflux with mechanical stirring under N_2. Water formed as a byproduct was captured by an azeotropic condensation trap. The mixture was allowed to reflux for 8 hours, and ~7.2 g water was isolated. Toluene was removed by roto-evaporation and 65.2g of product (C10DS) was recovered.

Preparation of $C_4F_9SO_2N(CH_2CH_2OH)_2$ (FBSEE):

$C_4F_9SO_2N(C_2H_4OH)_2$, a fluorochemical diol, can be prepared as described in Example 8 of U.S. Pat. No. 3,787,351 (Olson), except that an equimolar amount of $C_4F_9SO_2NH_2$ is substituted for $C_8F_{17}SO_2NH_2$.

Preparation of $C_4F_9SO_2N(CH_2CH_2OC(O)CH_2SH)_2$ (FBSEESS):

A 250ml three necked round-bottom flask was charged with 23.22 g FBSEE (MW=387, 60 mmol), 11.06 g mercaptoacetic acid (MW=92, 120 mmol), 150 g Toluene, and 0.15 g CH3PhSO3H (catalyst). The mixture was heated to reflux with mechanical stirring under N2. Water formed as a byproduct was captured by azeotropic condensation trap. The mixture was allowed to reflux for 8 hours, and 2.20 g water was isolated. Toluene was removed by roto-evaporation to give 32.5 g product, FBSEESS.

Preparation of $HSC_2H_4NHC(O)$-LTM-$C(O)NHC_2H_4SH$ (LTMDS):

A 150 ml Pyrex tube was charged with 79g LTMDME (MW=2000, 39.5 mmol) and 6.13g cyteamine (MW=77, 79 mmol). The tube was flushed with N_2 sealed, and the mixture was heated to 120°C with a magnetic stirring for 6 hours. Infrared analysis confirmed complete conversion to LTMDS.

General Procedure for Polymer Preparation:

For each example and comparative example, a 120 ml bottle was charged with fluorinated monomer, dimercaptan and optionally a third hydrocarbon (meth)acrylate monomer in different mole ratios as described in Table 1, 0.5~1% VAZO-67 initiator (by weight), and sufficient solvent to yield a 15-30% solids by weight concentration of monomers. After purging with nitrogen for 35-60 seconds, the bottle was sealed and the mixture polymerized in a 70°C oil bath for 24 hrs. The advancing and receding contact angles for the resulting polymers were determined as described above and the results were reported in Table 1 below.

Detailed Procedure for Selected Examples and Comparative Example

Example 2: C4MH/PEGDS-1048 (12/1)

A 120ml bottle was charged with 5.85g C4MH (MW=723, 8.095 mmol), 0.71g PEGDS-1048 (MW = 1048, 0.672 mmol), 40.34g ethyl acetate and 0.058g VAZO-67. A magnetic stir bar was added. The solution was bubbled with nitrogen for two minutes. The sealed bottle was put in a 70°C oil bath and polymerized with a magnetic stirring for 24 hours. The obtained solution showed precipitation at room temperature. Addition of 5.g DMF turned it clear solution with 12.8% solid. Contact angle data was reported in Table 1 below.

Example 3: C4MH/PEGDS-1048/HEMAPA (2.9/0.3/1)

A 120ml bottle was charged with 5.03g C4MH (MW=723, 6.956 mmol), 0.72g PEGDS-1048 (MW = 1048, 0.691 mmol), 0.50g HEMAPA (MW=210.13, 2.379 mmol), 25.2 g EtOAc and 0.058 g VAZO-67. A magnetic stir bar was added. The solution was bubbled with nitrogen for two minutes. The sealed bottle was put in a 70°C oil bath and polymerized with a magnetic stirring for 24 hours. The obtained solution showed precipitation at room temperature. Addition of 5.g DMF turned it clear solution with 13.61% solid. Contact angle data was reported in Table 1.

