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(54) **PERFLUOROPOLYETHER URETHANE
ADDITIVES HAVING (METH)ACRYL
GROUPS AND HARD COATS**

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(75) Inventors: **Thomas P. Klun**, Lakeland, MN (US);
Naiyong Jing, Woodbury, MN (US);
Richard J. Pokorny, Maplewood, MN
(US); **Zai-Ming Qiu**, Woodbury, MN
(US); **Mark J. Pellerite**, Woodbury,
MN (US); **William D. Coggio**, Hudson,
WI (US)

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Correspondence Address:

**3M INNOVATIVE PROPERTIES COMPANY
PO BOX 33427
ST. PAUL, MN 55133-3427 (US)**

(57) **ABSTRACT**

Fluorocarbon- and urethane-(meth)acryl-containing addi-
tives and hardcoats. The hardcoats are particularly useful as
a surface layer on an optical device.

(73) Assignee: **3M Innovative Properties Company**

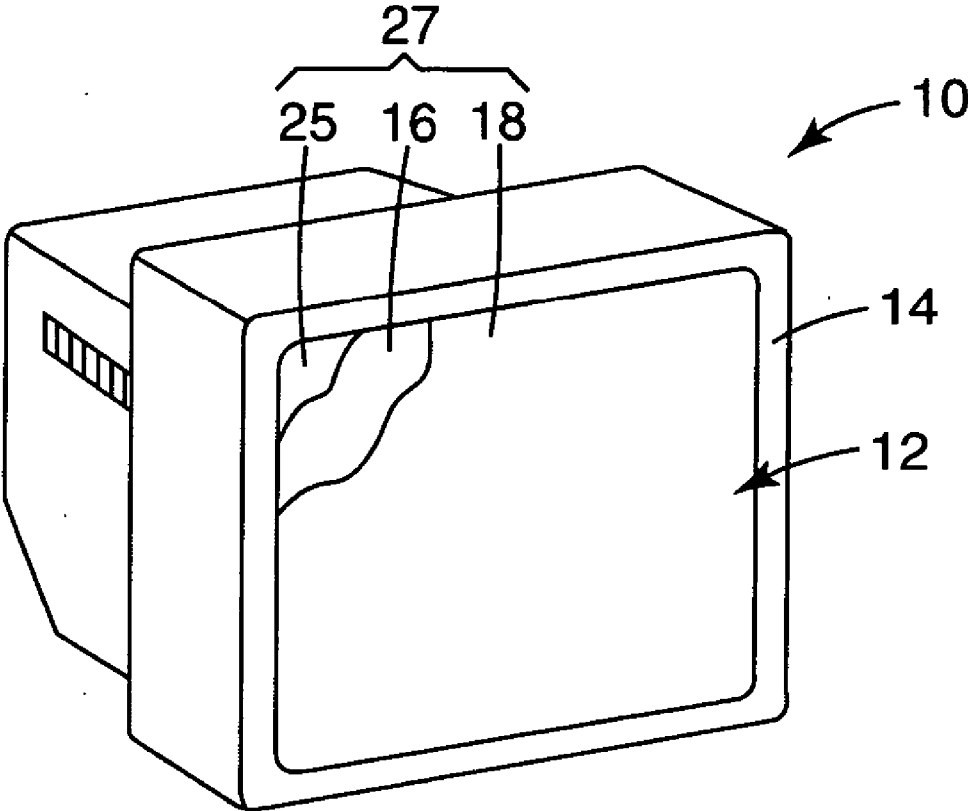


Fig. 1

**PERFLUOROPOLYETHER URETHANE
ADDITIVES HAVING (METH)ACRYL GROUPS
AND HARD COATS**

BACKGROUND OF THE INVENTION

[0001] Optical hard coats are applied to optical display surfaces to protect them from scratching and marking. Desirable product features in optical hard coats include durability to scratches and abrasions, and resistance to inks and stains.

[0002] Materials that have been used to date for surface protection include fluorinated polymers, or fluoropolymers. Fluoropolymers provide advantages over conventional hydrocarbon based materials in terms of high chemical inertness (in terms of solvent, acid, and base resistance), dirt and stain resistance (due to low surface energy), low moisture absorption, and resistance to weather and solar conditions.

[0003] Fluoropolymers have also been investigated that are crosslinked to a hydrocarbon-based hard coating formulation that improves hardness and interfacial adhesion to a substrate. For example, it is known that free-radically curable perfluoropolyethers provide good repellency to inks from pens and permanent markers when added to ceramer hard coat compositions, which comprise a plurality of colloidal inorganic oxide particles and a free-radically curable binder precursor, such as described in U.S. Pat. No. 6,238,798 to Kang, and assigned to 3M Innovative Properties Company of St. Paul, Minn.

[0004] Industry would find advantage in other fluoropolymer-based hard coatings, particularly those having improved properties.

SUMMARY OF THE INVENTION

[0005] In one aspect, the invention relates to fluorocarbon and urethane-(meth)acryl-containing additives.

[0006] In one embodiment, the additive comprises a perfluoropolyether urethane having a monovalent perfluoropolyether moiety and a multi-(meth)acryl terminal group and is described in the detailed description below as formula (1).

[0007] In another embodiment, the additive comprises a perfluoropolyether-substituted urethane acrylate having a monovalent perfluoropolyether moiety described in the detailed description below as formula (3A) and more preferably as formula (3B).

[0008] In a third embodiment, the additive comprises one or more perfluoropolyether urethanes having a monovalent perfluoropolyether moiety and a multi-(meth)acryl group of the formula (4) as described further in the detailed description below.

[0009] In a fourth embodiment, the additive comprises one or more perfluoropolyether urethanes having a monovalent perfluoropolyether moiety and a multi-(meth)acryl group of the formula (5) as described below in the detailed description.

[0010] In a fifth embodiment, the additive comprises one or more perfluoropolyether urethanes with multi-(meth)acryl groups of the formula (6) as described below in the detailed description.

[0011] In another aspect, the invention relates to a hardcoat composition comprising a (e.g. small amount of a) hardcoat-compatible, monovalent perfluoropolyether moiety-containing urethane multi-(meth)acryl additive, a hydrocarbon hardcoat composition; and optionally a plurality of surface modified inorganic nanoparticles. The hardcoat preferably comprises one or more of the embodied additives just described. The hardcoat is preferably provided as a surface layer on an optical substrate. The hardcoat may be provided as a single layer disposed on an optical substrate. Alternatively, a first (e.g. different composition) hardcoat layer may be disposed on the optical substrate with a hardcoat of the invention disposed on the first hardcoat layer. Further, a particulate matting agent may be incorporated to impart anti-glare properties to the optical hard coating layer. The particulate matting agent can also prevent the reflectance decrease and uneven coloration caused by interference of the hard coat layer with the underlying substrate layer. In preferred embodiments, the hardcoats provide any one or combination of enhanced stain and ink repellency properties, adequate smoothness, and improved durability.

[0012] The (e.g. optical) hard coats having these fluorocarbon additives described herein generally do not need compatibilizers to enhance the compatibility between a fluoropolymer additive and the conventional hard coat material. Alternatively, however, free-radically reactive fluoroalkyl or fluoroalkylene group-containing compatibilizers can also be employed such as a perfluorobutyl-substituted acrylate or a fluoroalkyl- or fluoroalkylene-substituted thiol or polythiol.

[0013] Other objects and advantages of the present invention will become apparent upon considering the following detailed description and appended claims, and upon reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] **FIG. 1** illustrates an article having a hard coated optical display formed in accordance with a preferred embodiment of the present invention.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

[0015] For the following defined terms, these definitions shall be applied, unless a different definition is given in the claims or elsewhere in the specification.

[0016] The term “(meth)acryl” refers to functional groups including acrylates, methacrylates, acrylamides, methacrylamides, alpha-fluoroacrylates, thioacrylates and thio-methacrylates. A preferred (meth)acryl group is acrylate.

[0017] The term “monovalent perfluoropolyether moiety”, refers to a perfluoropolyether chain having one end terminated by a perfluoroalkyl group.

[0018] The term “ceramer” is a composition having inorganic oxide particles, e.g. silica, of nanometer dimensions dispersed in a binder matrix. The phrase “ceramer composition” is meant to indicate a ceramer formulation in accordance with the present invention that has not been at least partially cured with radiation energy, and thus is a flowing, coatable liquid. The phrase “ceramer composite” or “coating layer” is meant to indicate a ceramer formulation in accordance with the present invention that has been at least

partially cured with radiation energy, so that it is a substantially non-flowing solid. Additionally, the phrase “free-radically polymerizable” refers to the ability of monomers, oligomers, polymers or the like to participate in crosslinking reactions upon exposure to a suitable source of curing energy.

[0019] The term “polymer” will be understood to include polymers, copolymers (e.g. polymers using two or more different monomers), oligomers and combinations thereof, as well as polymers, oligomers, or copolymers that can be formed in a miscible blend.

[0020] Unless otherwise noted, “HFPO—” refers to the end group $F(CF_2(CF_3)CF_2O)_aCF_2(CF_3)—$ of the methyl ester $F(CF_2(CF_3)CF_2O)_aCF_2(CF_3)C(O)OCH_3$, wherein “a” averages about 6.2, and the methyl ester has 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.), the disclosure of which is incorporated herein by reference, with purification by fractional distillation.

[0021] The recitation of numerical ranges by endpoints includes all numbers subsumed within the range (e.g. the range 1 to 10 includes 1, 1.5, 3.33, and 10).

[0022] As used in this specification and the appended claims, the singular forms “a”, “an”, and “the” include plural referents unless the content clearly indicates otherwise. Thus, for example, reference to a composition containing “a compound” includes a mixture of two or more compounds. As used in this specification and the appended claims, the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

[0023] Unless otherwise indicated, all numbers expressing quantities of ingredients, measurements of properties such as contact angle, and so like as used in the specification and claims are to be understood to be modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings of the present invention. At the very 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 be at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters set forth in the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as accurately as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviations found in their respective testing measurements.

[0024] The term “optical display”, or “display panel”, can refer to any conventional optical displays, including but not limited to multi-character multi-line displays such as liquid crystal displays (“LCDs”), plasma displays, front and rear projection displays, cathode ray tubes (“CRTs”), and signage, as well as single-character or binary displays such as light emitting diodes (“LEDs”), signal lamps and switches. The exposed surface of such display panels may be referred to as a “lens.” The invention is particularly useful for displays having a viewing surface that is susceptible to being

touched or contacted by ink pens, markers and other marking devices, wiping cloths, paper items and the like.

[0025] The protective coatings of the invention can be employed in a variety of portable and non-portable information display articles. These articles include PDAs, cell phones (including combination PDA/cell phones), LCD televisions (direct lit and edge lit), touch sensitive screens, wrist watches, car navigation systems, global positioning systems, depth finders, calculators, electronic books, CD and DVD players, projection television screens, computer monitors, notebook computer displays, instrument gauges, instrument panel covers, signage such as graphic displays and the like. The viewing surfaces can have any conventional size and shape and can be planar or non-planar, although flat panel displays are preferred.

[0026] A combination of low surface energy (e.g. anti-soiling, stain resistant, oil and/or water repellency) and durability (e.g. abrasion resistance) is desired for the coating layer for these displays while maintaining optical clarity. The hard coating layer functions to decrease glare loss while improving durability and optical clarity.

[0027] The surface energy can be characterized by various methods such as contact angle and ink repellency, as determined by the test methods described in the Examples. In this application, “stain repellent” refers to a surface treatment exhibiting a static contact angle with water of at least 70 degrees. More preferably, the contact angle is at least 80 degrees and most preferably at least 90 degrees. Alternatively, or in addition thereto, the advancing contact angle with hexadecane is at least 50 degrees and more preferably at least 60 degrees. Low surface energy results in anti-soiling and stain repellent properties as well as rendering the exposed surface easy to clean.

[0028] Another indicator of low surface energy relates to the extent to which ink from a pen or marker beads up when applied to the exposed surface. The surface layer and articles exhibit “ink repellency” when ink from pens and markers can be easily removed by wiping the exposed surface with tissues or paper towels, such as tissues available from the Kimberly Clark Corporation, Roswell, Ga. under the trade designation “SURPASS FACIAL TISSUE.” Durability can be defined in terms of results from a modified oscillating sand test (Method ASTM F 735-94) carried out at 300 rpm for 15 minutes as described in Experiment 1 of this application. Preferably, a durable coating exhibits an ink repellency value of 65 mm or less, more preferably 40 mm or less, most preferably 0 mm in this test.

