



(86) Date de dépôt PCT/PCT Filing Date: 2005/12/29
(87) Date publication PCT/PCT Publication Date: 2006/07/13
(45) Date de délivrance/Issue Date: 2014/04/08
(85) Entrée phase nationale/National Entry: 2007/06/26
(86) N° demande PCT/PCT Application No.: US 2005/047350
(87) N° publication PCT/PCT Publication No.: 2006/074033
(30) Priorité/Priority: 2004/12/30 (US60/640,471)

(51) Cl.Int./Int.Cl. *C09D 133/04* (2006.01),
C09D 133/16 (2006.01)
(72) Inventeurs/Inventors:
CHANG, CHENG-CHUNG, US;
QIU, ZAI-MING, US;
JING, NAIYONG, US;
ELSBERND, CHERYL L. S., US
(73) Propriétaire/Owner:
3M INNOVATIVE PROPERTIES COMPANY, US
(74) Agent: SMART & BIGGAR

(54) Titre : COMPOSITIONS FLUOREES RESISTANTES AUX TACHES
(54) Title: STAIN-RESISTANT FLUORO-CHEMICAL COMPOSITIONS

(57) **Abrégé/Abstract:**

The invention features a coating composition that comprises a non-urethane acrylate or methacrylate compound in combination with a fluorochemical. Typically, the non-urethane (meth)acrylate is an aliphatic or aromatic (meth)acrylate compound and the fluorochemical typically comprises a monofunctional (per)fluoropolyether (meth)acrylate compound. The coating compositions can provide a protective topcoat layer to a variety of substrates, including wood and vinyl.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 July 2006 (13.07.2006)

PCT

(10) International Publication Number
WO 2006/074033 A1

(51) International Patent Classification:

C09D 133/04 (2006.01) *C09D 133/16* (2006.01)

(21) International Application Number:

PCT/US2005/047350

(22) International Filing Date:

29 December 2005 (29.12.2005)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

60/640,471 30 December 2004 (30.12.2004) US

(71) Applicant (for all designated States except US): **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: **CHANG, Cheng-chung**; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **QIU, Zai-Ming**; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **JING, Naiyong**; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **ELSBERND, Cheryl, L., S.**; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: **EDMAN, Sean, J.**, et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: STAIN-RESISTANT FLUOROCHEMICAL COMPOSITIONS

(57) Abstract: The invention features a coating composition that comprises a non-urethane acrylate or methacrylate compound in combination with a fluorochemical. Typically, the non-urethane (meth)acrylate is an aliphatic or aromatic (meth)acrylate compound and the fluorochemical typically comprises a monofunctional (per)fluoropolyether (meth)acrylate compound. The coating compositions can provide a protective topcoat layer to a variety of substrates, including wood and vinyl.

WO 2006/074033 A1

60557-7763

STAIN-RESISTANT FLUOROCHEMICAL COMPOSITIONS

Field of the Invention

5 The present invention relates to coating compositions. More specifically, the invention relates to coating compositions comprising a non-urethane (meth)acryl compound and a fluorochemical.

Background

10 Certain commonly used materials, such as optical displays, textiles, metals, stone, wood, leather, etc, are susceptible to scratches, abrasion, and soiling during routine use. In some instances, protective films or coatings may be applied to the surfaces of these materials in order to provide protection and enhance durability, performance, and appearance.

15 UV-curable systems based on the polymerization of an acrylic resin, such as a urethane (meth)acrylate compound, have been used as protective coating compositions for a variety of surfaces. In some instances, it may be desirable to modify or enhance the performance of these coatings by introducing particular structures, such as fluorinated groups, into the polymeric network. Fluorinated
20 groups can be incorporated into these compositions through the copolymerization of the acrylic resin with a low amount (<1%, w/w) of a fluorinated monomer, such as a fluorinated acrylate compound.

 Although various protective coatings have been developed using fluorinated polymers, a need remains for improved coating compositions with better
25 performance and longevity than existing systems.

Summary of Invention

It is often desirable for a protective topcoat layer to be stain-resistant in order to improve the look and appearance of the coated surface. One approach for providing stain resistance is to incorporate a fluorochemical compound into the topcoat composition. We found that, under certain circumstances, ambient light can degrade urethane-containing topcoats thus reducing the stain resistance of the fluorochemical additives. We have also found that certain stains and dyes have a high affinity for the urethane-groups present in many of the acrylate materials that are typically used in protective surface coating compositions, thereby hindering the improved stain resistance provided by the fluorochemical.

Accordingly, the present invention features a coating composition that comprises a non-urethane acryl or methacryl compound in combination with a fluorochemical. Typically, the non-urethane (meth)acryl compound is an aliphatic or aromatic (meth)acryl compound. The fluorochemical typically comprises a monofunctional (per)fluoropolyether (meth)acryl compound or a $C_8F_{17}C_2H_4O_2CCH=CH_2$ telomer. In other embodiments, the fluorochemical may be $C_4F_9SO_2NMrC_2H_4OC(O)CRCH_2$, $C_4F_9CH_2CH_2OC(O)CH=CH_2$, or $C_6F_{13}CH_2CH_2OC(O)CRCH_2$ wherein R is H, methyl or other lower alkyl.

In yet another embodiment, the fluorochemical may comprise a compound represented by the structure $C_pF_{2p+1}SO_2(R)C_2H_4O_2CCH=CH_2$, where R is a O, to C_6 alkyl group.

In yet another embodiment, the fluorochemical may comprise a compound represented by the formula $C_pF_{2p+1}C_2H_4O_2CCH=CH_2$, where p is a 3, to 20 and preferably averages between 6 and 8.

In some embodiments of the invention, the coating composition may comprise a combination of a urethane (meth)acryl compound and a non-urethane (meth)acryl compound. Typically, the coating composition contains less than 50 percent, more typically less than 30 percent, most typically less than 10 percent by weight of a urethane-containing (meth)acrylate. In other embodiments, the coating composition is substantially free of urethane (meth)acrylate.

60557-7763

The compositions of the invention are typically photopolymerizable and thus may further include a photoinitiator. The compositions may be coated onto a substrate and then polymerized, for example, by exposure to UV radiation. The reaction product of the non-urethane (meth)acryl compound and the fluorochemical monomer(s) forms a stain-
5 resistance protective topcoat on the substrate that maintains its stain resistance even after prolonged exposure to ambient light conditions.

The coating composition of the invention may be used to provide a protective topcoat on a variety of substrate surfaces, such as, for example, wood and vinyl.

According to another aspect of the present invention, there is provided a
10 coating composition comprising at least one non-urethane aliphatic (meth)acryl compound that is a monomer or oligomer having at least two acryl or methacryl groups and is not a fluorochemical; and at least one polymerizable fluorochemical, which comprises a (per)fluoropolyether (meth)acryl compound.