Example 5: C4MH/PEGDS-1598 (12/1)

A 120ml bottle was charged with 5.0g C4MH (MW=723, 6.91 mmol), 0.87g PEGDS-1598 (MW = 1524, 0.57 mmol), 35.0g EtOAc and 0.056g VAZO-67. A magnetic stir bar was added. The solution was bubbled with nitrogen for two minutes. The sealed bottle was put in a 70°C oil bath and polymerized with a magnetic stirring for 24 hours. The obtained solution showed precipitation at room temperature. Addition of 5.0 g DMF turned it clear. Contact angle data was reported in Table 1 below.

Example 7: C4MH/EGDS (8.07/1)

A 120ml bottle was charged with 5.0g C4MH (MW=723, 6.912 mmol), 0.18g $(HSCH_2CO_2CH_2)_2$ (MW = 210.27, 0.856 mmol), 11.94g EtOAc and 0.047g VAZO-67. A magnetic stir bar was added. The solution was bubbled with nitrogen for two minutes. The sealed bottle was put in a 70°C oil bath and polymerized with a magnetic stirring for 24 hours. The obtained solution showed precipitation at room temperature. Addition of 2.40 g DMSO turned the solution clear with 14.3% solids. Size exclusion chromatography analysis showed the conversion of 94.0%; Mn = 6,700; Mw = 8,710, Mw/Mn = 1.3. Contact angle data was reported in Table 1 below.

Example 9: C4MH/DOODS (5.8/1)

A 120ml bottle was charged with 3.00g C4MH (MW=723, 4.154 mmol), 0.13g $HSC_2H_4OC_2H_4OC_2H_4SH$ (MW = 182.31, 0.713 mmol), 17.74g EtOAc and 0.033 g VAZO-67. A magnetic stir bar was added. The solution was bubbled with nitrogen for two minutes. The sealed bottle was put in a 70°C oil bath and polymerized with a magnetic stirring for 24 hours. The obtained solution showed precipitation at room temperature. Addition of 5.0 g DMF turned the solution clear at 12% solids. Contact angle data was reported in Table 1 below.

Example 11: C4MH/MeOPEGA/DOODS (11.46/1.8/1)

A 120ml bottle was charged with 5.0g C4MH (MW=723, 6.916 mmol), 0.50g $CH_3O(C_2H_4O)_nC(O)CH=CH_2$ (MW= 454, 1.10 mmol), 0.11g $HSC_2H_4OC_2H_4OC_2H_4SH$ (MW = 182.31, 0.603 mmol), 10.53 g EtOAc and 0.055 g VAZO-67. A magnetic stir bar was added. The solution was bubbled with nitrogen for two minutes. The sealed bottle was put in a 70°C oil bath and polymerized with a magnetic stirring for 24 hours. The obtained solution showed precipitation at room temperature. Addition of 5.0 g DMF cleared the solution at 16.9% solids. Contact angle data was reported in Table 1 below.

Example 13: C4MH/C10DS (8/1)

A 120ml bottle was charged with 31.62g C4MH (36.6% in EtOAc, MW=723, 16 mmol), 0.65 g C10DS (MW = 322, 2 mmol), 28.85g EtOAc and 0.15g VAZO-67. A magnetic stir bar was added. The solution was bubbled with nitrogen for two minutes. The sealed bottle was put in a 70°C oil bath and polymerized with a magnetic stirring for 24 hours. The obtained 20% solution showed precipitation at room temperature. Addition of 5.0g DMF cleared the solution. Contact angle data was reported in Table 1 below.