[0029] Coatings appropriate for use as optical hard coatings must be substantially free of visual defects. Visual defects that may be observed include but are not limited to pock marks, fish eyes, mottle, lumps or substantial waviness, or other visual indicators known to one of ordinary skill in the art in the optics and coating fields. Thus, a “rough” surface as described in the Experimental has one or more of these characteristics, and may be indicative of a coating material in which one or more components of the composition are incompatible with each other. Conversely, a substantially smooth coating, characterized below as “smooth” for the purpose of the present invention, presumes to have a coating composition in which the various components, in the reacted final state, form a coating in which the components

are compatible or have been modified to be compatible with one another and further has little, if any, of the characteristics of a "rough" surface.

[0030] Additionally, the surface layer preferably exhibits an initial haze of less than 2% and/or an initial transmission of at least 90%.

[0031] Referring now to FIG. 1, a perspective view of an article (here a computer monitor 10) is illustrated as having an optical display 12 coupled within a housing 14. The optical display 12 is a substantially transparent material having optically enhancing properties through which a user can view text, graphics or other displayed information. The optical display 12 includes hard coating layer 18 applied to an optical substrate 16. The thickness of the hardcoat layer is typically at least 0.5 microns, preferably at least 1 micron, and more preferably at least 2 microns. The thickness of the hardcoat layer is generally no greater than 25 microns. Preferably the thickness ranges from 3 microns to 5 microns.

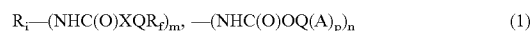
[0032] In another embodiment (not shown), the hardcoat layer described herein (i.e. comprising at least one fluorocarbon- and urethane-(meth)acryl-containing additive and at least one non-fluorinated crosslinking agent) may be provided as a surface layer having an additional hard coat layer underlying the hardcoat surface layer. In this embodiment, the surface layer preferably has a thickness ranging from about 10 to 200 nanometers.

[0033] Various permanent and removable grade adhesive compositions may be coated on the opposite side of the substrate 16 (i.e. to that of the hardcoat 16) so the article can be easily mounted to a display surface. Suitable adhesive compositions include (e.g. hydrogenated) block copolymers such as those commercially available from Kraton Polymers of Westhollow, Tex. under the trade designation "Kraton G-1657", as well as other (e.g. similar) thermoplastic rubbers. Other exemplary adhesives include acrylic-based, urethane-based, silicone-based and epoxy-based adhesives. Preferred adhesives are of sufficient optical quality and light stability such that the adhesive does not yellow with time or upon weather exposure so as to degrade the viewing quality of the optical display. The adhesive can be applied using a variety of known coating techniques such as transfer coating, knife coating, spin coating, die coating and the like. Exemplary adhesives are described in U.S. Patent Application Publication No. 2003/0012936. Several of such adhesives are commercially available from 3M Company, St. Paul, Minn. under the trade designations 8141, 8142, and 8161.

[0034] The substrate layer 16 may consist of any of a wide variety of non-polymeric materials, such as glass, or polymeric materials, such as polyethylene terephthalate (PET), bisphenol A polycarbonate, cellulose triacetate, poly(methyl methacrylate), and biaxially oriented polypropylene which are commonly used in various optical devices.

[0035] The composition of the hard coating layer 18, prior to application and curing to the optical substrate 16, is formed from a mixture of a conventional hydrocarbon-based, and more preferably acrylate-based, hard coat composition and a fluorocarbon- and urethane-acrylate-containing additive described in formulas (1), (3A), (4), (5) and (6) below. Methods for forming the hard coating compositions for each of the preferred embodiments are described below in the experimental section.

[0036] In one preferred embodiment of the present invention, the fluorocarbon- and urethane-acrylate-containing additive is a perfluoropolyether urethane having a monovalent perfluoropolyether moiety and a multi-acrylate terminal group combined with a conventional hydrocarbon-based (more preferably acrylate-based) hard coat material. The perfluoropolyether urethane having a monovalent perfluoropolyether moiety and a multi-acrylate terminal group is added at between about 0.01% and 10%, and more preferably between about 0.1% and 1%, of the total solids of the hard coat composition. The additive is of the formula (1):



wherein R_1 is the residue of a multi-isocyanate; X is O, S or NR, where R is H or lower alkyl of 1 to 4 carbon atoms; R_f is a monovalent perfluoropolyether moiety composed of groups comprising the formula: $\text{F}(\text{R}_{fc}\text{O})_x\text{C}_d\text{F}_{2d}$, wherein each R_{fc} independently represents a fluorinated alkylene group having from 1 to 6 carbon atoms, each x independently represents an integer greater than or equal to 2, and wherein d is an integer from 1 to 6; Q is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof; A is a (meth)acryl functional group $-\text{XC(O)C(R}_2)=\text{CH}_2$, where R_2 is a lower alkyl of 1 to 4 carbon atoms or H or F; m is at least 1; n is at least 1; p is 2 to 6, m+n is 2 to 10, and in which each unit referred to by the subscripts m and n is attached to an R_1 unit.

[0037] By their method of synthesis, these materials are necessarily mixtures. If the mole fraction of isocyanate groups is arbitrarily given a value of 1.0, then the total mole fraction of m and n units used in making materials of formula (1) is 1.0 or greater. The mole fractions of m:n ranges from 0.95:0.05 to 0.05:0.95. Preferably, the mole fractions of m:n are from 0.50:0.50 to 0.05:0.95. More preferably, the mole fractions of m:n are from 0.25:0.75 to 0.05:0.95 and most preferably, the mole fractions of m:n are from 0.25:0.75 to 0.10:0.95. In the instances the mole fractions of m:n total more than one, such as 0.15:0.90, the m unit is reacted onto the isocyanate first, and a slight excess (0.05 mole fraction) of the n units are used.

[0038] In a formulation, for instance, in which 0.15 mole fractions of m and 0.85 mole fraction of n units are introduced, a distribution of products is formed in which some fraction of products formed contain no m units. There will, however, be present in this product distribution, materials of formula (1).

[0039] Numerous diisocyanates (di-functional isocyanates), modified diisocyanate materials, and higher functional isocyanates may be used as R_1 in the present invention as the residue of multi-isocyanate and still fall within the spirit of the present invention. Most preferably, multifunctional materials based on hexamethylene diisocyanate ("HDI") are utilized. One commercially available derivative of HDI is Desmodur™ N100, available from Bayer Polymers LLC of Pittsburgh, Pa.

[0040] Further, other diisocyanates such as toluene diisocyanate ("TDI") or isophorone diisocyanate ("IPDI") may

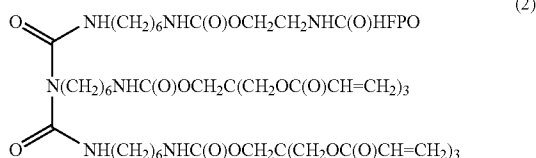
also be utilized as R_f in the present invention. Non-limiting examples of aliphatic and aromatic isocyanate materials, for example, that may be used include Desmodur™ 3300, Desmodur™ TPLS2294, and Desmodur™ N 3600, all obtained from Bayer Polymers LLC of Pittsburgh, Pa.

[0041] Materials used to make the additive of formula (1) may be described by the formula: $\text{HOQ}(\text{A})_p$, which are exemplified by, for instance, 1,3-glycerol dimethacrylate, available from Echo Resins Inc. of Versailles, Mo.; and pentaerythritol triacrylate, available as SR444C from Sartomer of Exton, Pa.

[0042] Preferably, the monovalent perfluoropolyether moiety R_f is a hexafluoropropylene oxide ("HFPO") moiety of the formula: $\text{F}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_a\text{CF}(\text{CF}_3)\text{—}$, wherein a is between about 3 and 10. Such species generally exist as a distribution or mixture of oligomers with a range of values for a , so that the average value of a may be non-integer.

[0043] Typically, the additives of this preferred embodiment are made by first reacting the polyisocyanate with the perfluoropolyether-containing alcohol, thiol, or amine, followed by reaction with the hydroxyl functional multiacrylate, usually in a non-hydroxylic solvent and in the presence of a catalyst such as an organotin compound. Alternately, the additives of this preferred embodiment are made by reacting the polyisocyanate with the hydroxyl functional multiacrylate, followed by reaction with the perfluoropolyether-containing alcohol, thiol, or amine, usually in a non-hydroxylic solvent and in the presence of a catalyst such as an organotin compound. In addition, the additives could be made by reacting all three components simultaneously, usually in a non-hydroxylic solvent and in the presence of a catalyst such as an organotin compound.

[0044] One representative structure (2) of perfluoropolyether urethanes with multi-acrylates terminal groups of formula (1) is shown below as:

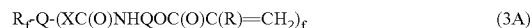


which is the reaction product of the biuret of HDI with one equivalent of HFPO oligomer amidol ($\text{F}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_{6,5}\text{CF}(\text{CF}_3)\text{C}(\text{O})\text{NHCH}_2\text{CH}_2\text{OH}$), and further with two equivalents of pentaerythritol triacrylate.

[0045] In a slight alternative preferred variation of formula (1), a hard coating composition may be formed by the addition of a perfluoropolyether urethane with a monoacrylate terminal group according to the formula $R_f\text{—}(\text{NH}\text{C}(\text{O})\text{XQR}_i)_m\text{—}(\text{NHC}(\text{O})\text{OQA})_n$ to a hydrocarbon-based hard coating formulation.

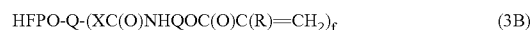
[0046] In another preferred embodiment of the present invention, the fluorocarbon- and urethane-acrylate-containing additive comprises a perfluoropolyether-substituted urethane acrylate having a monovalent perfluoropolyether moiety added at between about 0.01% and 10%, and more

preferably between about 0.1% and 1%, of the total solids of the hard coat composition. The additive is of the formula (3A):



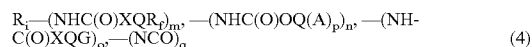
where R_f is a monovalent perfluoropolyether moiety composed of groups comprising the formula: $\text{F}(\text{R}_{fc}\text{O})_x\text{C}_d\text{F}_{2d}\text{—}$, wherein each R_{fc} independently represents a fluorinated alkylene group having from 1 to 6 carbon atoms, each x independently represents an integer greater than or equal to 2, and wherein d is an integer from 1 to 6; a is 2-15; Q is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof; X is independently O, S or NR, where R is H or lower alkyl of 1 to 4 carbon atoms and f is 1-5.

[0047] One preferred perfluoropolyether-substituted urethane(meth)acrylate that meets the description of formula (3A) is described more specifically in formula (3B):



where HFPO is $\text{F}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_a\text{CF}(\text{CF}_3)\text{—}$; a is 2-15; Q is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof; X is independently O, S or NR, where R is H or lower alkyl of 1 to 4 carbon atoms and f is 1-5. Two preferred HFPO-substituted urethane acrylates that can be utilized include: $\text{HFPO}\text{—}C(\text{O})\text{NHC}(\text{C}_2\text{H}_4\text{OC}(\text{O})\text{NHC}(\text{C}_2\text{H}_4\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2)$ and $\text{HFPO}\text{—}C(\text{O})\text{NHC}(\text{C}_2\text{H}_5)(\text{CH}_2\text{OC}(\text{O})\text{NHC}(\text{C}_2\text{H}_4\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2)_2$.

[0048] In another preferred embodiment of the present invention, the fluorocarbon- and urethane-acrylate-containing additive is formed from one or more perfluoropolyether urethanes having a monovalent perfluoropolyether moiety and multi-meth(acryl) groups added at between about 0.01% and 10%, and more preferably between about 0.1% and 1%, of the total solids of the hard coat composition. The additive is of the formula (4):

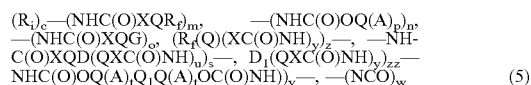


wherein R_i is the residue of a multi-isocyanate; X is independently O, S or NR, where R is H or lower alkyl of 1 to 4 carbon atoms; R_f is a monovalent perfluoropolyether moiety composed of groups comprising the formula: $\text{F}(\text{R}_{fc}\text{O})_x\text{C}_d\text{F}_{2d}\text{—}$, wherein each R_{fc} independently represents a fluorinated alkylene group having from 1 to 6 carbon atoms, each x independently represents an integer greater than or equal to 2, and wherein d is an integer from 1 to 6; Q is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and

S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof; A is a (meth)acryl functional group $-\text{XC}(\text{O})\text{C}(\text{R}_2)=\text{CH}_2$, where R_2 is a lower alkyl of 1 to 4 carbon atoms or H or F; G is selected from the group consisting of an alkyl, an aryl, an alkaryl and an aralkyl, wherein G optionally contains heteroatoms such as O, N, and S and optionally has heteroatom-containing functional groups such as carbonyl and sulfonyl and combinations of heteroatoms and heteroatom-containing functional groups; and G optionally contains pendant or terminal reactive groups selected from the group consisting of (meth)acryl groups, vinyl groups, allyl groups and $-\text{Si}(\text{OR}_3)_3$ groups, where R_3 is a lower alkyl of 1 to 4 carbon atoms; wherein G also optionally has fluoroalkyl or perfluoroalkyl groups; m is at least 1; n is at least 1; o is 0 or greater; p is 2 to 6; q is 0 or greater; $(m+n+o+q)=N_{\text{NCO}}$, where N_{NCO} is the number of isocyanate groups originally appended to R_i ; and the quantity $(m+n+o)/N_{\text{NCO}}$ is greater than or equal to 0.67, and in which each unit referred to by the subscripts m, n, o, and q is attached to an R_i unit. Preferably R_{fc} is $-\text{CF}(\text{CF}_3)\text{CF}_2-$.