According to still another aspect of the present invention, there is provided a
15 coating composition comprising at least one non-urethane (meth)acryl compound that is a monomer or oligomer having at least two acryl or methacryl groups and is not a fluorochemical; and at least one monoterminated (per)fluoropolyether (meth)acryl compound.

According to yet another aspect of the present invention, there is provided a method of protecting a substrate surface, the method comprising providing a surface layer on
20 the substrate, wherein the surface layer comprises the reaction product of a composition comprising at least one non-urethane aliphatic (meth)acryl compound that is a monomer or oligomer having at least two acryl or methacryl groups and is not a fluorochemical; and at least one polymerizable fluorochemical, which comprises a (per)fluoropolyether (meth)acryl compound.

60557-7763

According to a further aspect of the present invention, there is provided a method of protecting a substrate surface, the method comprising providing a surface layer on the substrate, wherein the surface layer comprises the reaction product of a composition comprising at least one non-urethane (meth)acryl compound that is a monomer or oligomer
5 having at least two acryl or methacryl groups and is not a fluorochemical; and at least one monoterminated (per)fluoropolyether (meth)acryl compound.

According to yet a further aspect of the present invention, there is provided an article comprising a substrate and surface layer, wherein the surface layer comprises the reaction product of a composition comprising at least one non-urethane aliphatic (meth)acryl
10 compound that is a monomer or oligomer having at least two acryl or methacryl groups and is not a fluorochemical; and at least one polymerizable fluorochemical, which comprises a (per)fluoropolyether (meth)acryl compound.

According to still a further aspect of the present invention, there is provided an article comprising a substrate and surface layer, wherein the surface layer comprises the
15 reaction product of a composition comprising at least one non-urethane (meth)acryl compound that is a monomer or oligomer having at least two acryl or methacryl groups and is not a fluorochemical; and at least one monoterminated (per)fluoropolyether (meth)acryl compound.

Other features and advantages of the present invention will be apparent from
20 the following detailed description thereof, and from the claims.

60557-7763

Definitions

As used herein, the term "non-urethane (meth)acryl compound" means a monomer or oligomer having at least one, preferably two or more acryl or methacryl groups without any urethane groups. The term "(meth)acryl" includes both acryl
5 and methacryl compounds.

By "aliphatic (meth)acryl compound" is meant a monomer or oligomer having at least one, preferably two or more acryl or methacryl groups which are linked by an aliphatic segment that is acyclic or cyclic with one or more optional heteroatoms independently selected from the group consisting of O, N, and S.

10 By "aromatic (meth)acryl" is meant a monomer or oligomer having at least one, preferably two or more acryl or methacryl groups and at least one or more aromatic rings.

By "(per)fluoropolyether (meth)acryl compound" is meant a compound comprising at least one (per)fluoropolyether group and at least one (meth)acryl
15 group, which are typically joined by a linking group. Typically, the (meth)acryl group is a (meth)acrylate group optionally substituted with hydrogen or fluorine. In at least some embodiments, acrylate groups are preferred. As used herein, (meth)acryl groups includes those class of compounds such as (meth)acrylate

60557-7763

esters, (meth)acrylamides, and N-alkyl (meth)acrylamides, optionally substituted with hydrogen or fluorine. Preferably, the (meth)acryl group is a (meth)acrylate group optionally substituted with hydrogen or fluorine. In at least some embodiments, acrylate groups are preferred.

5 By "monoterminated (per)fluoropolyether (meth)acryl compound" is meant a compound that can be represented by the following Formula I:



wherein R' is F, CF₃, C₂F₅, or C₃F₇; X is a (per)fluoropolyether group; Q is -C(O)NH(CH₂)_a or -(CH₂)_bO(CH₂)_a wherein a is 1-5 and b is 1-5, preferably 1; and
 10 R'' is -OC(O)CH=CH₂, -C(O)NH(C₂H₄O)_b(CH₂)_a, -OC(O)CMe=CH₂,
 -OC(O)NHCH₂CH₂OC(O)CMe=CH₂, -CH(OC(O)CH=CH₂)₂,
 -CH(OC(O)CMe=CH₂)₂, -N(CH₂CH₂OC(O)CH=CH₂)₂,
 -N(CH₂CH₂OC(O)CMe=CH₂)₂, -N(-C(O)CH=CH₂)(-CH₂CH₂OC(O)CH=CH₂),
 -NMeCH₂CH₂CO₂CH₂CEt(CH₂OC(O)CH=CH₂)₂ or
 15 -O-triurethane(NHCO₂CH₂CH₂OC(O)CH=CH₂)₂

or a compound that can be represented by the following Formula II



20

wherein R_f is a monofunctional terminal group selected from the group consisting of (per)fluoropolyether groups; X and W are optional linking groups, which may or may not be present and each W may be the same or different, and R_A is a (meth)acryl group or -C(O)CF=CH₂; and y is 1 or 2.

25 By "hardcoat" or "topcoat" is meant a crosslinkable or crosslinked composition that optionally comprises inorganic articles.

As used herein "wt-%" refers to weight percent solids based on the coating composition or reaction product thereof unless specified otherwise.

60557-7763

The recitation herein of numerical ranges by endpoints includes all numbers subsumed within that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4 and 5).

As used in this specification and the appended claims, the singular forms “a”, “an”, and “the” also include the plural forms unless the context clearly dictates otherwise. Thus, for example, reference to a composition containing “a compound”
5 includes a mixture of two or more compounds. In addition, the term “or” is generally used in the sense of “and/or” unless the context clearly dictates otherwise.

Unless otherwise indicated, all numbers expressing quantities of ingredients, measurement of properties such as surface energy, contact angles, and so forth used
10 in the instant specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that can vary depending upon the desired properties sought by those skilled in the art utilizing the teachings of the present invention. At the very
15 least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth
20 in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors and uncertainties necessarily resulting from the standard deviations found in their respective testing measurements.

25

Detailed Description

The present invention features polymerizable coating compositions comprising at least one non-urethane (meth)acryl compound and at least one fluorochemical. The non-urethane (meth)acryl compound can be an aliphatic or aromatic (meth)acryl compound and is typically not a fluorochemical. In some

60557-7763

embodiments, the fluorochemical component of the composition is a monoterminated (per)fluoropolyether (meth)acryl compound.

The coating compositions of the invention may be applied to the surface of a substrate, such as, for example, vinyl or wood, and then polymerized to provide a stain-resistant topcoat. This protective layer generally has good light stability and can be exposed to fluorescent lighting for prolonged periods of time without undue deterioration of its stain-resistance properties.