Table 1: Examples 1-18 and Comparative Examples C1-C2

Example	Formulation	Mole Ratio	Contact Angle (advancing/receding)	
			Water	Hexadecane
1	C4MH/PEGDS-1048	8/1	128/98	82/67
2	C4MH/PEGDS-1048	12/1	127/102	81/67
C1	MeFBSEA/PEGDS-1048	6/1	65/46	80/44
C2	MeFBSEA/PEGDS-1048	6/1	98/47	64/35
3	C4MH/PEGDS-1048/HEMAPA	2.9/0.3/1	124/99	82/67
4	C4MH/PEGDS-1048/HEMAPA	5.2/0.5/1	127/101	82/68
5	C4MH/PEGDS-1598	12/1	120/89	81/64
6	C4MH/EGDS	4/1	132/115	80/68
7	C4MH/EGDS	8/1	128/103	79/68
8	C4MH/EGDS	12/1	132/115	81/68
9	C4MH/DOODS	5.8/1	123/103	81/68
10	C4MH/DOODS	10.8/1	121/98	80/71
11	C4MH/MeOPEGA/DOODS	11/1.8/1	121/98	80/71
12	C4MH/C10DS	12/1	131/108	81/66
13	C4MH/C10DS	8/1	132/108	81/66
C3	MeFBSEA/C10DS	12/1	122/75	75/33
14	C4MH/FBSEESS	4/1	121/91	82/70
15	C4MH/FBSEESS/ODA	8/1/2	120/91	81/69
16	C4MH/LTMDS	4/1	125/109	81/69
17	C4MH/LTMDS	16/1	127/106	82/68
18	C4MH/LTMDS/ODA	8/1/2	128/93	81/66

Example 19: C4MH/KF-2001 (90/10)

A 120ml bottle was charged with 4.50g C4MH (MW=723, 6.22 mmol), 0.49g KF-2001, 28.4g EtOAc and 0.056 g VAZO-67. A magnetic stir bar was added, and the solution was bubbled with nitrogen for two minutes. The sealed bottle was put in a 70°C oil bath and polymerized with a magnetic stirring for 24 hours. The obtained solution was slightly cloudy.

Addition of 5g DMF cleared the solution (13.16% solids). Size exclusion chromatography analysis showed the conversion was 93.4%, Mn = 11,600, Mw = 21,800 and Mw/Mn = 1.9. Contact angle data was reported in Table 2 below.

Example 20: C4MH/KF-2001 (80/20)

A 120ml bottle was charged with 3.98g C4MH (MW=723, 5.510 mmol), 1.01 g KF-2001, 27.62g EtOAc and 0.050g VAZO-67. A magnetic stir bar was added, and the solution was bubbled with nitrogen for two minutes. The sealed bottle was put in a 70°C oil bath and polymerized with a magnetic stirring for 24 hours. The obtained solution was slightly cloudy. Addition of 5g DMF cleared the solution (13.37% solids). Size exclusion chromatography analysis showed the conversion was 87.4%, Mn = 12,500, Mw = 23,700 and Mw/Mn = 1.9. Contact angle data was reported in Table 2 below.

Example 21: C4MH/KF-2001 (70/30)

A 120ml bottle was charged with 3.51g C4MH (MW=723, 4.849 mmol), 1.52g KF-2001, 26.75g EtOAc and 0.053g VAZO-67. A magnetic stir bar was added, and the solution was bubbled with nitrogen for two minutes. The sealed bottle was put in a 70°C oil bath and polymerized with a magnetic stirring for 24 hours. The obtained solution was slightly cloudy. Addition of 5 g DMF turned the solution clear (13.78% solid). Size exclusion chromatography analysis showed the conversion was 87.7%, Mn = 12,300, Mw = 24,900 and Mw/Mn = 2. Contact angle data was reported in Table 2 below.

Example 22: C4MH/KF-2001/AA (60/30/10)

A 120ml bottle was charged with 2.99g C4MH (MW=723, 4.142 mmol), 1.50g KF-2001, 0.50 g acrylic acid (AA, MW =-72, 6.944 mmol), 25.76 g EtOAc and 0.055g VAZO-67. A magnetic stir bar was added, and the solution was bubbled with nitrogen for two minutes. The sealed bottle was put in a 70°C oil bath and polymerized with a magnetic stirring for 24 hours. The obtained solution was clear (16.40% solids). Size exclusion chromatography analysis showed the conversion was 84.8%, Mn = 6,420, Mw = 14,600 and Mw/Mn = 2.3. Contact angle data was reported in Table 2 below.