[0049] The monoalcohol, monothiol or monoamine HXQG used in making materials of formula (4) may include materials such as $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$, $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2(\text{SiOCH}_3)_3$, $\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$, and HEA ("hydroxyethylacrylate").

[0050] In still another preferred embodiment of the present invention, the fluorocarbon- and urethane-acrylate-containing additive is formed from one or more perfluoropolyether urethanes having a monovalent perfluoropolyether moiety and multi-meth(acryl) groups added at between about 0.01% and 10%, and more preferably between about 0.1% and 1%, of the total solids of the hard coat composition. The additive is of the formula (5):



wherein R_i is the residue of a multi-isocyanate; c is 1 to 50; X is independently O, S or NR, where R is H or lower alkyl; R_f is a monovalent perfluoropolyether moiety composed of groups comprising the formula: $\text{F}(\text{R}_{\text{fc}}\text{O})_x\text{C}_d\text{F}_{2d-4}$, each R_{fc} independently represents a fluorinated alkylene group having from 1 to 6 carbon atoms and each x independently represents an integer greater than or equal to 2 and wherein d is an integer from 1 to 6; Q is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof; A is a (meth)acryl functional group having the chemical formula: $(-\text{XC}(\text{O})\text{C}(\text{R}_2)=\text{CH}_2)$, where R_2 is a lower alkyl of 1 to 4 carbon atoms or H or F; G is selected from the group consisting of an alkyl, an aryl, an alkaryl and an aralkyl, wherein G optionally contains heteroatoms such as O, N, and S and optionally has heteroatom-containing functional groups such as carbonyl and sulfonyl and combinations of heteroatoms and heteroatom-containing functional groups; and wherein G optionally contains pendant or terminal reactive groups selected from the group consisting of (meth)

acryl groups, vinyl groups, allyl groups and $-\text{Si}(\text{OR}_3)_3$ groups, where R_3 is a lower alkyl of 1 to 4 carbon atoms; wherein G also optionally has fluoroalkyl or perfluoroalkyl groups; D is selected from the group consisting of an alkylene, an arylene, an alkarylene, a fluoroalkylene, a perfluoroalkylene and an aralkylene and optionally contains heteroatoms such as O, N, and S; D_1 is selected from the group consisting of an alkyl, an aryl, an alkaryl, a fluoroalkyl, a perfluoroalkyl and an aralkyl group and optionally contains heteroatoms such as O, N, and S; Q_1 is a connecting group defined in the same way as Q; m or z is at least 1; n or v is at least 1; y is independently 2 or greater; o, s, v, w, z and zz are 0 or greater; $(m+n+o+[(u+1)s]+2v+w+yz+y(zz))=cN_{\text{NCO}}$, where N_{NCO} is the number of isocyanate groups originally appended to R_i ; the quantity $(m+n+o+[(u+1)s]+2v+yz+y(zz))/(cN_{\text{NCO}})$ is greater than or equal to least 0.75; p is 2 to 6; t is 1 to 6; and u is independently 1 to 3; in which each unit referred to by the subscripts m, n, o, s, v, w, z and zz is attached to an R_i unit; and preferably R_{fc} is $-\text{CF}(\text{CF}_3)\text{CF}_2-$.

[0051] In this embodiment, when added to the conventional hydrocarbon-based hard coating material, care must be taken in choosing the ratios and amounts of reactive components to avoid highly crosslinked urethane polymer gels. For instance, if a trifunctional isocyanate is to be used with a multifunctional alcohol, the amount of multifunctional alcohol should be limited to avoid forming a crosslinked network. For higher numbers of c for $(\text{R}_i)_c$ groups, it is preferred that diols and diisocyanates be primarily used.

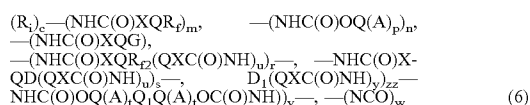
[0052] The materials used to make the additive of formula (5) include those of the formula: $\text{R}_f(\text{Q})(\text{XH})_y$, which is exemplified by HFPO— $\text{C}(\text{O})\text{NHCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$.

[0053] The materials used to make the additive of formula (5) include those of the formula: HXQDQXH, which is exemplified by hydrocarbon polyols such as $\text{HO}(\text{CH}_2)_{10}\text{OH}$ and fluorochemical diols such as $\text{HOCH}_2(\text{CF}_2)_4\text{CH}_2\text{OH}$.

[0054] The materials used to make the additive of formula (5) may include those of the formula: $\text{D}(\text{QXH})_y)_{zz}$, which is exemplified by fluorochemical diols $\text{C}_4\text{F}_9\text{SO}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$.

[0055] The materials used to make the additive of formula (5) may also include those of the formula: $\text{HOQ}(\text{A})_t\text{Q}_1\text{Q}(\text{A})_t\text{OH}$, which is exemplified by Hydantoin hexaacrylate (HHA), prepared as described in Example 1 of U.S. patent application No. 4,262,072 to Wendling et al, and $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{O}(\text{CH}_2)_4\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$.

[0056] In still another preferred embodiment of the present invention, the fluorocarbon- and urethane-acrylate-containing additive is formed from one or more perfluoropolyether urethanes with multi-meth(acryl) groups added at between about 0.01% and 10%, and more preferably between about 0.1% and 1%, of the total solids of the hard coat composition. The additive is of the formula (6):



wherein R_1 is the residue of a multi-isocyanate; c is 1 to 50; X is independently O, S or NR, where R is H or lower alkyl; R_f is a monovalent perfluoropolyether moiety composed of groups comprising the formula: $F(R_{fc}O)_x C_d F_{2d}$, each R_{fc} independently represents a fluorinated alkylene group having from 1 to 6 carbon atoms and each x independently represents an integer greater than or equal to 2 and wherein d is an integer from 1 to 6; Q is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof; A is a (meth)acryl functional group having the chemical formula: $(-XC(O)C(R_2)=CH_2)$, where R_2 is a lower alkyl of 1 to 4 carbon atoms or H or F; G is selected from the group consisting of an alkyl, an aryl, an alkaryl and an aralkyl, wherein G optionally contains heteroatoms such as O, N, and S and optionally has heteroatom-containing functional groups such as carbonyl and sulfonyl and combinations of heteroatoms and heteroatom-containing functional groups; and wherein G optionally contains pendant or terminal reactive groups selected from the group consisting of (meth)acryl groups, vinyl groups, allyl groups and $-Si(OR_3)_3$ groups, where R_3 is a lower alkyl of 1 to 4 carbon atoms; G also optionally has fluoroalkyl or perfluoroalkyl groups; R_{f2} is a multi-valent fluoropolyether moiety, R_{f2} is composed of groups comprising the formula: $Y((R_{fc1}O)_x C_{d1} F_{2d1})_b$, wherein each R_{fc1} independently represents a fluorinated alkylene group having from 1 to 6 carbon atoms: each x independently represents an integer greater than or equal to 2, and $d1$ is an integer from 0 to 6; Y represents a polyvalent organic group or covalent bond having a valence of b , and b represents an integer greater than or equal to 2; D is selected from the group consisting of an alkylene, an arylene, an alkarylene, a fluoroalkylene, a perfluoroalkylene and an aralkylene group and optionally contains heteroatoms such as O, N, and S; D_1 is selected from the group consisting of an alkyl, an aryl, an alkaryl, a fluoroalkyl, a perfluoroalkyl and an aralkyl group and optionally contains heteroatoms such as O, N, and S; Q_1 is a connecting group defined in the same way as Q ; r is at least 1; n or v is at least 1; y is independently 2 or greater; m , o , s , v , w and z are 0 or greater; $(m+n+o+[(u+1)r]+[(u+1)s]+2v+w+y(zz))=cN_{NCO}$, where N_{NCO} is the number of isocyanate groups originally appended to R_1 ; the quantity $(m+n+o+[(u+1)r]+[(u+1)s]+2v+y(zz))/(cN_{NCO})$ is greater than or equal to least 0.75; p is 2 to 6; t is 1 to 6; u is independently 1 to 3; in which each unit referred to by the subscripts m , n , o , r , s , v , w , and z is attached to an R_1 unit; and R_{fc1} is preferably independently selected from: $-CF(CF_3)CF_2-$, $-CF_2CF_2CF_2-$, and $(-CH_2C(R)(CH_2OCH_2C_d F_{2d+1})CH_2-)_a$ where aa is 2 or greater and d and R are defined above.

[0057] The materials used to make the additive of formula (9) may also include those of the formula: $HXQR_{f2}QXH$, which is exemplified by $(H(OCH_2C(CH_3)(CH_2OCH_2CF_3)CH_2)_{aa}OH)$ (Fox-Diol, having a MW about 1342 and available from Omnova Solutions Inc. of Akron, Ohio).

[0058] In preferred embodiments the fluorocarbon- and urethane-(meth)acryl additive(s) described herein are employed as the sole perfluoropolyether containing additive

in a hardcoat composition. Alternatively, however, the additive(s) described herein may be employed in combination with various other perfluoropolyether fluorocarbon-(meth)acryl materials such as HFPO— $C(O)NHCH_2CH_2OC(O)CH=CH_2$ and various (per)fluoropolyether acryl compounds such as described in U.S. application Ser. No. 10/841159, filed May 7, 2004; (Docket No. 59727US002) and U.S. Provisional Application Ser. No. 60/569351, filed May 7, 2004 (Docket No. 59795US002); incorporated by reference. Exemplary materials include compound of the structures: HFPO— $C(O)N(H)C(CH_2OC(O)CH=CH_2)_2CH_2CH_3$, and HFPO— $C(O)N(H)C(CH_2OC(O)CH=CH_2)_2H$.

[0059] The hardcoat may be provided as a single layer disposed on an optical substrate. In this construction, the total of all (per)fluoropolyether acryl compounds, (i.e. the fluorocarbon- and urethane-(meth)acryl additive(s) of the invention and other perfluoropolyether fluorocarbon-(meth)acryl materials) ranges from 0.01% to 10%, and more preferably from 0.1% to 1%, of the total solids of the hard coat composition. For embodiments wherein a first (e.g. different composition) hardcoat layer is disposed on the optical substrate with a hardcoat of the invention disposed on the first hardcoat layer the fluorocarbon- and urethane-(meth)acryl-containing additives described herein may be present in the surface coating at amounts ranging from 0.01 to 50 wt-% solids, and more preferably from 1 to 25 wt-% solids; whereas the various other (per)fluoropolyether acryl compounds may be present at weight percents from 1 to 20%, and preferably from 1 to 10%. Preferably, the ratio of fluorocarbon- and urethane-(meth)acryl-containing additive to other (per)fluoropolyether acryl compounds is at least 1 to 1 and more preferably is about 3 to 1.

[0060] The fluorocarbon- and urethane(meth)acryl additives (e.g. those of formulas (1), (3A), (4), (5) or (6)) optionally in combination with various other (per)fluoropolyether(meth)acryl compounds may be combined with one or more compatibilizers.