(Meth)acryl monomers and oligomers

The non-urethane (meth)acryl compound used in the coating compositions of the present invention can be any monomer or oligomer having at least two acryl or methacryl groups without any urethane groups. Examples of suitable non-urethane (meth)acryl compounds include, but are not limited to, tripropyleneglycol diacrylate available under the trade designation "SR306", trimethylolpropane ethoxylated (3) triacrylate available under the trade designation "SR454", and trimethylolpropane propoxylated (3) triacrylate, available under the trade designation "SR492", bis-phenol A ethoxylated diacrylate, available under the trade designation "SR349", all from Sartomer Company, Exton, PA.

The non-urethane (meth)acryl compound may optionally be blended with one or more additional poly(meth)acrylates, including urethane (meth)acryl compounds and/or other non-urethane (meth)acryl compounds. For example, the non-urethane (meth)acryl compound may be combined with a urethane-containing (meth)acryl compound in a weight ratio of 9 to 1, 5 to 1, 4 to 1, 3 to 1, or 1 to 1 (non-urethane to urethane (meth)acrylate)). In blended formulations, typically the compositions comprise less than about 50%, more typically less than 30%, and most typically less than 10% by weight of a urethane-containing (meth)acryl compound.

Useful additional poly(meth)acrylates include, for example, di(meth)acryl containing compounds such as 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol monoacrylate monomethacrylate, ethylene glycol diacrylate, alkoxylated aliphatic diacrylate,

alkoxylated cyclohexane dimethanol diacrylate, alkoxylated hexanediol diacrylate, alkoxylated neopentyl glycol diacrylate, caprolactone modified neopentylglycol hydroxypivalate diacrylate, caprolactone modified neopentylglycol hydroxypivalate diacrylate, cyclohexanedimethanol diacrylate, diethylene glycol diacrylate, 5 dipropylene glycol diacrylate, ethoxylated (10) bisphenol A diacrylate, ethoxylated (3) bisphenol A diacrylate, ethoxylated (30) bisphenol A diacrylate, ethoxylated (4) bisphenol A diacrylate, hydroxypivalaldehyde modified trimethylolpropane diacrylate, neopentyl glycol diacrylate, polyethylene glycol (200) diacrylate, polyethylene glycol (400) diacrylate, polyethylene glycol (600) diacrylate, 10 propoxylated neopentyl glycol diacrylate, tetraethylene glycol diacrylate, tricyclodecanedimethanol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate; tri(meth)acryl containing compounds such as glycerol triacrylate, trimethylolpropane triacrylate, ethoxylated triacrylates (e.g., ethoxylated (3) trimethylolpropane triacrylate, ethoxylated (6) trimethylolpropane triacrylate, 15 ethoxylated (9) trimethylolpropane triacrylate, ethoxylated (20) trimethylolpropane triacrylate), pentaerythritol triacrylate, propoxylated triacrylates (e.g., propoxylated (3) glyceryl triacrylate, propoxylated (5.5) glyceryl triacrylate, propoxylated (3) trimethylolpropane triacrylate, propoxylated (6) trimethylolpropane triacrylate), trimethylolpropane triacrylate, tris(2-hydroxyethyl)isocyanurate triacrylate; higher 20 functionality (meth)acryl containing compounds such as ditrimethylolpropane tetraacrylate, dipentaerythritol pentaacrylate, ethoxylated (4) pentaerythritol tetraacrylate, pentaerythritol tetraacrylate, caprolactone modified dipentaerythritol hexaacrylate; oligomeric (meth)acryl compounds such as, for example, polyester acrylates, epoxy acrylates; polyacrylamide analogues of the foregoing; and 25 combinations thereof. Such compounds are widely available from vendors such as, for example, Sartomer Company, Exton, PA; UCB Chemicals Corporation, Smyrna, GA; and Aldrich Chemical Company, Milwaukee, WI. Additional useful (meth)acrylate materials include hydantoin moiety-containing poly(meth)acrylates, for example, as described in U.S. 4,262,072 (Wendling et al.).

60557-7763

Fluorochemicals

The coating compositions of the invention also include a fluorochemical component, which may comprise a single (per)fluoropolyether (meth)acryl compound, or various combinations of monofunctional (per)fluoropolyether (meth)acryl compound(s), combinations of polyfunctional (per)fluoropolyether (meth)acryl compounds, as well as combinations of one or more monofunctional (per)fluoropolyether (meth)acryl compound(s) in combination with one or more polyfunctional (per)fluoropolyether (meth)acryl compounds.

Typically the (per)fluoropolyether (meth)acryl component comprises less than 0.5 % of the total coating composition, and the non-fluorinated (meth)acryl component (e.g., the non-urethane (meth)acrylate or poly(meth)acrylate blend) comprises 99.5% or greater and more preferably 99.9 % or greater of the total composition. The total amount of (per)fluoropolyether (meth)acryl compound in the coating composition that is polymerized to form the topcoat is typically less than 0.5 wt-% (e.g. less than about 0.1 wt-%, 0.2 wt-%, 0.3 wt-%, and 0.4 wt-%).

A variety of (per)fluoropolyether (meth)acryl compounds may be employed in the coating compositions of the invention. In some implementations of the invention, it is preferred to use a monoterminated (per)fluoropolyether (meth)acrylate compound represented by the following Formula I:



wherein R' is F, CF₃, C₂F₅, or C₃F₇; X is a (per)fluoropolyether group; Q is -C(O)NH(CH₂)_a or -(CH₂)_bO(CH₂)_a wherein a is 1-5 and b is 1; and R'' is -OC(O)CH=CH₂, -OC(O)CMe=CH₂, -OC(O)NHCH₂CH₂OC(O)CMe=CH₂, -CH(OC(O)CH=CH₂)₂, -CH(OC(O)CMe=CH₂)₂, -N(CH₂CH₂OC(O)CH=CH₂)₂, -N(CH₂CH₂OC(O)CMe=CH₂)₂, -N(-C(O)CH=CH₂)(-CH₂CH₂OC(O)CH=CH₂), -NMeCH₂CH₂CO₂CH₂CEt(CH₂OC(O)CH=CH₂)₂ or -O-triurethane(NHCO₂CH₂CH₂OC(O)CH=CH₂)₂.

Other suitable perfluoropolyether (meth)acryl compounds that may be used in the coating composition include those represented by the following Formula II:



wherein R_f is (per)fluoropolyether group; W is a linking group; and R_A is a (meth)acryl group or $-\text{COCF}=\text{CH}_2$; and w is 1 or 2.