Table 2: Examples 19-22 and Comparative Example C4

Example	Formulation	Weight Ratio	Contact Angle (advancing/receding)	
			Water	Hexadecane
19	C4MH/KF2001	90/10	121/101	69/48
20	C4MH/KF2001	80/20	119/94	68/48
21	C4MH/KF2001	70/30	120/93	69/45
C4	MeFBSEA/KF-2001	70/30	112/77	34/32
22	C4MH/KF2001/AA	60/30/10	112/87	54/37

Examples 23-25 and Comparative Example C5

The copolymers of the invention were diluted to 5% solids with toluene. The solution was then coated with a #6 wire wound (Mayer) rod onto a 1.6 mil primed polyester terephthalate film. The coated film was attached to a fiberboard frame and dried for 15 minutes at 65° C.

The test method used to evaluate the release coatings was a modification of the industry standard peel adhesion test used to evaluate pressure sensitive adhesive coated materials. The standard test is described in detail in various publications of the American Society for Testing and Materials (ASTM), Philadelphia, Pa., and the Pressure Sensitive Tape Council (PSTC), Glenview, Ill. The modified standard method is described in detail below. The reference source of the standard test method is ASTM D3330-78 PSTC-1 (11/75)

2.54 cm by 15.24 cm strips of SCOTCH PERFORMANCE MASKING TAPE 233+ (available from 3M Company, St. Paul, MN) were rolled down onto the coated polyester film with a 2.04 kg rubber roller. The laminated samples were then aged 7 days at 22°C and 50% relative humidity or 16 hours at 65°C. Prior to testing, the heat-aged samples were equilibrated to 22°C and 50% relative humidity for 24 hours.

Release testing was conducted by mounting the masking tape/coated film laminate to the stage of an Instrumentors, Inc. slip/peel tester (model 3M90) with double coated tape. The force required to remove the masking tape at 180 degrees and 228.6 cm/minute was then measured. Tape re-adhesions were also measured by adhering the freshly peeled masking tape to a clean glass plate and measuring the peel adhesion in normal fashion using the same Instrumentors slip/peel tester indicated above, again peeling at 228.6 cm/min and at a 180 degree peel angle. The results of these peel tests are shown in Table 3

The backside of a strip of SCOTCH PERFORMANCE MASKING TAPE 233+ served as a control sample.

Table 3 Examples 23-25 and Comparative Example C5

Example	Formulation	7 days 22°C		16 hr at 65°C	
		Peel Force from Release Coating, g/cm	Re-adhesion Peel Force from Glass g/cm	Peel Force from Release Coating, g/cm	Re-adhesion Peel Force from Glass g/cm
23	C4MH/KF-2001, 80/20	36	462	51	364
24	C4MH/KF-2001, 70/30	19	485	36	430
25	C4MH/KF-2001/AA, 60/30/10	37	433	54	406
C5	PERFORMANCE MASKING TAPE 233+	220	527	385	422

Examples 26-28 and Comparative Example C6

The copolymers of the invention were coated and tested according to the methods described above with the exception that SCOTCH MAGIC TAPE 810 (Available from 3M Company) was used in place of SCOTCH PERFORMANCE MASKING TAPE 233+. The backside of a strip of SCOTCH MAGIC TAPE 810 served as a control sample. The results are shown in Table 4 below.

Table 4 Examples 26-28 and Comparative Example C6

Example	Formulation	7 days 22°C		16 hr at 65°C	
		Peel Force from Release Coating, g/cm	Re-adhesion Peel Force from Glass g/cm	Peel Force from Release Coating, g/cm	Re-adhesion Peel Force from Glass g/cm
26	C4MH/KF-2001, 80/20	95	147	88	115
27	C4MH/KF-2001, 70/30	79	141	81	95
28	C4MH/KF-2001/AA, 60/30/10	95	236	78	177
C6	SCOTCH MAGIC TAPE 810	79	201	166	131

Various modifications and alteration to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows.