[0061] A class of free-radically reactive fluoroalkyl or fluoroalkylene group-containing compatibilizers of the respective chemical formulas: $R_{ff}Q_3(X_1)_{n1}$ and $(X_1)_{n1}Q_3R_{ff2}Q_3(X_1)_{n1}$, where R_{ff} is a fluoroalkyl, R_{ff2} is a fluoroalkylene, Q_3 is a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene group, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof; X_1 is a free-radically reactive group selected from (meth)acryl, $-SH$, allyl, or vinyl groups and $n1$ is independently 1 to 3. Typical Q_3 groups include: $-SO_2N(R)CH_2CH_2-$; $-SO_2N(CH_2CH_2)_2-$; $-(CH_2)_m-$; $-CH_2O(CH_2)_3-$; and $-C(O)NRCH_2CH_2-$, where R is H or lower alkyl of 1 to 4 carbon atoms and m is 1 to 6. Preferably the fluoroalkyl or fluoroalkylene group is a perfluoroalkyl or perfluoroalkylene group. One preferred class of fluoroalkyl- or alkylene-substituted compatibilizers meeting these criteria for use in the composition of the hard coat layer 18 is the perfluorobutyl-substituted acrylate compatibilizers. Exemplary, non-limiting perfluorobutyl-substituted acrylate compatibilizers meeting these criteria and useful in the present inven-

tion include one or more of $C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$, $C_4F_9SO_2N(CH_2CH_2OC(O)CH=CH_2)_2$, or $C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)C(CH_3)=CH_2$. The free-radically reactive fluoroalkyl or fluoroalkylene group-containing compatibilizers described above are preferably added at between about 0.5% and 20%, and more preferably between about 1% and 10%, of the total solids of the hard coat composition.

[0062] One non-limiting example of a preferred fluoroalkyl-substituted compatibilizer that may be utilized in the composition of the hard coat layer 18 is: (1H,1H,2H,2H)-perfluorodecyl acrylate, available from Lancaster Synthesis of Windham, N.H. Numerous other (meth)acryl compounds with perfluoroalkyl moieties that may also be utilized in the composition of the hard coat layer are mentioned in U.S. Pat. No. 4,968,116, to Hulme-Lowe et al., and in U.S. Pat. No. 5,239,026 (including perfluorocyclohexylmethyl methacrylate), to Babirad et al., which are assigned to Minnesota Mining and Manufacturing Company of St. Paul, Minn. and are herein incorporated by reference. Other fluorochemical (meth)acrylates that meet these criteria and may be utilized include, for example, 2,2,3,3,4,4,5,5-octafluorohexanediol diacrylate and ω -hydro 2,2,3,3,4,4,5,5-octafluoropentyl acrylate ($H-C_4F_8-CH_2O-C(O)-CH=CH_2$). Other fluorochemical (meth)acrylates that may be used alone, or as mixtures, are described in U.S. Pat. No. 6,238,798, to Kang et al., and assigned to Minnesota Mining and Manufacturing Company of St. Paul, Minn., and herein incorporated by reference.

[0063] Another compatibilizer that may be used is a fluoroalkyl- or fluoroalkylene-substituted thiol or polythiol to a ceramer hard coating composition. Non-limiting examples of this type of compatibilizer includes one or more of the following: $C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)CH_2SH$, $C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)CH_2CH_2SH$, $C_4F_9SO_2N(CH_3)CH_2CH_2SH$, and $C_4F_9SO_2N(CH_3)CH(OC(O)CH_2SH)CH_2OC(O)CH_2SH$.

[0064] The conventional hard coat material used as a portion of layer 18 in any of the preferred embodiments described above is a hydrocarbon-based material well known to those of ordinary skill in the optical arts. Most preferably, the hydrocarbon-based material is an acrylate-based hard coat material. One preferable hard coat material for use in the present invention is based on PETA (pentaerythritol tri/tetra acrylate). One commercially available form of pentaerythritol triacrylate ("PET3A") is SR444C and one commercially available form of pentaerythritol tetraacrylate ("PET4A") is SR295, each available from Sartomer Company of Exton, Pa.

[0065] However, other crosslinking agents may be used in the present invention. Useful crosslinking agents include, for example, poly(meth)acryl monomers selected from the group consisting of (a) 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, alkoxyated aliphatic diacrylate, alkoxyated cyclohexane dimethanol diacrylate, alkoxyated hexanediol diacrylate, alkoxyated neopentyl glycol diacrylate, caprolactone modified neopentylglycol hydroxypivalate diacrylate, caprolactone modified neopentylglycol hydroxypivalate dia-

crylate, cyclohexanedimethanol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, ethoxylated (10) bisphenol A diacrylate, ethoxylated (3) bisphenol A diacrylate, ethoxylated (30) bisphenol A diacrylate, ethoxylated (4) bisphenol A diacrylate, hydroxypivaldehyde modified trimethylolpropane diacrylate, neopentyl glycol diacrylate, polyethylene glycol (200) diacrylate, polyethylene glycol (400) diacrylate, polyethylene glycol (600) diacrylate, propoxylated neopentyl glycol diacrylate, tetraethylene glycol diacrylate, tricyclodecanedimethanol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate; (b) tri(meth)acryl containing compounds such as glycerol triacrylate, trimethylolpropane triacrylate, ethoxylated triacrylates (e.g., ethoxylated (3) trimethylolpropane triacrylate, ethoxylated (6) trimethylolpropane triacrylate, ethoxylated (9) trimethylolpropane triacrylate, ethoxylated (20) trimethylolpropane 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; (c) higher functionality (meth)acryl containing compounds such as ditrimethylolpropane tetraacrylate, dipentaerythritol pentaacrylate, ethoxylated (4) pentaerythritol tetraacrylate, caprolactone modified dipentaerythritol hexaacrylate; (d) oligomeric (meth)acryl compounds such as, for example, urethane acrylates, polyester acrylates, epoxy acrylates; polyacrylamide analogues of the foregoing; and combinations thereof. Such compounds are widely available from vendors such as, for example, Sartomer Company of Exton, Pa.; UCB Chemicals Corporation of Smyrna, Ga.; and Aldrich Chemical Company of Milwaukee, Wis. Additional useful (meth)acrylate materials include hydantoin moiety-containing poly(meth)acrylates, for example, as described in U.S. Pat. No. 4,262,072 (Wendling et al.).

[0066] 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 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. No. 4,654,233 (Grant et al.); U.S. Pat. No. 4,855,184 (Klun et al.); and U.S. Pat. No. 6,224,949 (Wright et al.).

[0067] Useful free-radical thermal initiators include, for example, azo, peroxide, persulfate, and redox initiators, and combinations thereof.

[0068] Useful free-radical photoinitiators include, for example, those known as useful in the UV cure of acrylate polymers. Such initiators include benzophenone 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" from Ciba Specialty Chemicals Corporation of Tarrytown, N.Y.), benzoin methyl ether, benzoin ethyl ether, benzoin n-butyl

ether; acetophenone and its derivatives such as 2-hydroxy-2-methyl-1-phenyl-1-propanone (commercially available under the trade designation "DAROCUR 1173" from Ciba Specialty Chemicals Corporation) and 1-hydroxycyclohexyl phenyl ketone (commercially available under the trade designation "IRGACURE 184", also from Ciba Specialty Chemicals Corporation); 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone commercially available under the trade designation "IRGACURE 907", also from Ciba Specialty Chemicals Corporation); 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone commercially available under the trade designation "IRGACURE 369" 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", 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", "IRGACURE 1800", "IRGACURE 1850", "IRGACURE 819", "IRGACURE 2005", "IRGACURE 2010", "IRGACURE 2020" and "DAROCUR 4265". Combinations of two or more photoinitiators may be used. Further, sensitizers such as 2-isopropyl thioxanthone, commercially available from First Chemical Corporation, Pascagoula, Miss., may be used in conjunction with photoinitiator(s) such as "IRGACURE 369".

[0069] The composition of any of these preferred embodiments is applied to an optical substrate layer **16** of an optical display **12** and photocured to form the easy to clean, stain and ink repellent optical hard coating layer **18**. The presence of the urethane functionality, in addition to the fluorocarbon component, in the additive eliminates the need for comonomers introduced to the composition to compatibilize the fluorochemical component with the hydrocarbon-based crosslinker.

[0070] In still another preferred embodiment, the hard coat material forming layer **18** of any of the above-preferred embodiments further contains surface modified inorganic particles that add mechanical strength to the resultant coating. One example of such particles is colloidal silica reacted with a methacryl silane coupling agent such as A-174 (available from Natrochem, Inc.), other dispersant aids such as N,N dimethylacrylamide and various other additives (stabilizers, initiators, etc.).

[0071] In still another preferred embodiment of any of the above preferred embodiments described above, a particulate matting agent is incorporated into the composition of the layer **18** in order to impart anti-glare properties to the layer **18**. The particulate matting agent also prevents the reflectance decrease and uneven coloration caused by interference with an associated hard coat layer. The particulate matting agent should preferably be transparent, exhibiting transmission values of greater than about 90%. Alternatively, or in addition thereto, the haze value is preferably less than about 5%, and more preferably less than about 2%, and most preferably less than about 1%.

[0072] Exemplary systems incorporating matting agents into a hard coating layer, but having a different hard coating

composition, are described, for example, in U.S. Pat. No. 6,693,746, and herein incorporated by reference. Further, exemplary matte films are commercially available from U.S.A. Kimoto Tech of Cedartown, Ga., under the trade designation "N4D2A."

[0073] The amount of particulate matting agent added is between about 0.5 and 10% of the total solids of the composition, depending upon the thickness of the layer **18**, with a preferred amount around 2%. The anti-glare layer **18** preferably has a thickness of 0.5 to 10 microns, more preferably 0.8 to 7 microns, which is generally in the same thickness range of gloss hard coatings.

[0074] The average particle diameter of the particulate matting agent has a predefined minimum and maximum that is partially dependent upon the thickness of the layer. However, generally speaking, average particle diameters below 1.0 microns do not provide the degree of anti-glare sufficient to warrant inclusion, while average particle diameters exceeding 10.0 microns deteriorate the sharpness of the transmission image. The average particle size is thus preferably between about 1.0 and 10.0 microns, and more preferably between 1.7 and 3.5 microns, in terms of the number-averaged value measured by the Coulter method.

[0075] As the particulate matting agent, inorganic particles or resin particles are used including, for example, amorphous silica particles, TiO₂ particles, Al₂O₃ particles, cross-linked acrylic polymer particles such as those made of cross-linked poly(methyl methacrylate), cross-linked polystyrene particles, melamine resin particles, benzoguanamine resin particles, and cross-linked polysiloxane particles. By taking into account the dispersion stability and sedimentation stability of the particles in the coating mixture for the anti-glare layer and/or the hard coat layer during the manufacturing process, resin particles are more preferred, and in particular cross-linked polystyrene particles are preferably used since resin particles have a high affinity for the binder material and a small specific gravity.

[0076] As for the shape of the particulate matting agent, spherical and amorphous particles can be used. However, to obtain a consistent anti-glare property, spherical particles are desirable. Two or more kinds of particulate materials may also be used in combination.

[0077] Thin coating layers **18** of any of the preferred embodiments can be applied to the optical substrate **16** using a variety of techniques, including dip coating, forward and reverse roll coating, wire wound rod coating, and die coating. Die coaters include knife coaters, slot coaters, slide coaters, fluid bearing coaters, slide curtain coaters, drop die curtain coaters, and extrusion coaters among others. Many types of die coaters are described in the literature such as by Edward Cohen and Edgar Guttoff, *Modern Coating and Drying Technology*, VCH Publishers, NY 1992, ISBN 3-527-28246-7 and Guttoff and Cohen, *Coating and Drying Defects: Troubleshooting Operating Problems*, Wiley Interscience, NY ISBN 0-471-59810-0.

[0078] A die coater generally refers to an apparatus that utilizes a first die block and a second die block to form a manifold cavity and a die slot. The coating fluid, under pressure, flows through the manifold cavity and out the coating slot to form a ribbon of coating material. Coatings can be applied as a single layer or as two or more superimposed layers. Although it is usually convenient for the substrate to be in the form of a continuous web, the substrate may also be a succession of discrete sheets.

[0079] To prove the effectiveness of the hard coat formulations according to each preferred embodiment of the present invention described above, sample hard coats having the given compositions were formulated and applied to PET substrates and compared to hard coat formulations having less than all the desired components. The coatings were visually inspected and tested for ink repellency, durability and surface roughness. The experimental procedures and tabulated results are described below:

I. EXPERIMENTAL PROCEDURES

A: Ingredients

[0080] Unless otherwise noted, as used in the examples, "HFPO—" refers to the end group $F(CF(CF_3)CF_2O)_aCF(CF_3)$ — wherein a averages about 6.22, with an average molecular weight of 1,211 g/mol, can be prepared according to the method reported in U.S. Pat. No. 3,250,808 (Moore et al.), the disclosure of which is incorporated herein by reference, with purification by fractional distillation.

[0081] Polyisocyanates Desmodur™ (Des) N100, Desmodur™ 3300, Desmodur™ TPLS2294, Desmodur™ N 3600, and Isophorone diisocyanate (IPDI) were obtained from Bayer Polymers LLC, of Pittsburgh, Pa.

[0082] PAPI (Poly[(phenyl isocyanate)-co-formaldehyde]) (MW about 375), is available from Sigma Aldrich of Milwaukee, Wis.