The perfluoropolyether group R_f can be linear, branched, cyclic, or combinations thereof and can be saturated or unsaturated. The perfluoropolyether has at least two catenated oxygen heteroatoms. Exemplary perfluoropolyethers include, but are not limited to, those that have perfluorinated repeating units selected from the group of $-(\text{C}_p\text{F}_{2p})-$, $-(\text{C}_p\text{F}_{2p}\text{O})-$, $-(\text{CF}(\text{Z}))-$, $-(\text{CF}(\text{Z})\text{O})-$, $-(\text{CF}(\text{Z})\text{C}_p\text{F}_{2p}\text{O})-$, $-(\text{C}_p\text{F}_{2p}\text{CF}(\text{Z})\text{O})-$, $-(\text{CF}_2\text{CF}(\text{Z})\text{O})-$, or combinations thereof. In these repeating units, p is typically an integer of 1 to 10. In some embodiments, p is an integer of 1 to 8, 1 to 6, 1 to 4, or 1 to 3. The group Z is a perfluoroalkyl group, perfluoroether group, perfluoropolyether, or a perfluoroalkoxy group, all of which can be linear, branched, or cyclic. The Z group typically has no more than 12 carbon atoms, no more than 10 carbon atoms, or no more than 9 carbon atoms, no more than 4 carbon atoms, no more than 3 carbon atoms, no more than 2 carbon atoms, or no more than 1 carbon atom. In some embodiments, the Z group can have no more than 4, no more than 3, no more than 2, no more than 1, or no oxygen atoms. In these perfluoropolyether structures, the different repeat units can be distributed randomly along the chain.

In certain embodiments, R_f can be monovalent or divalent. Where R_f is monovalent, the terminal groups can be $(\text{C}_p\text{F}_{2p+1})-$, $(\text{C}_p\text{F}_{2p+1}\text{O})-$, $(\text{X}'\text{C}_p\text{F}_{2p}\text{O})-$, or $(\text{X}'\text{C}_p\text{F}_{2p+1})-$ where X' is hydrogen, chlorine, or bromine and p is an integer of 1 to 10. In some embodiments of monovalent R_f groups, the terminal group is perfluorinated and p is an integer of 1 to 10, 1 to 8, 1 to 6, 1 to 4, or 1 to 3. Exemplary monovalent R_f groups include $\text{CF}_3\text{O}(\text{C}_2\text{F}_4\text{O})_n\text{CF}_2-$, and

$C_3F_7O(CF(CF_3)CF_2O)_nCF(CF_3)-$ wherein n has an average value of 0 to 50, 1 to 50, 3 to 30, 3 to 15, or 3 to 10.

Suitable structures for divalent R_f groups include, but are not limited to, $-CF_2O(CF_2O)_q(C_2F_4O)_nCF_2-$, $-(CF_2)_3O(C_4F_8O)_n(CF_2)_3-$, $-CF_2O(C_2F_4O)_nCF_2-$, and $-CF(CF_3)(OCF_2CF(CF_3))_sOC_tF_{2t}O(CF(CF_3)CF_2O)_nCF(CF_3)-$, wherein q has an average value of 0 to 50, 1 to 50, 3 to 30, 3 to 15, or 3 to 10; n has an average value of 0 to 50, 3 to 30, 3 to 15, or 3 to 10; s has an average value of 0 to 50, 1 to 50, 3 to 30, 3 to 15, or 3 to 10; the sum $(n + s)$ has an average value of 0 to 50 or 4 to 40; the sum $(q + n)$ is greater than 0; and t is an integer of 2 to 6.

As synthesized, compounds according to Formula II typically include a mixture of R_f groups. The average structure is the structure averaged over the mixture components. The values of q , n , and s in these average structures can vary, as long as the compound has a number average molecular weight of at least about 400. Compounds of Formula I often have a molecular weight (number average) of 400 to 5000, 800 to 4000, or 1000 to 3000.

The linking group W between the perfluoropolyether segment and (meth)acryl or $-COCF=CH_2$ endgroup includes a divalent group selected from an alkylene, arylene, heteroalkylene, or combinations thereof and an optional divalent group selected from carbonyl, carbonyloxy, carbonylimino, sulfonamido, or combinations thereof. W can be unsubstituted or substituted with an alkyl, aryl, halo, or combinations thereof. The W group typically has no more than 30 carbon atoms. In some compounds, the W group has no more than 20 carbon atoms, no more than 10 carbon atoms, no more than 6 carbon atoms, or no more than 4 carbon atoms. For example, W can be an alkylene, an alkylene substituted with an aryl group, or an alkylene in combination with an arylene.

The perfluoropolyether acrylate compounds (e.g. of Formula II) can be synthesized by known techniques such as described in U.S. Patent Nos. 3,553,179 and 3,544,537.

60557-7763

Alternatively or in addition to at least one monofunctional (per)fluoropolyether acrylate compound, the (per)fluoropolyether acrylate compound may be polyfunctional, having two or more (meth)acryl groups such as (meth)acrylate groups.

5 One type of preferred polyfunctional perfluoropolyether acrylate compounds comprises at least one terminal $F(CF(CF_3)CF_2O)_aCF(CF_3)-$ group wherein a averages 4 to 15. In some embodiments, the polyfunctional perfluoropolyether acrylates comprises a terminal HFPO- group. As used herein "HFPO-" refers to the structure $F(CF(CF_3)CF_2O)_aCF(CF_3)-$ wherein a averages 6 to 7 (e.g. 6.3).

10 Exemplary compounds include for example

HFPO- $C(O)N(H)C(CH_2OC(O)CH=CH_2)_2CH_2CH_3$, and
 HFPO- $C(O)N(H)C(CH_2OC(O)CH=CH_2)_2H$.

15 The perfluoropolyether acrylate comprising at least one terminal HFPO- group and at least two (meth)acryl groups can be prepared in a two step process. The first step is by reaction of poly(hexafluoropropylene oxide) esters, such as HFPO- $C(O)OCH_3$ or acid halides HFPO- $C(O)F$, with materials containing at least 3 alcohol or primary or secondary amino groups to produce HFPO- amide polyols or
 20 polyamines, HFPO- ester polyols or polyamines, or HFPO- amides, or HFPO- esters with mixed amine and alcohol groups. The second is (meth)acrylation of the alcohol and/or amine groups with (meth)acryloyl halides, (meth)acrylic anhydrides or (meth)acrylic acid. Exemplary syntheses thereof are set forth in the examples.

In other embodiments, the (per)fluoropolyether acrylate compound may be a
 25 compound preparable by Michael-type addition of a reactive (per)fluoropolyether with a poly(meth)acrylate, such as the adduct of HFPO-
 $C(O)N(H)CH_2CH_2CH_2N(H)CH_3$ with trimethylolpropane triacrylate (TMPTA). Such (per)fluoropolyether acrylate compounds are further described in
 WO 2005/113,642.

The coating composition described herein may comprise a monofunctional fluorinated compound that can be represented by the following Formula III:



wherein R_A is as previously described (i.e. a (meth)acrylate or a $CH_2=CFCO$ group); R^{F1} is a fluoroalkylene group comprising 2 to 7 carbon atoms; and W' is a linking group. R_A of Formula III is preferably an acrylate group. R^{F1} may be a linear or branched perfluorinated alkylene moiety.