We claim:

1. A copolymer comprising repeating units derived from at least one co-reactant comprising two or more mercapto functional groups, and repeating units derived from a fluoroacrylate comprising the reaction product of:

(a) at least one fluorochemical alcohol represented by the formula:

$$C_4F_9\text{-}X\text{-}OH$$

wherein:

$$X = -SO_2-\underset{|}{\overset{R}{N}}-C_mH_{2m}- \quad , \quad -CO-\overset{H}{\underset{|}{N}}-C_mH_{2m}- \quad ,$$

$$-\underset{H}{\overset{R_f}{C}}-C_yH_{2y}- \quad , \text{ or } \quad -C_qH_{2q}- \quad ,$$

R = hydrogen or an alkyl group of 1 to 4 carbon atoms,

m = 2 to 8,

$R_f = C_nF_{2n+1}$,

n = 1 to 5,

y = 0 to 6, and

q = 1 to 8;

(b) at least one unbranched symmetric diisocyanate; and

(c) at least one hydroxy-terminated alkyl (meth)acrylate or 2-fluoroacrylate monomer having 2 to about 30 carbon atoms in its alkylene portion.

2. The copolymer of claim 1 wherein X is

$$-SO_2-N(R)-C_mH_{2m}-$$

3. The copolymer of claim 1 wherein the fluorochemical alcohol is $C_4F_9SO_2NCH_3(CH_2)_2OH$.

4. The copolymer of claim 1 wherein the unbranched symmetric diisocyanate is 4,4'-diphenylmethane diisocyanate.

5. The copolymer of claim 1 wherein the hydroxy-terminated alkyl (meth)acrylate or 2-fluoroacrylate monomer is 2-hydroxyethyl acrylate.

6. The copolymer of claim 1 wherein the reaction product of (a), (b), and (c) is represented by the formula:

$$C_4F_9\text{-}X\text{-}OC(O)NH\text{-}A\text{-}HNC(O)O\text{-}(C_pH_{2p})(O)COC(R')=CH_2$$

wherein:

$X = -SO_2-N(R)-C_mH_{2m}-$, $-CO-N(H)-C_mH_{2m}-$,

$-CH(R_f)-C_yH_{2y}-$, or $-C_qH_{2q}-$,

R = H or an alkyl group of 1 to 4 carbon atoms,

m = 2 to 8,

$R_f = C_nF_{2n+1}$,

n = 1 to 5,

y = 0 to 6,

q = 1 to 8,

A = an unbranched symmetric alkylene group, arylene group, or aralkylene group,

p = 2 to 30, and

R′ = H, CH_3, or F.

7. The copolymer of claim 6 wherein reaction product of (a), (b), and (c) is $C_4F_9SO_2N(CH_3)C_2H_4OC(O)NHC_6H_4CH_2C_6H_4NHCOOCH_2CH_2OC(O)CH{=}CH_2$.

8. The copolymer of claim 1 wherein the co-reactant is represented by the formula:

$$(B)_n(Q\text{-}SH)_k$$

wherein:

B = a multivalent segment selected from the group consisting of $-CH-(\overset{|}{C}H)_b-CH-$, $-(CH_2)_b-$, $-(CH_2CH_2O)_b-$, $-(CHCH_3CH_2O)_b-$, $-(CH_2CH_2O)_b-(CHCH_3CH_2O)_b$, $-C_4H_8(OC_4H_8)_b-$, $-C_2H_4OC_2H_4OC_2H_4-$, $C_6H_5CR''_2C_6H_5-$, and $-(C_2H_4O)_bC_6H_5CR''_2C_6H_5(OC_2H_4)_b-$;

b = 1 to 100;

R″ = CH_3, CF_3, or H;

Q = $-(CH_2)_b-$, $-C(O)(CH_2)_a-$, or $-OC(O)(CH_2)_a-$;

a = 1 to 10;

n = 1 or greater; and

k = 2 or greater.