[0083] $C_6F_{13}C_2H_4OH$ is available from Sigma Aldrich of Milwaukee, Wis.

[0084] 4-methoxy phenol (MEHQ) is available from Sigma Aldrich of Milwaukee, Wis.

[0085] $HO(CH_2)_{10}OH$ is available from Sigma Aldrich of Milwaukee, Wis.

[0086] FOX-diol ($H(OCH_2CCH_3(CH_2OCH_2CF_3)CH_2)_xOH$) (MW about 1342), is available from Omnova Solutions Inc. of Akron, Ohio.

[0087] Pentaerythritol tetracrylate ("PET4A"), under the trade designation "SR295", was obtained from Sartomer Company of Exton, Pa.

[0088] Pentaerythritol triacrylate ("PET3A"), under the trade designation "SR444C", was obtained from Sartomer Company of Exton, Pa.

[0089] Trimethylolpropane triacrylate ("TMPTA"), under the trade designation "SR351", was obtained from Sartomer Company of Exton, Pa.

[0090] Hydantoin hexaacrylate (HHA) was prepared as described in Example 1 of U.S. Pat. No. 4,262,072.

[0091] FBSEE ($C_4F_9SO_2N(C_2H_4OH)_2$), a fluorochemical diol, can be prepared as described in column 5, line 31 and in FIG. 9 of U.S. Pat. No. 3,734,962 (1973).

[0092] MeFBSE ($C_4F_9SO_2N(CH_3)CH_2CH_2OH$) was prepared by essentially following the procedure described in U.S. Pat. No. 6,664,354 (Savu et al.), Example 2, Part A.

[0093] FBSEA ($C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)CH=CH_2$) is made by the procedure of Examples 2A and 2B of WO 01/30873 to Savu et al.

[0094] HFPO AEA (HFPO— $C(O)NHCH_2CH_2OC(O)CH=CH_2$) was prepared as

described in File number U.S. application Ser. No. 10/841159, filed May 7, 2004 (Docket No. 57927US002); under Preparation of Monofunctional Perfluoropolyether Acrylate (FC-1).

[0095] Fomblin Zdol ($HOCH_2CF_2(OCF_2CF_2)_n(OCF_2)_mCH_2OH$) is available from Solvay Solexis, Inc. of Italy.

[0096] Hydroxyethyl acrylate (HEA) is available from Sigma Aldrich of Milwaukee, Wis.

[0097] $H_2NCH_2CH_2CH_2Si(OCH_3)_3$ is available from Sigma Aldrich of Milwaukee, Wis.

[0098] $HSCH_2CH_2CH_2Si(OCH_3)_3$ is available from Sigma Aldrich of Milwaukee, Wis.

[0099] 2-isocyanato-ethyl-methacrylate ("IEM") ($CH_2=C(CH_3)CO_2CH_2CH_2NCO$), is available from Sigma Aldrich of Milwaukee, Wis.

[0100] The amines, 2-amino-2-ethyl-1,3-propane diol, and 1,1-bis-(hydroxyethyl)-1,3 aminopropane were obtained from Sigma-Aldrich of Milwaukee, Wis.

[0101] Acryloyl chloride was obtained from Sigma-Aldrich of Milwaukee Wis.

[0102] The UV photoinitiator, 1-hydroxycyclohexyl phenyl ketone used was obtained from Ciba Specialty Products, Tarrytown, N.Y. and sold under the trade designation "Irgacure 184."

[0103] The photoinitiator 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one used was obtained from Ciba Specialty Products, Tarrytown, N.Y. and sold under the trade designation "Irgacure 907."

[0104] Methyl perfluorobutyl ether (HFE 7100) was obtained from 3M Company, St. Paul, Minn.

[0105] Dibutyltin dilaurate (DBTDL) was obtained from Sigma Aldrich of Milwaukee, Wis.

B. Preparation of Experimental Materials

[0106] Unless otherwise noted, "MW" refers to molecular weight and "EW" refers to equivalent weight. Further, "° C." may be used interchangeably with "degrees Celsius" and "mol" refers to moles of a particular material and "eq" refers to equivalents of a particular material. Further, "Me" constitutes a methyl group and may be used interchangeably with

Preparation No. 1. Preparation of HFPO— $C(O)CH_3$

[0107] As used in the examples, "HFPO—" refers to the end group $F(CF(CF_3)CF_2O)_aCF(CF_3)$ — wherein a has average values of about 4.41, 6.2, 6.85, and 8.07. The material $F(CF(CF_3)CF_2O)_aCF(CF_3)COOCH_3$ (HFPO— $C(O)OCH_3$) can be prepared according to the method reported in U.S. Pat. No. 3,250,808 (Moore et al.), the disclosure of which is incorporated herein by reference, with purification by fractional distillation.

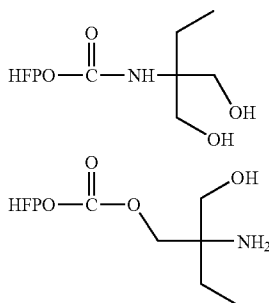
Preparation No. 2. Preparation of HFPO diol HFPO— $C(O)NHCH_2CH_2CH_2N(CH_2CH_2OH)_2$ (HFPODO, MW about 1341)

[0108] To a 500 ml 3-necked flask equipped with a stir bar and reflux condenser was charged 100 g (MW about 1210.6,

0.0826 mol) HFPO—C(O)OCH₃, and 13.40 g (MW=162.2, 0.0826 mol) H₂NCH₂CH₂CH₂N(CH₂CH₂OH)₂. The mixture was reacted neat at 130 degrees Celsius for 6 hours. From Fourier Transform Infrared Spectroscopy (FTIR) analysis, the amide —C(O)NH— was formed as the ester signal (—CO₂—) disappeared. The desired product, HFPO—C(O)NHCH₂CH₂CH₂N(CH₂CH₂OH)₂ was obtained as a viscous yellow liquid after concentration at 55 degrees Celsius under aspirator vacuum.

Preparation No. 3. Preparation of HFPO—C(O)N(H)C(CH₂OH)₂CH₂CH₃ Starting Material

[0109] To a 500 ml 3-necked flask equipped with a stir bar and reflux condenser was charged 11.91 g (0.1 mol) H₂NC(CH₂OH)₂CH₂CH₃ and 60 g tetrahydrofuran (“THF”). Next via dropping funnel was added 121.1 g (0.1 mol) HFPO—C(O)OCH₃ over about 80 minutes at a bath temperature of about 85 degrees Celsius. The reaction was cloudy at first, but became clear about 1 hour into the reaction. After addition was complete, the heating bath was shut off and the reaction was allowed to cool for three days. The material was concentrated at 55 degrees Celsius under aspirator vacuum to yield 130.03 g of a light colored syrup. NMR analysis showed the product to be an 87:13 mixture of the structures I and II as follows:



Preparation No. 4. Preparation of HFPO—C(O)NHCH₂CH₂OH of Different Molecular Weights

[0110] HFPO—C(O)N(H)CH₂CH₂OH of different molecular weights (938.5, 1344, and 1547.2) were made by a procedure similar to that described in U.S. Publication No. 2004-0077775 (Docket Number 57823), entitled “Fluorochemical Composition Comprising a Fluorinated Polymer and Treatment of a Fibrous Substrate Therewith,” filed on May 24, 2002, for Synthesis of HFPO-oligomer alcohols, substituting F(CF(CF₃)CF₂O)_aCF(CF₃)C(O)OCH₃ with a=4.41, 6.85, and 8.07 respectively, for F(CF(CF₃)CF₂O)_aCF(CF₃)C(O)CH₃ with a=6.2.

C. General Procedure-Synthesis of Perfluoropolyether Urethane Multiacrylate

Preparation No. 5. Preparation of Des N100/0.66 PET3A/0.33 HFPO

[0111] A 500 ml roundbottom flask equipped with magnetic stir bar was charged with 25.0 g (0.131 eq, 191 EW) Des N100, 43.13 g (0.087 eq, 494.3 EW) of Sartomer SR444C, 25.3 mg of MEHQ, and 126.77 g methyl ethyl ketone (MEK). The reaction was swirled to dissolve all the reactants, the flask was placed in a oil bath at 60 degrees Celsius, and fitted with a condenser under dry air. Two drops of dibutyltin dilaurate was added to the reaction. After 1 hour, 58.64 g (0.0436 eq, 1344 EW) F(CF(CF₃)CF₂O)_{6.85}CF(CF₃)C(O)NHCH₂CH₂OH was added to the reaction via addition funnel over about 75 minutes. The reaction was monitored by FTIR and showed a small isocyanate absorption at 2273 cm⁻¹ after about 5 hours of reaction, but no isocyanate absorption at 7.5 hours of reaction. The material was used as a 50% solids solution in MEK. The HFPO multiacrylate urethanes preparations shown in Table 1 below, listed as Preparation Nos. 5.1 through 5.19 respectively, were all made according to this general procedure, using the appropriate mole fractions of materials noted in the table. These preparations were then used to verify the inventive formulations of the present invention as used in hardcoat 18.

TABLE 1

Perfluoropolyether Urethane Multiacrylates			
Preparation Number	Isocyanate used (set at 100 Mole percent NCO in all cases)	Mole percent PET3A	Mole percent HFPO—C(O)NHCH ₂ CH ₂ OH (MW 1344)
5.1	Des N100	95	5
5.2	Des N100	85	15
5.3	Des N100	75	25
5.4	Des N100	66.6	33.3
5.5	Des N100	50	50
5.6	Des N100	33.3	66.6
5.7	Des N100	5	95
5.8	Des N3300	85	15
5.9	Des N3300	75	25
5.10	Des N3300	66.6	33.3
5.11	Des N3300	50	50
5.12	IPDI	75	25
5.13	Des TPLS2294	85	15
5.14	Des N3600	85	15

TABLE 1-continued

Perfluoropolyether Urethane Multiacrylates			
Preparation Number	Isocyanate used (set at 100 Mole percent NCO in all cases)	Mole percent PET3A	
			Mole percent HFPO—C(O)NH(CH ₂) ₃ NHCH ₃ (See Preparation number 22)
5.15	Des N100	85	15
			Mole percent HFPO—C(O)NHCH ₂ CH ₂ OH (MW 938.5)
5.16	Des N100	85	15
5.17	Des N100	75	25
			Mole percent HFPO—C(O)NHCH ₂ CH ₂ OH (MW 1547.2)
5.18	Des N100	85	15
5.19	Des N100	75	25

Preparation No. 6. Preparation of Des N100/0.90 PET3A/0.15 HFPO

[0112] A 500 ml roundbottom 2-necked flask equipped with magnetic stir bar was charged with 25.00 g (0.131 eq, 191 EW) Des N100, 26.39 g (0.0196 eq, 1344 EW) F(CF(CF₃)CF₂O)_{6.85} CF(CF₃)C(O)NHCH₂CH₂OH, and 109.62 g MEK, and was swirled to produce a homogeneous solution. The flask was placed in an 80 degrees Celsius bath, charged with 2 drops of dibutyltin dilaurate catalyst, and fitted with a condenser. The reaction was cloudy at first, but cleared within two minutes. At about 1.75 hours, the flask was removed from the bath and 2.42 g of MEK was added to compensate for lost solvent. A 2.0 g sample was removed from the flask, leaving (1-(2.0/161.01) or 0.9876 weight fraction, of the reaction, and 57.51 g (98.76% of 58.23 g) (0.116 mol, 494.3 equivalent weight) PET3A was added to the reaction, which was placed in a 63 degrees Celsius bath. At about 5.25 hours FTIR showed no isocyanate absorption at 2273 cm⁻¹, and 0.56 g MEK was added to compensate for solvent lost to bring the material to 50% solids.

Preparation No.7. Preparation of Des N100/0.90 HEA/0.10 HFPO

[0113] By a procedure similar to that for Preparation 5.1 shown in Table 1 above, 28.34 g (0.1484 eq) Des N100, 19.94 g (0.148 eq) F(CF(CF₃)CF₂O)_{6.85} CF(CF₃)C(O)NHCH₂CH₂OH, in 63.8 g MEK, with 2 drops of DBTDL, 0.03 g BHT were reacted for 1 hour, followed by addition of 15.51 g (0.1336 eq) HEA to provide, after reaction overnight, the desired material.