Other suitable perfluoropolyether monomers are described by Larson, et al., in U.S. Patent No. 4,614,667 at column 4, lines 24-55, cited portion.

The monofunctional fluorinated compounds of Formula III can be synthesized by known techniques. An exemplary monofunctional fluorinated compound of Formula III, ω -hydro 2,2,3,3,4,4,5,5-octafluoropentyl acrylate ($H-C_4F_8-CH_2O-C(O)-CH=CH_2$), is commercially available from Oakwood Products, West Columbia, S.C. Monofunctional fluorinated compounds of Formula III having the formula $H(CF_2)_nCH_2OCOCH=CH_2$ where $n=2, 4$, and 6 as well as $CF_3CHFCF_2CH_2OCOC(CH_3)CH_2$ (2,2,3,4,4,4 hexafluorobutyl methacrylate) are commercially available from Lancaster Chemical, Windham, NH.

The inclusion of one or more monofunctional fluorinated compounds of Formula III can further improve the compatibility of at least certain perfluoropolyether acrylate compounds with the poly(meth)acrylate crosslinking agents. This aspect is particularly advantageous for embodiments wherein a monofunctional perfluoropolyether acrylate compound is employed such as $HFPO-C(O)N(H)CH_2CH_2OC(O)CH=CH_2$.

The amount of monofunctional fluorinated compound(s) of Formula III utilized in the coating composition of the invention can vary depending on the kind and amount of (per)fluoropolyether acrylate compound employed. Typically, the amount ranges from about half the amount of the (per)fluoropolyether acrylate

60557-7763

compound to about twice the amount of the (per)fluoropolyether acrylate compound.

Initiators for polymerization of the coating composition

5 To facilitate curing, polymerizable compositions according to the present invention may further comprise at least one free-radical thermal initiator and/or photoinitiator. Typically, if such an initiator and/or photoinitiator are present, it comprises less than about 10 percent by weight, more typically less than about 5 percent of the polymerizable composition, based on the total weight of the
10 polymerizable composition. Free-radical curing techniques are well known in the art and include, for example, thermal curing methods as well as radiation curing methods such as electron beam or ultraviolet radiation. Further details concerning free radical thermal and photopolymerization techniques may be found in, for example, U.S. Pat. Nos. 4,654,233 (Grant et al.); 4,855,184 (Klun et al.); and
15 6,224,949 (Wright et al.).

Useful free-radical thermal initiators include, for example, azo, peroxide, persulfate, and redox initiators, and combinations thereof.

Useful free-radical photoinitiators include, for example, those known as useful in the UV cure of acrylate polymers. Such initiators include benzophenone
20 and its derivatives; benzoin, alpha-methylbenzoin, alpha-phenylbenzoin, alpha-allylbenzoin, alpha-benzylbenzoin; benzoin ethers such as benzil dimethyl ketal (commercially available under the trade designation "IRGACURE 651"TM from Ciba Specialty Chemicals Corporation of Tarrytown, New York), benzoin methyl ether, benzoin ethyl ether, benzoin n-butyl ether; acetophenone and its derivatives such as
25 2-hydroxy-2-methyl-1-phenyl-1-propanone (commercially available under the trade designation "DAROCUR 1173"TM from Ciba Specialty Chemicals Corporation) and 1-hydroxycyclohexyl phenyl ketone (commercially available under the trade designation "IRGACURE 184"TM, also from Ciba Specialty Chemicals Corporation); 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone commercially
30 available under the trade designation "IRGACURE 907"TM, also from Ciba Specialty

60557-7763

Chemicals Corporation); 2-benzyl-2- (dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone commercially available under the trade designation "IRGACURE 369"TM from Ciba Specialty Chemicals Corporation); aromatic ketones such as benzophenone and its derivatives and anthraquinone and its derivatives; onium salts such as diazonium salts, iodonium salts, sulfonium salts; titanium complexes such as, for example, that which is commercially available under the trade designation "CGI 784 DC"TM, also from Ciba Specialty Chemicals Corporation); halomethylnitrobenzenes; and mono- and bis-acylphosphines such as those available from Ciba Specialty Chemicals Corporation under the trade designations "IRGACURE 1700"TM, "IRGACURE 1800"TM, "IRGACURE 1850"TM, "IRGACURE 819"TM, "IRGACURE 2005"TM, "IRGACURE 2010"TM, "IRGACURE 2020"TM and "DAROCUR 4265"TM. Combinations of two or more photoinitiators may be used. Further, sensitizers such as 2-isopropyl thioxanthone, commercially available from First Chemical Corporation, Pascagoula, MS, may be used in conjunction with photoinitiator(s) such as "IRGACURE 369"TM.

Other reactive and non-reactive ingredients

A variety of inorganic oxide particles can be used in the coating compositions. The particles are typically substantially spherical in shape and relatively uniform in size. The particles can have a substantially monodisperse size distribution or a polymodal distribution obtained by blending two or more substantially monodisperse distributions. The inorganic oxide particles are typically non-aggregated (substantially discrete), as aggregation can result in precipitation of the inorganic oxide particles or gelation of the hardcoat. The inorganic oxide particles are typically colloidal in size, having an average particle diameter of about 0.001 to about 0.2 micrometers, less than about 0.05 micrometers, and less than about 0.03 micrometers. These size ranges facilitate dispersion of the inorganic oxide particles into the binder resin and provide ceramers with desirable surface properties and optical clarity. The average particle size of the inorganic oxide particles can be measured using transmission electron

microscopy to count the number of inorganic oxide particles of a given diameter.

Inorganic oxide particles include colloidal silica, colloidal titania, colloidal alumina, colloidal zirconia, colloidal vanadia, colloidal chromia, colloidal iron oxide, colloidal antimony oxide, colloidal tin oxide, and mixtures thereof. The

5 inorganic oxide particles can consist essentially of or consist of a single oxide such as silica, or can comprise a combination of oxides, such as silica and aluminum oxide, or a core of an oxide of one type (or a core of a material other than a metal oxide) on which is deposited an oxide of another type. Silica is a common

10 inorganic particle. The inorganic oxide particles are often provided in the form of a sol containing a colloidal dispersion of inorganic oxide particles in liquid media.

The sol can be prepared using a variety of techniques and in a variety of forms including hydrosols (where water serves as the liquid medium), organosols (where organic liquids so serve), and mixed sols (where the liquid medium contains both water and an organic liquid), e.g., as described in U.S. Pat. Nos. 5,648,407 (Goetz et al.); 5,677,050 (Bilkadi et al.) and 6,299,799 (Craig et al.). Aqueous sols (e.g. of 15 amorphous silica) can be employed. Sols generally contain at least 2 wt-%, at least 10 wt-%, at least 15 wt-%, at least 25 wt-%, and often at least 35 wt-% colloidal inorganic oxide particles based on the total weight of the sol. The amount of colloidal inorganic oxide particle is typically no more than 50 wt-% (e.g. 45 wt-%).