9. The copolymer of claim 1 wherein the co-reactant is represented by the formula:

$$HS(Q'-(B')_n-Q'S)_bH$$

wherein:

B′ = a multivalent segment selected from the group consisting of $-(CH_2)_b-$, $-(CH_2CH_2O)_b-$, $-(CHCH_3CH_2O)_b-$, $-(CH_2CH_2O)_b-(CHCH_3CH_2O)_b$, $-C_4H_8(OC_4H_8)_b-$, $-C_2H_4OC_2H_4OC_2H_4-$, $C_6H_5CR''_2C_6H_5-$, and $-(C_2H_4O)_bC_6H_5CR''_2C_6H_5(OC_2H_4)_b-$;

b = 1 to 100;

R″ = CH_3, CF_3, or H;

n = 1 or greater; and

Q′ = $-OC(O)CH_2CH_2-$ or $-C(O)CH_2CH_2-$.

10. The copolymer of claim 1 wherein the co-reactant is represented by the formula:

$$(R_{f'})_n(Q''-SH)_k$$

wherein:

$R_{f'}$ = a multivalent segment comprising a fluorinated alkyl or alkylene group;

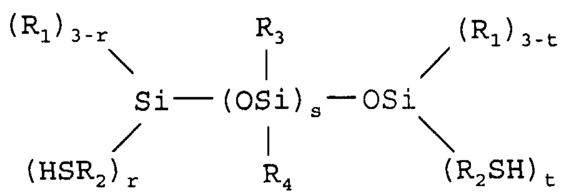
Q″ = $-C(O)NH(CH_2)_b-$ or $-OC(O)(CH_2)_b-$;

b = 2 to 12;

n = 1 or greater; and

k = 2 or greater.

11. The copolymer of claim 1 wherein the co-reactant is represented by the formula:



wherein:

R_1 = monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, hydroxyl, hydrogen, and fluoroalkyl;

R_2 = divalent linking groups which can independently be the same or different;

R_3 = monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, hydroxyl, hydrogen, fluoroalkyl, and -ZSH;

R_4 = monovalent moieties which can independently be the same or different and are selected from the group consisting of alkyl, aryl, alkaryl, alkoxy, alkylamino, hydroxyl, hydrogen, fluoroalkyl, and -ZSH;

wherein:

Z = a divalent linking group;

r = 0 to 3;

s = 10 or greater; and

t = 0 to 3;

wherein at least two of the following are true:

t = at least 1

r = at least 1

R_3 comprises at least one -ZSH moiety; and

R_4 comprises at least one -ZSH moiety.

12. The copolymer of claim 1 further comprising repeating units derived from at least one comonomer.

13. The copolymer of claim 12 wherein the comonomer is a (meth)acrylate or fluoro(meth)acrylate.

14. A composition comprising a solvent and the copolymer of claim 1.

15. The composition of claim 14 wherein the composition is a release coating composition.

16. An article comprising a substrate having one or more surfaces coated with the composition of claim 14.

17. The article of claim 16 wherein the substrate comprises a material selected from the group consisting of polyethylene terephthalate, polyolefins, and polyolefin coated paper.

18. The article of claim 16 wherein the substrate is a fibrous substrate.

19. The article of claim 16 wherein the substrate is a non-woven substrate.

20. An article comprising a substrate having one or more surfaces coated with the composition of claim 15.

21. The article of claim 20 wherein the article is a release liner.

INTERNATIONAL SEARCH REPORT

International application No
/US2005/045758

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F20/24 C08G75/26 C08F220/38
ADD. C08G18/00

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)
C08F C08G

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, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO 2005/066224 A (3M INNOVATIVE PROPERTIES COMPANY) 21 July 2005 (2005-07-21) claims; examples	1
A	US 5 144 056 A (LINA ET AL) 1 September 1992 (1992-09-01) claims	1
A	US 5 446 118 A (SHEN ET AL) 29 August 1995 (1995-08-29) the whole document	1

☐ Further documents are listed in the continuation of Box C.

☒ 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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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	Date of mailing of the international search report
12 April 2006	26/04/2006

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INTERNATIONAL SEARCH REPORT

Information on patent family members

ıtional application No
/US2005/045758

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2005066224	A	21-07-2005	NONE	
US 5144056	A	01-09-1992	NONE	
US 5446118	A	29-08-1995	NONE	