Preparation No. 8. Preparation of Des N100/HFPO—C(O)NHCH₂CH₂OH/MeFBSE/PET3A (in 30/10/10/10 Ratio):

[0114] A 120 ml bottle was charged with 5.73 g Des N100 (EW about 191, about 30 milliequivalents NCO), 3.57 g MeFBSE (MW=357, 10 milliequivalents OH), 13.44 g HFPO—C(O)NHCH₂CH₂OH (MW about 1344, 10 milliequivalents OH), 4.94 g PET3A (EW about 494.3, about 10 milliequivalents OH), 5 drops of dibutyltin dilaurate catalyst

and 42 g MEK (about 40% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 20 hours after sealing the bottle. A clear solution was obtained after reaction, which showed no unreacted —NCO signal in FTIR analysis.

Preparation No. 9. Preparation of Des N100/HFPO—C(O)NHCH₂CH₂OH/MeFBSE/PET3A (in 40/10/10/20 Ratio):

[0115] A 120 ml bottle was charged with 7.64 g Des N100 (EW about 191, about 40 milliequivalents NCO), 3.57 g MeFBSE (MW=357, 10 milliequivalents OH), 13.44 g HFPO—C(O)NHCH₂CH₂OH (MW about 1344, 10 milliequivalents OH), 9.89 g PET3A (EW about 494.3, about 20 milliequivalents OH), 5 drops of dibutyltin dilaurate catalyst and 52 g MEK (about 40% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 20 hours after sealing the bottle. A clear solution was obtained after reaction, which showed no unreacted —NCO signal in FTIR analysis.

Preparation No. 10. Preparation of Des 100/C₆F₁₃C₂H₄OH/PET3A (in 20/10/10 Ratio)

[0116] A 120 ml bottle was charged with 3.82 g Des N100 (EW about 191, about 20 milliequivalents NCO), 3.64 g C₆F₁₃C₂H₄OH (MW=363, 10 milliequivalents OH), 4.94 g PET3A (EW about 494.3, about 10 milliequivalents OH), 3 drops of dibutyltin dilaurate catalyst and 19 g MEK (about 40% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 20 hours after sealing the bottle. A clear solution was obtained after reaction, which showed no unreacted —NCO signal in FTIR analysis.

Preparation No. 11. Preparation of Des 100/HO(CH₂)₁₀OH/HFPO—C(O)NHCH₂CH₂OH/PET3A (in 60/20/15/25 Ratio)

[0117] A 120 ml bottle was charged with 11.46 g Des N100 (EW about 191, about 60 milliequivalents NCO), 1.74 g HO(CH₂)₁₀OH (MW=174, 20 milliequivalents OH), 20.16 g HFPO—C(O)NHCH₂CH₂OH (MW about 1344, 15 mil-

liequivalents OH), 12.36 g PET3A (EW about 494.3, about 25 milliequivalents OH), 5 drops of dibutyltin dilaurate catalyst and 106 g MEK (about 30% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 20 hours after sealing the bottle. A clear solution was obtained after reaction, which showed no unreacted —NCO signal in FTIR analysis.

Preparation No. 12. Preparation of Des N100/FBSEE/HFPO—C(O)NHCH₂CH₂OH/PET3A (in 30/10/7.5/12.5 Ratio)

[0118] A 120 ml bottle was charged with 5.73 g Des N100 (EW about 191, about 30 milliequivalents NCO), 1.94 g FBSEE (MW=387, 10 milliequivalents OH), 10.08 g HFPO—C(O)NHCH₂CH₂OH (MW about 1344, 7.5 milliequivalents OH), 6.18 g PET3A (EW about 494.3, about 12.5 milliequivalents OH), 5 drops of dibutyltin dilaurate catalyst and 56 g MEK (about 30% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 20 hours after sealing the bottle. A clear solution was obtained after reaction, which showed no unreacted —NCO signal in FTIR analysis.

Preparation No. 13. Preparation of Des N3300/HFPODO/PET3A (in 30/10/20 Ratio)

[0119] A 240 ml bottle was charged with 5.79 g Des N3300 (EW about 193, about 30 milliequivalents NCO), 6.71 g HFPODO (MW about 1341, 10 milliequivalents OH), 9.89 g PET3A (EW about 494.3, about 20 milliequivalents OH), 5 drops of dibutyltin dilaurate catalyst and 52 g MEK (about 30% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 10 hours after sealing the bottle. There was a small amount of precipitate formed upon standing at room temperature. FTIR analysis showed no unreacted —NCO signal.

Preparation No. 14. Preparation of Des N3300/HFPODO/HFPO—C(O)NHCH₂CH₂OH/PET3A (in 30/10/5/15 Ratio)

[0120] A 240 ml bottle was charged with 5.79 g Des N3300 (EW about 193, about 30 milliequivalents NCO), 6.71 g HFPODO (MW about 1341, 10 milliequivalents OH), 6.72 g HFPO—C(O)NHCH₂CH₂OH (MW about 1344, 5 milliequivalents OH), 7.42 g PET3A (EW about 494.3, about 15 milliequivalents OH), 5 drops of dibutyltin dilaurate catalyst, 27 g MEK and 10 g C₄F₉OCH₃ (about 20% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 10 hours after sealing the bottle. Separation into two liquid phases occurred upon standing at room temperature. Addition of more C₄F₉OCH₃ produced a clear homogeneous solution at about 17% solids. FTIR analysis showed no unreacted —NCO signal.

Preparation No. 15. Preparation of Des N3300/HFPODO/MeFBSE/PET3A (in 30/10/5/15 Ratio)

[0121] A 120 ml bottle was charged with 5.79 g Des N3300 (EW about 191, about 30 milliequivalents NCO), 6.71 g HFPODO (MW about 1341, 10 milliequivalents OH), 1.79 g MeFBSE (MW=357, 5 milliequivalents OH), 7.42 g PET3A (EW about 494.3, about 15 milliequivalents OH), 5 drops of dibutyltin dilaurate catalyst and 51 g MEK (about 30% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 10 hours after sealing the bottle. A clear solution was obtained at 70 degrees Celsius after reaction, but there was a small amount of precipitate formed upon standing at room temperature. FTIR analysis showed no unreacted —NCO signal.

Preparation No. 16. Preparation of Des N3300/Fox-Diol/HFPO—C(O)NHCH₂CH₂OH/PET3A (in 30/10/5/15 Ratio)

[0122] A 240 ml bottle was charged with 5.79 g Des N3300 (EW about 191, about 30 milliequivalents NCO), 6.71 g Fox-Diol (MW about 1341, 10 milliequivalents OH), 6.72 g HFPO—C(O)NHCH₂CH₂OH (MW about 1344, 5 milliequivalents OH), 7.40 g PET3A (EW about 494.3, about 15 milliequivalents OH), 5 drops of dibutyltin dilaurate catalyst, 56 g MEK and 50 g C₄F₉OCH₃ (about 19% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 10 hours after sealing the bottle. A clear solution was obtained after reaction. FTIR analysis showed no unreacted —NCO signal.

Preparation No. 17. Preparation of Des N3300/Fomblin Zdol/PET3A (in 30/10/20 Ratio)

[0123] A 240 ml bottle was charged with 5.79 g Des N3300 (EW about 191, about 30 milliequivalents NCO), 10.0 g Fomblin Zdol (MW about 2000, 10 milliequivalents OH), 9.89 g PET3A (EW about 494.3, about 20 milliequivalents OH), 5 drops of dibutyltin dilaurate catalyst, 63 g MEK and 40 g C₄F₉OCH₃ (about 18% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 10 hours after sealing the bottle. A clear solution was obtained after reaction. FTIR analysis showed no unreacted —NCO signal.

Preparation No. 18. Preparation of Des N3300/HHA/HFPO—C(O)NHCH₂CH₂OH/PET3A (in 30/10/10/10 Ratio)

[0124] A 240 ml bottle was charged with 5.79 g Des N3300 (EW about 191, about 30 milliequivalents NCO), 6.14 g HHA (MW about 1228, 10 milliequivalents OH), 12.29 g HFPO—C(O)NHCH₂CH₂OH (MW about 1229, 10 milliequivalents OH), 4.93 g PET3A (EW about 494.3, about 10 milliequivalents OH), 5 drops of dibutyltin dilaurate catalyst, 85 g MEK and 25 g C₄F₉OCH₃ (about 20% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 10 hours after sealing the bottle. A clear solution was obtained after reaction. FTIR analysis showed no unreacted —NCO signal.

Preparation No. 19. Preparation of PAPI/HFPO—C(O)NHCH₂CH₂OH/PET3A (in 28/8/20 Ratio)

[0125] A 120 ml bottle was charged with 3.75 g PAPI (EW about 134, about 28 milliequivalents NCO), 10.75 g HFPO—C(O)NHCH₂CH₂OH (MW about 1344, 8 milliequivalents OH), 9.88 g PET3A (EW about 494.3, about 20 milliequivalents OH), 5 drops of dibutyltin dilaurate catalyst and 37 g MEK (about 40% solid) under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 5 hours after sealing the bottle. A clear solution was obtained after reaction. FTIR analysis showed no unreacted —NCO.

D. General Preparation of perfluoropolyether urethane multiacrylates Containing trialkoxysilane Functionality

Preparation No. 20. Preparation of Des N100/0.75 PET3A/0.15 HFPO/0.15 H₂N(CH₂)₃Si(OCH₃)₃

[0126] A 500 ml roundbottom flask equipped with stir bar was charged with 25.00 g (0.1309 eq) Des N100, 103.43 g MEK, 2 drops of DBTDL, 26.39 g (0.0196 eq) HFPO—C(O)NHCH₂CH₂OH, 1344 equivalent weight, and 0.05 g BHT, and placed in a 60 degrees Celsius oil bath. After 1

hour, 3.52 g (0.0196 eq) $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ was added to the reaction, followed in 10 minutes by the addition of 48.52 g (0.0982 eq, 494.3 equivalent weight) SR444C. The reaction showed no residual isocyanate by FTIR after a total reaction time of 5.75 hours.

[0127] The preparation of other perfluoropolyether urethane multiacrylates containing trialkoxysilane functionality was done by a similar procedure, substituting the appropriate amounts of materials, and are summarized in Table 2 as Preparation Nos. 20.1 through 20.4:

TABLE 2

Preparation Number	Isocyanate used (set at 100 Mole percent NCO in all cases)	Mole percent PET3A	Mole percent	
			HFPO—C(O)NHCH ₂ CH ₂ OH	H ₂ N(CH ₂) ₃ -Si(OCH ₃) ₃
20.1	Des N100	75	15	15
20.2	Des N100	60	15	30
20.3	Des N100	45	15	45
20.4	Des N100	30	15	60

Preparation No. 21. Preparation of Des N3300HFPO—C(O)NHCH₂CH₂OH/HSC₃H₆Si(OCH₃)₃/PET3A (in 30/8/2/20 Ratio)

[0128] A 240 ml bottle was charged with 5.79 g Des N3300 (EW about 193, about 30 milliequivalents NCO), 9.83 g HFPO—C(O)NHCH₂CH₂OH (MW about 1229, 8 milliequivalents OH), 0.39 g HSC₃H₆Si(OMe)₃ (MW=196, 2 milliequivalents SH), 5 drops of dibutyltin dilaurate catalyst, 40 g MEK and 20 g C₄F₉OCH₃ under nitrogen. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 2 hours after sealing the bottle. Then, 4.46 g PET3A (EW about 494.3, about 20 milliequivalents OH) was added at room temperature under nitrogen. The solution was allowed to react for another 6 hours at 70 degrees Celsius. A clear solution was obtained after reaction, which showed no unreacted —NCO signal in FTIR analysis.

Preparation No. 22. Preparation of HFPO—C(O)NHCH₂CH₂CH₂NHCH₃ Starting material

[0129] A 1-liter round-bottom flask was charged with 291.24 g (0.2405 mol) of HFPO—C(O)OCH₃ and 21.2 g (0.2405 mol) N-methyl-1,3-propanediamine, both at room temperature, resulting in a cloudy solution. The flask was swirled and the temperature of the mixture rose to 45 degrees Celsius, and to give a water-white liquid, which was heated overnight at 55 degrees Celsius. The product was then placed on a rotary evaporator at 75 degrees Celsius and 28 inches of Hg vacuum to remove methanol, yielding 301.88 g of a viscous slightly yellow liquid, nominal molecular weight is equal to 1267.15 g/mol.

Preparation No. 23. Preparation of HFPO—C(O)NHC(CH₂CH₃)(CH₂OC(=O)NHC₂H₄OC(O)C(CH₃)=CH₂)₂

[0130] A 240 ml bottle was charged with 6.49 g HFPO—C(O)NHC(CH₂CH₃)(CH₂OH)₂ (1298.5 MW, 5 mmol) ("Preparation No. 3"), 1.55 g IEM (OCNC₂H₄OC(O)C(CH₃)=CH₂, MW=155, 10 mmol), 3 drops of dibutyltin dilaurate catalyst, 50 mg BHT, 32 g ethyl acetate and 10 g C₄F₉OCH₃. The solution was reacted at 70 degrees Celsius in an oil bath with a magnetic stir bar for 8

hours after sealing the bottle. A clear solution was obtained after reaction, which showed no unreacted —NCO by in FTIR analysis, providing a solution of the product HFPO—C(O)NHC(CH₂CH₃)(CH₂OC(=O)NHC₂H₄OC(O)C(CH₃)=CH₂)₂.