20 The surface of the inorganic particles can be "acrylate functionalized" as described in Bilkadi et al. The sols can also be matched to the pH of the binder, and can contain counterions or water-soluble compounds (e.g., sodium aluminate).

The coating compositions can conveniently be prepared by mixing an aqueous sol of inorganic oxide particles with a free-radically curable binder precursor (e.g., one or more free-radically curable monomers, oligomers or 25 polymers that can participate in a crosslinking reaction upon exposure to a suitable source of curing energy). The resulting composition usually is dried before it is applied, in order to remove substantially all of the water. This drying step is sometimes referred to as "stripping". An organic solvent can be added to the 30 resulting ceramer composition before it is applied, in order to impart improved

viscosity characteristics and assist in coating the ceramer composition onto the substrate. After coating, the ceramer composition can be dried to remove any added solvent, and then can be at least partially hardened by exposing the dried composition to a suitable source of energy in order to bring about at least partial
5 cure of the free-radically curable binder precursor.

The coating composition described herein may further various other reactive and non-reactive ingredients. For example the composition may comprise polymerizable (meth)acryl compounds with alkyl, perfluoroalkyl, and perfluoroalkylene moieties. Examples of these compounds include butyl acrylate, 1H,1H-2,2,3,3,4,4,4-
10 heptafluorobutyl acrylate, available from Sigma-Aldrich; 1H,1H,2H,2H-perfluorodecyl acrylate, available from Lancaster Synthesis, Windham, NH; and $C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$ made by the procedure of Examples 2A and 2B of WO01/30873A. Numerous other (meth)acryl compounds with perfluoroalkyl moieties are mentioned in US 4,968,116 and in US 5,239,026 (including
15 (perfluorocyclohexyl)methyl acrylate).

The compositions described herein are typically, though not always, free of hydrophilic ingredients since the inclusion of such tends to reduce anti-soiling properties as well as stain certain media. Hydrophilic components are also susceptible to degradation upon exposure to aqueous based cleaning agents.

Those skilled in the art appreciate that the coating compositions can contain other optional adjuvants, such as, binders, surfactants, antistatic agents (e.g.,
20 conductive polymers), leveling agents, matting agents (e.g., silica particles), photosensitizers, ultraviolet ("UV") absorbers, stabilizers, antioxidants, lubricants, pigments, dyes, plasticizers, suspending agents and the like. Other particles which may be included in the compositions are described in U.S. Patent No. 6,730,388.
25

The hardcoat formulation can be water-based or solvent-based or 100% solids with no solvent. Where appropriate, polymerizable components can optionally be diluted, for example, to 10 percent by weight total solids in methyl ethyl ketone. Two percent by weight of a photoinitiator such as DAROCUE 1173
30 (Ciba Specialty Products, Terrytown, NY) may be included in the polymerizable

60557-7763

compositions using a 10 percent solids photoinitiator solutions in methyl ethyl ketone. The photoinitiator can be added before dilution to the final percent by weight total solids. Dilution to the final percent by weight total solids can be achieved. achieved using methyl isobutyl ketone.

5

Application of coating composition to the substrate

The coating composition can be applied to the hardcoat using a variety of conventional coating methods. Suitable coating methods include, for example, spin coating, knife coating, die coating, wire coating, flood coating, padding, spraying, roll coating, dipping, brushing, foam application, and the like. The coating is dried, typically using a forced air oven. The dried coating is at least partially and typically completely cured using an energy source.

Preferred energy sources include ultraviolet light curing devices that provide a UV "C" dosage of about 5 to 60 millijoules per square centimeter (mJ/cm^2). Preferably curing takes place in an environment containing low amounts of oxygen, e.g., less than about 100 parts per million. Nitrogen gas is a preferred environment.

Preferably the coating composition is applied at a sufficient amount to provide a cured layer having a thickness of at least about 10 nanometers, and preferably at least about 25 nanometers. Typically, the cured layer has a thickness of less than about 50 mils, preferably less than about 10 mils, and more preferably less than about 5 mils. Accordingly, the bulk of the durability is provided by the underlying coating layer.

The coating compositions may be applied to a variety of substrates, including those identified in WO 2006/074,085.

Further features and advantages of this invention are further illustrated by the following examples, which are in no way intended to be limiting thereof. The present invention should not be considered limited to the particular examples described herein, but rather should be understood to cover all aspects of the

invention as fairly set out in the attached claims. Various modifications, equivalent processes, as well as numerous structures to which the present invention can be applicable will be readily apparent to those of skill in the art to which the present invention is directed upon review of the instant specification.

5

EXAMPLES

As used in the following examples, "HFPO-" refers to the end group $F(CF(CF_3)CF_2O)_aCF(CF_3)-$ wherein "a" ranges between 5 and 12, and averages about 6.3, with an average molecular weight of 1,211 g/mol, and which can be prepared according to the method reported in U.S. Pat. No. 3,250,808 (Moore et al.).

10

Preparation of Fluorochemical Compounds

The following fluorochemical compounds HFPO-MA and LTMDA, designated herein as FC-1 and FC-2, respectively, and shown in Table 1, were used the following examples. The preparation of HFPO-MA and LTMDA are described below.

15

Table 1. Fluorochemical compounds

Fluorochemical	Name/Description
FC-1 (HFPO-MA)	HFPO-MA, having the formula $F(CF(CF_3)CF_2O)_aCF(CF_3)C(O)N(H)CH_2CH_2OC(O)C(CH_3)=CH_2$, wherein a averages between 5 to 12
FC-2 (LTMDA)	LTMDA having the approximate formula $H_2C=CHCO_2CH_2CF_2O(CF_2O)_x(CF_2CF_2O)_y$ $CF_2CH_2O_2CHC=CH_2$

1. Preparation of Monofunctional Perfluoropolyether Methacrylate, HFPO-C(O)N(H)CH₂CH₂OC(O)C(CH₃)=CH₂, (FC-1)

5 HFPO-C(O)N(H)CH₂CH₂OC(O)C(CH₃)=CH₂ (HFPO-AEMA) (FC-2) is made by a procedure similar to that described in U.S. Publication No. 2004-0077775, entitled "Fluorochemical Composition Comprising a Fluorinated Polymer and Treatment of a Fibrous Substrate Therewith," filed on May 24, 2002, for Synthesis of (HFPO)_k-methacrylate, substituting

10 F(CF(CF₃)CF₂O)_aCF(CF₃)C(O)NHCH₂CH₂OH with a=6.8, molecular weight 1344, for the F(CF(CF₃)CF₂O)_aCF(CF₃)C(O)NHCH₂CH₂OH with a=10.5.

2. Preparation of LTMDA (FC-2)

15 LTMDA was prepared essentially in the same manner as described in example 15 of U.S. Patent No. 3,810,874, except that instead of making a dimethacrylate from the diol, a diacrylate was made.