Preparation No. 24. Preparation of HFPO—C(O)NHCH₂CH₂OC(=O)NHC₂H₄OC(O)C(CH₃)=CH₂) (HFPO—IEM)

[0131] A 120 ml bottle was charged with 71.20 g (MW 1229, 57.9 mmol) HFPO—C(O)NHC₂H₄OH, 9.0 g of

CH₂=C(CH₃)CO₂C₂H₄NCO (MW=155, 58 mmol), 52 g EtOAc, 3 drops of DBTDL and 1.5 mg of phenothiazine under nitrogen. The solution was heated in a oil bath at 70 degrees Celsius for 6 hours with a magnetic stirring after sealing the bottle. Fourier Transform Infrared Spectroscopy (FTIR) analysis indicated no remaining isocyanate.

E. Test Methods

[0132] Steel Wool Testing: The abrasion resistance of the cured films was tested cross-web to the coating direction by use of a mechanical device capable of oscillating cheesecloth or steel wool fastened to a stylus (by means of a rubber gasket) across the film's surface. The stylus oscillated over a 10 cm wide sweep width at a rate of 3.5 wipes/second wherein a "wipe" is defined as a single travel of 10 cm. The stylus had a flat, cylindrical geometry with a diameter of 1.25 inch (3.2 cm). The device was equipped with a platform on which weights were placed to increase the force exerted by the stylus normal to the film's surface. The cheesecloth was obtained from Summers Optical, EMS Packaging, a subdivision of EMS Acquisition Corp., Hatsfield, Pa. under the trade designation "Mil Spec CCC-c-440 Product #S12905". The cheesecloth was folded into 12 layers. The steel wool was obtained from Rhodes-American, a division of Homax Products, Bellingham, Wash. under the trade designation "#0000-Super-Fine" and was used as received. A single sample was tested for each example, with the weight in grams applied to the stylus and the number of wipes employed during testing reported.

[0133] Taber Testing: The Taber test was run according to ASTM D1044-99 using CS-10 wheels.

[0134] Contact Angle: 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, Mass.), on a video contact angle analyzer available as product number VCA-2500XE from AST Products (Billerica, Mass.). Reported values are the averages of measure-

ments on at least three drops measured on the right and the left sides of the drops. Drop volumes were 5 μL for static measurements and 1-3 μL for advancing and receding. For hexadecane, only advancing and receding contact angles are reported because static and advancing values were found to be nearly equal.

[0135] Surface Smoothness (Dewetting): For some of the tables below, a visual inspection was made regarding the smoothness of the applied dry film. While the measurement of smoothness by visual inspection is a subjective determination, a smooth film, for the purposes of the present invention, is deemed to be a surface layer that is substantially continuous and free of visible defects in reflected light as observed by visual observation of the coating surface at a wide variety of possible angles. Typically, visual observation is accomplished by looking at the reflection of a light source from the coating surface at an angle of about 60 degrees from perpendicular. Visual defects that may be observed include but are not limited to pock marks, fish eyes, mottle, lumps or substantial waviness, or other visual indicators known to one of ordinary skill in the art in the optics and coating fields. Thus, a "rough" surface as described below has one or more of these characteristics, and may be indicative of a coating material in which one or more components of the composition are incompatible with each other. Conversely, a substantially smooth coating, characterized below as "smooth" for the purpose of the present invention, presumes to have a coating composition in which the various components, in the reacted final state, form a coating in which the components are compatible or have been modified to be compatible with one another and further has little, if any, of the characteristics of a "rough" surface.

[0136] The surfaces may also be classified for dewetting as "good," "very slight" (v.sl), "slight" (sl), "fair," or "poor." A "good" surface meaning a substantially smooth surface having little dewetting. A "very slight," "slight", or "fair" categorization means that the surface has an increasing portion of defects but is still substantially acceptable for smoothness. A "poor" surface has a substantial amount of defects, indicating a rough surface that has a substantial amount of dewetting.

F. Experiments

[0137] The ceramer hardcoat ("HC-1") used in the examples was made as described in column 10, line 25-39 and Example 1 of U.S. Pat. No. 5,677,050 to Bilkadi, et al.

Experiment 1

[0138] Solutions as generally described in Tables 3-5 below were prepared at 30% solids in a solvent blend of 1:1 isopropanol:ethyl acetate and coated at a dry thickness of about 4 microns using a number 9 wire wound rod onto 5-mil Melinex 618 film. The coatings were dried in an 80 degree Celsius oven for 1 minute and then placed on a conveyer belt coupled to a ultraviolet ("UV") light curing device and UV cured under nitrogen using a Fusion 500 watt H bulb at 20 ft/min. The values reported in the Tables refer to the percent solids of each component of the dried coating. The coatings were then visually inspected for surface smoothness (dewetting). The coatings were also tested for durability of ink repellency. Durability was assessed using a modified Oscillating Sand Method (ASTM F 735-94). An

orbital shaker was used (VWR DS-500E, from VWR Bristol, Conn.). A disk of diameter 85 mm was cut from the sample, placed in a 16 ounce jar lid (jar W216922 from Wheaton, Millville, N.J.), and covered with 50 grams of 20-30 mesh Ottawa sand (VWR, Bristol, Conn.). The jar was capped and placed in the shaker set at 300 rpm for 15 minutes. After shaking, a Sharpie permanent marker was used to draw a line across the diameter of the disk surface. The portion of the ink line that did not bead up was measured. A measure of 85 mm would be no repellency; a measure of 0 mm would be perfect durability. Results are shown in Tables 3 and 4.

TABLE 3

Percentage HC-1 in coating	Preparation number	Percentage Preparation in coating	Dewet	Ink Repel.
99.9	5.5	0.1	good	65
99.8	5.5	0.2	v. sl	53
99.7	5.5	0.3	fair	49
99.86	5.4	0.14	sl	51
99.72	5.4	0.28	sl	44
99.58	5.4	0.42	sl	40
99.7	5.3	0.3	good	35
99.4	5.3	0.6	v. sl	34
99.1	5.3	0.9	sl	31
99.9	5.11	0.1	good	65
99.8	5.11	0.2	v. sl	49
99.7	5.11	0.3	sl	50
99.86	5.10	0.14	good	60
99.72	5.10	0.28	good	37
99.58	5.10	0.42	v. sl	38
99.7	5.9	0.3	good	42
99.4	5.9	0.6	good	43
99.1	5.9	0.9	v. sl	47

[0139] Selected coatings, before sand testing, from another coating run were analyzed for contact angles and the results are shown in Table 4.

TABLE 4

Preparation number	Wt % in HC-1	Water static/Adv/Rec CA (deg)	Hexadecane Adv/Rec CA (deg)
5.3	0.3	108/119/91	71/65
5.3	0.6	109/120/90	72/67
5.5	1.2	108/120/90	73/67
5.9	1.2	109/121/89	74/67
4.11	1.2	108/118/85	74/64

[0140] Another set of examples was run according to the same procedure as examples in Table 1. The results are shown in Table 5.

TABLE 5

Percentage HC-1 in coating	Preparation number	Percentage Preparation in coating	Smoothness	Ink Repellency
99.8	5.3	0.2	good	32
99.7	5.3	0.3	good	22
99.6	5.3	0.4	v. sl	23
99.76	5.2	0.24	good	46
99.52	5.2	0.48	good	26
99.33	5.2	0.67	good	42

TABLE 5-continued

Percentage HC-1 in coating	Preparation number	Percentage Preparation in coating	Smoothness	Ink Repellency
99.8	5.10	0.2	good	25
99.7	5.10	0.3	good	42
99.6	5.10	0.4	v. sl	42
99.64	5.9	0.36	good	26
99.43	5.9	0.57	good	12
99.22	5.9	0.78	good	33
99.76	5.8	0.24	good	47
99.52	5.8	0.48	good	18
99.33	5.8	0.67	v. sl	33

[0141] Table 6 shows the results of another set of examples that was run at two levels of additives in an HC-1 hardcoat in which the sand test was run for 25 minutes at 300 rpm. The examples were run according to the same procedure as examples in Table 1 described above.

TABLE 6

Percentage HC-1 in coating	Preparation number	Percentage Preparation in coating	Smoothness	Ink Repellency
99.8	9	0.2	sl	20
99.0	9	1.0	sl	10
99.8	8	0.2	good	29
99.0	8	1.0	poor	25
99.8	10	0.2	good	38
99.0	10	1.0	good	30
99.8	11	0.2	good	40
99.0	11	1.0	fair	20
99.8	12	0.2	good	36
99.0	12	1.0	poor	22
99.8	19	0.2	good	20
99.0	19	1.0	sl	49
99.8	5.2	0.2	good	5

[0142] Table 7 shows the results of another set of examples that was run at two levels of additives in an HC-1 hardcoat in which the sand test was run for 25 minutes at 300 rpm and in a separate set for 35 minutes at 300 rpm. The examples were run according to the same procedure as examples in Table 1 described above.

TABLE 7

% HC-1 in coating	Preparation number	Percentage Preparation in coating	Smoothness	Repellency 25 min at 300 rpm	Repellency 35 min at 300 rpm
99.5	5.2	0.5	good	0	
99.5	5.2	0.5	good		10
99.8	5.1	0.2	good	35	
99.0	5.1	1.0	good	0	
99.0	5.1	1.0	good		36
99.8	5.6	0.2	sl	0	
99.0	5.6	1.0	poor	0	
99.8	5.7	0.2	poor	62	
99.0	5.7	1.0	poor	26	
99.8	5.12	0.2	good	0	
99.0	5.12	1.0	fair	0	
99.8	5.12	0.2	good		54
99.8	5.13	0.2	good	0	
99.0	5.13	1.0	good	0	
99.0	5.13	1.0	good		38
99.8	5.14	0.2	good	0	

TABLE 7-continued

% HC-1 in coating	Preparation number	Percentage Preparation in coating	Smoothness	Repellency 25 min at 300 rpm	Repellency 35 min at 300 rpm
99.0	5.14	1.0	good	0	
99.0	5.14	1.0	good		35
99.8	5.15	0.2	good	5	
99.0	5.15	1.0	good	0	
99.0	5.15	1.0	slight		11
99.8	5.3	0.2	good	0	
99.2	5.3	1.0	sl	0	
99.5	5.3	0.5	good		25
99.8	5.16	0.2	good	10	
99.0	5.16	1.0	good	0	
99.0	5.16	1.0	good		38
99.8	5.17	0.2	good	0	
99.0	5.17	1.0	v. sl	0	
99.5	5.17	0.5	good		25
99.8	5.18	0.2	good	0	
99.0	5.18	1.0	sl	0	
99.8	5.18	0.2	good		47
99.8	5.19	0.2	good	0	
99.0	5.19	1.0	sl	0	
99.8	5.19	0.2	sl		36
99.8	8	0.2	good		27
98.5	10	1.5	good		30

[0143] An example set illustrating the use of perfluoropolyether diols in the invention was run according to the same procedure as examples in Table 1. These results are shown in Table 8.

TABLE 8

% HC-1 in coating	Preparation Number	Percentage Preparation in coating	Smoothness	Ink repellency 35 min at 300 rpm	Ink repellency 55 min at 300 rpm
98.8	13	0.2	good	37	
99.0	13	1.0	v. sl	27	
99.5	14	0.5	v. sl	0	26
99.8	15	0.2	good	34	
99.0	15	1.0	v. sl	31	
99.8	16	0.2	good	0	28
99.0	16	1.0	good	0	26
99.8	17	0.2	good	26	
99.0	17	1.0	v. sl	34	

[0144] Another set illustrating the use of a multi acrylate diol in the invention, and a thiol functional trialkoxysilane was run according to the same procedure as examples in Table 1. These results are shown in Table 9.

TABLE 9

Percentage HC-1 in coating	Preparation number	Percentage Preparation in coating	Smoothness	Ink repellency 40 min at 300 rpm
99.3	18	0.7	good	32
99.3	21	0.7	good	40
99.3	4.2	0.7	good	0

[0145] An example set illustrating the trialkoxysilane functional perfluoropolyether urethane multiacrylates, a perfluoropolyether urethane acrylate made using hydroxyethyl acrylate, and a perfluoropolyether diol functionalized with isocyanatoethyl methacrylate was run according to the same

procedure as examples in Table 1. These results are shown in Table 10.