Preparation of the Coating Composition.

20 Substrates were coated with polymerizable compositions using materials and amounts by weight as reported in the following examples (100% solids unless specified). The commercially available hardcoat compositions listed in Table 2 were used in the coating compositions as described below.

60557-7763

Table 2. Hardcoat compositions

Hardcoat	Name	Description
HC-1	SR 306™, available from Sartomer Company, Exton, PA.	Tripropyleneglycol diacrylate
HC-2	SR 454™, available from Sartomer Company, Exton, PA.	Trimethylolpropane ethoxylated (3) triacrylate
HC-3	SR 492™, available from Sartomer Company, Exton, PA.	Trimethylolpropane propoxylated (3) triacrylate
HC-4	BHEDA™, available from Sartomer Company, Exton, PA, under the trade designation "SR 349"	Bis-phenol A ethoxylated diacrylate
HC-5	CN 965A80™, available from Sartomer Company, Exton, PA.	Urethane acrylate blended with Tripropyleneglycol diacrylate
HC-6	CN 984™, available from Sartomer Company, Exton, PA.	Urethane acrylate

Contact Angle Test

5 The coatings were rinsed for 1 minute by hand agitation in IPA before being
 subjected to measurement of water and hexadecane contact angles. Measurements
 were made using as-received reagent-grade hexadecane (Aldrich) and deionized
 water filtered through a filtration system obtained from Millipore Corporation
 (Billerica, MA), on a video contact angle analyzer available as product number
 VCA-2500XE™ from AST Products (Billerica, MA). Reported values are the
 10 averages of measurements on at least three drops measured on the right and the left

60557-7763

sides of the drops, and are shown in Table 2. Drop volumes were 1 μ L for receding contact angle.

Marker Resistance Test

5 The tip of a SANFORD (R) KING SIZETM permanent black marker was cut with a razor blade at an angle to allow for a wide marking width. Using a ruler, a straight line was drawn on the test sample using the marking at a speed of approximately 6 inches per second. The marked sample was then placed next to a 1-5 rating standard with 1 being the lightest and 5 being the darkest. The process
10 was repeated three times and the average of the three tests was taken.

Example 1

0.1g of FC-1, 9.9 g of HC-1, and 0.1g of DAROCUR 1173TM photoinitiator were added to a vial and shaken for 5 minutes before coating. A piece of vinyl
15 substrate (4" x 6") was coated with the above acrylate mixture using a Meyer Bar (#10) to give a 1 mil thickness. The acrylate mixture was then polymerized using a PRC UV processor (Model #84-502) at a line speed of 13 ft/min. The coating layer cured to provide a shiny, smooth hardcoat on the vinyl substrate. The coated vinyl had a receding C₁₆H₃₄ contact angle at 60 degrees.

20

Examples 2-13

The coating compositions listed in Table 3 below, containing one of each of the fluorochemical compounds FC-1 and FC-2 in combination with one of each of the hardcoat compositions HC-1, HC-2, HC-3, HC-4, HC-5 and HC-6, were
25 prepared as follows. 0.025 g of fluorinated polyether acrylate (either FC-1 or FC-2), 9.975 g of the hardcoat composition (either HC-1, HC-2, HC-3, HC-4, HC-5, HC-6), and 0.1 g of DAROCUR 1173TM photoinitiator were added to a vial and shaken on a for 5 minutes before coating. Each of the compositions was then hand coated onto a white vinyl substrate (4" x 6") using a rubber glove to give a thin layer of the
30 coating composition, which was then photopolymerized as described above in

60557-7763

example 1. Each of the samples of coated substrate were then exposed to a fluorescent light. The samples were then tested with the Marker Resistance test described above, after 1, 5, 13 and 27 days exposure to the fluorescent light. The results are summarized in Table 4, below.

5

Table 3. Coating formulations E2-E13

Sample	Fluorochemical Component	Non-Fluorine-Containing Acrylate Monomer
E2	FC-1	HC-1
E3	FC-2	HC-1
E4	FC-1	HC-2
E5	FC-2	HC-2
E6	FC-1	HC-3
E7	FC-2	HC-3
E8	FC-1	HC-4
E9	FC-2	HC-4
E10	FC-1	HC-5
E11	FC-2	HC-5
E12	FC-1	HC-6
E13	FC-2	HC-6

60557-7763

Table 4. Performance of samples E2-E13 on Black Marker Test after 1, 5, 13, and 27 days.

Sample	Day 1	Day 5	Day 13	Day 27
E2	1	1	1	1
E3	1	1	1	1
E4	1	1	1	1
E5	1	1	1	1
E6	1	1	1	1
E7	1	1	1	1
E8	3	5	5	5
E9	1	4	4	4
E10	5	5	5	5
E11	5	5	5	5
E12	5	5	5	5
E13	5	5	5	5

The above data indicate that the urethane-acrylates HC-5 and HC-6 (E10-
 5 E13) did not perform as well on the Marker Resistance Test as the non-urethane-
 containing acrylates HC-1, HC-2, HC-3, and HC-4 (E2-E9). The aliphatic acrylates
 HC-1, HC-2, and HC-3 (E2-E7) generally performed better than the aromatic
 acrylate HC-4 (E8-E9). It was also observed that fluorochemical coatings derived
 from aliphatic non-urethane hardcoat compositions gave much better performance
 10 stabilities to ambient fluorescent light regardless of which fluorochemicals were
 used, whereas the aromatic non-urethane hardcoat composition performed better
 with some fluorochemicals than with others.

Examples 14-21

15 The compositions listed in Table 5 were prepared and coated onto a vinyl
 substrate using the same procedures described above for examples 2-19, except that

a mixture of HC-3 (non-urethane acrylate) and HC-6 (urethane acrylate) were used at the following weight ratios: 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 25/75, and 0/100. FC-1 was used as the fluorochemical component. The samples were tested with the Marker Resistance test described above, after 1, 8, 13 and 22 days exposure to the fluorescent light. The results are summarized in Table 6, below.

Table 5. Coating formulations E14-E21

Sample	Weight Ratio HC-3 / HC-7
E14	100 / 0
E15	90 / 10
E16	80 / 20
E17	70 / 30
E18	60 / 40
E19	50 / 50
E20	25 / 75
E21	0 / 100

60557-7763

Table 6. Performance of samples E14-E21 on Black Marker Test after 1, 8, 13, and 22 days.

Sample	Day 1	Day 8	Day 13	Day 22
E14	1	1	1	1
E15	1	1	1	1
E16	1	1	1	1
E17	1	1	1	2
E18	1	2	2	2
E19	1	4	5	5
E20	4	5	5	5
E21	5	5	5	5

The above data show that the stain resistance of the compositions, as measured by the Marker Resistance Test, decreases as more of the urethane-containing acrylate HC-7 is added to the composition. Thus, in topcoat systems involving the copolymerization of an acrylic resin with a fluorinated monomer, such as a fluorinated (meth)acrylate compound, the particular non-fluorochemical (meth)acrylates used can have a significant impact on the stain-resistance characteristics of the topcoat composition. The data presented herein show that compositions which contain an aliphatic or aromatic non-urethane-containing acrylate as the non-fluorochemical (meth)acrylate monomer component generally exhibit better stain resistance than compositions containing a urethane (meth)acrylate as the non-fluorochemical component of the composition.

Examples 22-23

The formulations show in Table 8 were prepared and coated onto a vinyl substrate using the procedures described above. About 1 wt-% of photoinitiator was added to each of the formulations.

Table 8. Coating formulations E22-23 (with FC-1)

Sample	wt-% acrylate monomer	Wt-% HFPO monomer
E22	99% HC-6 (SR984)	1%
E23	99% HC-1 (SR306)	1%

Once applied to the substrate and polymerized, the samples were passed under a UV light (H bulb) 1, 5, 10, and 15 times and the Black Marker Test was performed in order to test the effect of increasing amounts of light exposure on the stain resistant properties of the coating compositions. Three contact angle measurements were also taken after the final pass under the UV light. The results are shown below in Tables 9 and 10

60557-7763

Table 9. Black Marker Resistant and Contact Angle (hexadecane) measurements for E22

Number of passes under UV light	Black Marker Test Score	Receding left contact angel	Receding right contact angle
1	2	--	--
5	3	--	--
10	4	--	--
15	3-4	38.0	32.2
		45.0	47.0
		43.3	45.1

5 Table 10. Black Marker Resistant and Contact Angle (hexadecane) measurements for E23

Number of passes under UV light	Black Marker Test Score	Receding left contact angel	Receding right contact angle
1	1	--	--
5	1	--	--
10	1	--	--
15	1	49.0	51.0
		44.5	45.6
		50.1	51.0

10 The above results show that the stain resistance of the urethane acrylate-containing composition HC-6 (E22) degraded after repeated exposure to UV light, while the stain resistance of the non-urethane acrylate composition HC-1 (E23) remained relatively constant.

60557-7763

Various modifications and alterations to this invention will be apparent to those skilled in the art. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments set forth herein, and the scope of the claims should not be limited by these illustrative embodiments but should be given the broadest interpretation consistent with

5 the description as a whole.

60557-7763

CLAIMS:

1. A coating composition comprising at least one non-urethane aliphatic (meth)acryl compound that is a monomer or oligomer having at least two acryl or methacryl groups and is not a fluorochemical; and at least one polymerizable fluorochemical, which
5 comprises a (per)fluoropolyether (meth)acryl compound.
2. A coating composition comprising at least one non-urethane (meth)acryl compound that is a monomer or oligomer having at least two acryl or methacryl groups and is not a fluorochemical; and at least one monoterminated (per)fluoropolyether (meth)acryl compound.
- 10 3. The coating composition of claim 1, wherein the polymerizable fluorochemical is selected from the group consisting of (per)fluoroether-containing acrylates and methacrylates.
4. The coating composition of claim 2, wherein the non-urethane (meth)acryl compound is selected from the group consisting of aliphatic (meth)acrylates and aromatic
15 (meth)acrylates.
5. The coating composition of claim 1 or 2, wherein the composition contains less than 50 percent by weight of a urethane-containing (meth)acryl compound.
6. The coating composition of claim 1 or 2, wherein the composition contains less than 40 percent by weight of a urethane-containing (meth)acryl compound.
- 20 7. The coating composition of claim 1 or 2, wherein the composition contains less than 30 percent by weight of a urethane-containing (meth)acryl compound.
8. The coating composition of claim 1 or 2, wherein the composition contains less than 20 percent by weight of a urethane-containing (meth)acryl compound.
9. The coating composition of claim 1 or 2, wherein the composition contains less
25 than 10 percent by weight of a urethane-containing (meth)acryl compound.

60557-7763

10. The coating composition of claim 1 or 2, wherein the composition is substantially free of urethane (meth)acrylate.

11. The coating composition of claim 1 or 2, where the composition is photopolymerizable.

5 12. A method of protecting a substrate surface, the method comprising providing a surface layer on the substrate, wherein the surface layer comprises the reaction product of a composition comprising at least one non-urethane aliphatic (meth)acryl compound that is a monomer or oligomer having at least two acryl or methacryl groups and is not a fluorochemical; and at least one polymerizable fluorochemical, which comprises a
10 (per)fluoropolyether (meth)acryl compound.

13. A method of protecting a substrate surface, the method comprising providing a surface layer on the substrate, wherein the surface layer comprises the reaction product of a composition comprising at least one non-urethane (meth)acryl compound that is a monomer or oligomer having at least two acryl or methacryl groups and is not a fluorochemical; and at
15 least one monoterminated (per)fluoropolyether (meth)acryl compound.

14. The method of claim 12 or 13, wherein the surface layer is provided by coating the composition onto the substrate.

15. The method of claim 12 or 13, wherein the substrate comprises vinyl or wood.

16. The method of claim 12, wherein the fluorochemical is selected from the group
20 consisting of perfluoroether-containing acrylates and methacrylates.

17. The method of claim 13, wherein the non-urethane (meth)acryl compound is selected from the group consisting of aliphatic (meth)acrylates and aromatic (meth)acrylates.

18. The method of claim 12 or 13, wherein the surface layer is stain resistant.

19. An article comprising a substrate and surface layer, wherein the surface layer
25 comprises the reaction product of a composition comprising at least one non-urethane

60557-7763

aliphatic (meth)acryl compound that is a monomer or oligomer having at least two acryl or methacryl groups and is not a fluorochemical; and at least one polymerizable fluorochemical, which comprises a (per)fluoropolyether (meth)acryl compound.

20. An article comprising a substrate and surface layer, wherein the surface layer
5 comprises the reaction product of a composition comprising at least one non-urethane (meth)acryl compound that is a monomer or oligomer having at least two acryl or methacryl groups and is not a fluorochemical; and at least one monoterminated (per)fluoropolyether (meth)acryl compound.
21. The article of claim 19 or 20, wherein the surface layer is provided by coating
10 the composition onto the substrate.
22. The article of claim 19 or 20, wherein the substrate comprises vinyl or wood.
23. The article of claim 19, wherein the fluorochemical is selected from the group consisting of perfluoroether-containing acrylates and methacrylates.
24. The article of claim 20, wherein the non-urethane (meth)acryl compound is
15 selected from the group consisting of aliphatic (meth)acrylates and aromatic (meth)acrylates.
25. The article of claim 19 or 20, wherein the surface layer is stain resistant.
26. The coating composition of claim 1 or 2, which further comprises a photoinitiator.