TABLE 10

Percentage HC-1 in coating	Preparation Number	Percentage Preparation in coating	Smoothness	Repellency 20 min at 300 rpm
99.6	20.1	0.4	good	0
99.6	20.2	0.4	good	0
99.6	20.3	0.4	good	0
99.6	20.4	0.4	good	0
99.6	7	0.4	good	0
99.6	23	0.4	good	0

[0146] A 30% solids (in a solvent blend of 1:1 isopropanol:ethyl acetate) sample of 99.4% PET4A/0.6% Des N100/0.85 PET3A/0.15 HFPO (Preparation 5.2) with 2% added Irgacure 907 was prepared. The solution was coated and cured by the same procedure as above. The smooth coating gave an ink repellency of 0 after a 20 minute sand test at 300 rpm.

[0147] Another set of examples using a perfluoropolyether alcohol functionalized with isocyanatoethyl methacrylate in combination with a compatibilizer was run according to the same procedure as examples in Table 1. The results are shown in Table 11.

TABLE 11

Percentage HC-1 in coating	Preparation Number	Percentage Preparation in coating	Percentage FBSEA in coating	Smoothness	Repellency 15 min. at 300 rpm
99.7	24	0.03	0	Dewet/rough	not run
97.67	24	0.03	2.3	good	25
94.97	24	0.03	5	good	0
90.97	24	0.03	9	good	33
85.97	24	0.03	14	good	33

[0148] Another experiment was run in which HC-1 was applied to the 5-mil Melinex 618 film with a metered, precision die coating process. The hardcoat formulation with HC-1 and Des N100/0.85 PET3A/0.15 HFPO (Preparation 5.2) was diluted to 30 wt-% solids in isopropanol and coated onto the 5-mil PET backing to achieve a dry thickness of 5 microns. A flow meter was used to monitor and set the flow rate of the material from a pressurized container. The flow rate was adjusted by changing the air pressure inside the

sealed container which forces liquid out through a tube, through a filter, the flow meter and then through the die. The dried and cured film was wound on a take up roll.

[0149] The coatings were dried in a 10-foot oven at 100 degrees Celsius, and cured with a 300-watt Fusion Systems H bulb at 100, 75, 50, and 25% power. The coating shown in Table 12 below was evaluated in a series of tests. The sand test was run for 15 minutes at 300 rpm. The Steel Wool Test was run checking for damage to the coating at 100, 250, 500, 750, and 1000 cycles. The results are summarized in Table 12. Contact angles were also run on selected samples before and after testing and these results are shown in Table 13.

TABLE 12

Wt. % HC-1 in coating	(Preparation Number 5.2) Weight % in coating	UV dose % power	UV Ink repellency	Steel Wool (Cycles without scratches)	Taber testing % haze after 500 cycles	Taber testing Change in haze from initial value in % after 500 cycles
99.27	0.73	100	0	1000	10.83	10.51
99.27	0.73	75	0	1000	8.38	8.04
99.27	0.73	50	0	1000	11.05	10.62
99.27	0.73	25	0	1000	8.35	8.04

[0150] Selected coatings from Table 12 were tested for contact angles with water and hexadecane, and are identified by the UV dose % power used in curing the coatings. The results are summarized in Table 13:

TABLE 13

UV dose % power	Liquid used to test contact angle	Initial Advancing/Static/Receding Contact angles	After Sand Testing Advancing/Static/Receding Contact angles	After 1000 Steel Wool Samples Advancing/Static/Receding Contact angles
100	Water	110/123/98	94/111/68	107/119/89
100	Hexadecane	—/72/64	—/61/49	—/69/62
25	Water	107/120/84	91/105/53	103/118/72
25	Hexadecane	—/71/62	—/56/40	—/63/55

[0151] The present invention provides fluorocarbon- and urethane-acrylate-containing additives that can be used in coating compositions to provide coating layers having high surface energies and smoothness.

[0152] These fluorocarbon- and urethane-acrylate-containing additives are preferably introduced to conventional hard coating materials and cured to form optical hard coating layers having enhanced stain and ink repellency properties, adequate smoothness, and improved durability. Further, optical hard coatings having these additives do not need compatibilizers designed to enhance the compatibility between a fluoropolymer additive and the conventional hard coat material.

[0153] A transparent polyethylene terephthalate (PET) film obtained from e.i. duPont de Nemours and Company,

Wilmington, Del. under the trade designation "Melinex 618" having a thickness of 5.0 mils and a primed surface. A hardcoat composition substantially the same as Example 3 of U.S. Pat. No. 6,299,799 (S-1) was coated onto the primed surface with a metered, precision die coating process. The hardcoat was diluted in IPA to 30 wt-% solids and coated onto the 5-mil PET backing to achieve a dry thickness of 5 microns.

[0154] A flow meter was used to monitor and set the flow rate of the material from a pressurized container. The flow rate was adjusted by changing the air pressure inside the sealed container which forces liquid out through a tube, through a filter, the flow meter and then through the die. The dried and cured film was wound on a take up roll and used as the input backing for the coating solutions described below.

[0155] The hardcoat coating and drying parameters were as follows:

Coating width:	6" (15 cm)
Web Speed:	30 feet (9.1 m) per minute
Solution % Solids:	30.2%
Filter:	2.5 micron absolute
Pressure Pot:	1.5 gallon capacity (5.7 l)
Flow rate:	35 g/min
Wet Coating Thickness:	24.9 microns
Dry Coating Thickness:	4.9 microns
Conventional Oven Temps:	Zone 1 - 140° F. (60° C.) Zone 2 - 160° F. (53° C.) Zone 3 - 180° F. (82° C.)

Each zone was 10 ft (3 m) in length.

[0156] The coating compositions of the surface layer were coated onto the hardcoat layer of either the first or the second substrate using a precision, metered die coater. For this step, a syringe pump was used to meter the solution into the die. The solutions were diluted with MEK to a concentration of 1% and coated onto the hardcoat layer to achieve a dry thickness of 60 nm. The material was dried in a conventional air flotation oven and then cured a 600 watt Fusion Systems bulb under nitrogen using the conditions show below:

Coating width:	4" (10 cm)
Web Speed:	20 feet per minute
Solution % Solids:	1.0%
Pump:	60 cc Syringe Pump
Flow rate:	1.2 cc/min
Wet Coating Thickness:	4.1 microns
Dry Coating Thickness:	60 nm
Conventional Oven Temps:	Zone 1 - 65° C. Zone 2 - 65° C.

Both zones at 10 ft (3 m) in length.

[0157] The following surface layer coatings were made and tested for ink repellency after a sand test at 300 rpm for 15 min and for initial water static contact angle.

TABLE 14

TMPTA (%)	Preparation number 6 (%)	HFPO AEA	Darocure 1173	% Ink Repellency loss	Static water Contact angle (range in degrees)
95	3.75	1.25	4	0	100-101
90	7.5	2.5	4	0	
85	11.25	3.75	4	0	110-111
80	15	5	4	0	
90	10		4	0	93-94
80	20		4	0	103-104

[0158] While the invention has been described in terms of preferred embodiments, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art, particularly in light of the foregoing teachings.

What is claimed is:

1. A fluorocarbon- and urethane-(meth)acryl-containing additive comprising a perfluoropolyether urethane having a perfluoropolyether moiety and a multi-(meth)acry terminal group and having the formula: $R_1-(NHC(O)XQR_f)_m-(NHC(O)OQ(A)_p)_n$;

wherein R_1 is the residue of a multi-isocyanate;

wherein X is O, S or NR, where R is H or lower alkyl of 1 to 4 carbon atoms;

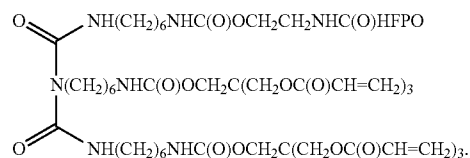
wherein R_f is a monovalent perfluoropolyether moiety composed of groups comprising the formula: $F(R_{fc}O)_x C_d F_{2d}$, wherein each R_{fc} independently represents a fluorinated alkylene group having from 1 to 6 carbon atoms, each x independently represents an integer greater than or equal to 2, and wherein d is an integer from 1 to 6;

wherein Q is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof; and

wherein A is a (meth)acryl functional group $-XC(O)C(R_2)=CH_2$, where R_2 is a lower alkyl of 1 to 4 carbon atoms or H or F; m is at least 1; n is at least 1; p is 2 to 6; m+n is 2 to 10;

and in which each unit referred to by the subscripts m and n is attached to an R_1 unit.

2. The additive of claim 1, wherein said fluorocarbon- and urethane-(meth)acryl-containing additive comprises:



3. A fluorocarbon- and urethane-acrylate-containing additive comprising a perfluoropolyether-substituted urethane (meth)acryl having the chemical formula: $R_f-Q-(XC(O)NHQOC(O)C(R)=CH_2)_f$;

wherein R_f is a monovalent perfluoropolyether moiety composed of groups comprising the formula: $F(R_{fc}O)_x C_d F_{2d}$, wherein each R_{fc} independently represents a fluorinated alkylene group having from 1 to 6 carbon atoms, each x independently represents an integer greater than or equal to 2, and wherein d is an integer from 1 to 6;

wherein a is 2-15;

wherein Q is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof;

wherein X is O or S; and

wherein f is 1-5.

4. The additive of claim 3, wherein R_f is HFPO.

5. The additive of claim 3, wherein said fluorocarbon- and urethane-acrylate-containing additive comprises: $HFPO-C(O)NHC(C_2H_5)(CH_2OC(O)NHC_2H_4OC(O)C(CH_3)=CH_2)_2$, where HFPO is $F(CF(CF_3)CF_2O)_a CF(CF_3)-$.

6. The additive of claim 3, wherein f is 2-5.

7. A fluorocarbon- and urethane-acrylate-containing additive comprising one or more perfluoropolyether urethanes with multi-(meth)acryl groups of the formula: $R_f-(NHC(O)XQR_f)_m$, $-(NHC(O)OQ(A)_p)_n$, $-(NHC(O)XQG)_o$, $-(NCO)_q$;

wherein R_f is the residue of a multi-isocyanate;

where X is O, S or NR, where R is H or lower alkyl of 1 to 4 carbon atoms;

where R_f is a monovalent perfluoropolyether moiety composed of groups comprising the formula: $F(R_{fc}O)_x C_d F_{2d}$, wherein each R_{fc} independently represents a fluorinated alkylene group having from 1 to 6 carbon atoms, each x independently represents an integer greater than or equal to 2, and wherein d is an integer from 1 to 6;

where Q is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof;

where G is selected from the group consisting of an alkyl, an aryl, an alkaryl and an aralkyl, wherein G optionally contains heteroatoms such as O, N, and S and optionally has heteroatom-containing functional groups such as carbonyl and sulfonyl and combinations of heteroatoms and heteroatom-containing functional groups; and G optionally contains pendant or terminal reactive groups selected from the group consisting of (meth)

acryl groups, vinyl groups, allyl groups and $-Si(OR_3)_3$ groups, where R_3 is a lower alkyl of 1 to 4 carbon atoms, wherein G also optionally has fluoroalkyl or perfluoroalkyl groups;

where m is at least 1;

where n is at least 1;

where o is 0 or greater;

where p is 2 to 6;

where q is 0 or greater;

wherein $(m+n+o+q)=N_{NCO}$, where N_{NCO} is the number of isocyanate groups originally appended to R_f ; and

wherein the quantity $(m+n+o)/N_{NCO}$ is greater than or equal to 0.67, and in which each unit referred to by the subscripts m , n , o , and q is attached to an R_f unit.

8. A fluorocarbon- and urethane-acrylate-containing additive comprising one or more perfluoropolyether urethanes with multi-meth(acryl) groups having the chemical formula: $(R_i)_c-(NHC(O)XQR_f)_m$, $-(NHC(O)OQ(A)_p)_n$, $-(NHC(O)XQG)_o$, $R_f(Q)(XC(O)NH)_y$, $-NHC(O)XQD(QX-C(O)NH)_u$, $-D_1(QXC(O)NH)_y$, $-NHC(O)OQ(A)_q$, $Q_1Q(A)_t$, $OC(O)NH)_v$, $-(NCO)_w$;

wherein R_i is the residue of a multi-isocyanate;

where c is 1 to 50;

where X is O, S or NR, where R is H or lower alkyl;

where R_f is a monovalent perfluoropolyether moiety composed of groups comprising the formula: $F(R_{fc}O)_x C_d F_{2d}$, each R_{fc} independently represents a fluorinated alkylene group having from 1 to 6 carbon atoms and each x independently represents an integer greater than or equal to 2 and wherein d is an integer from 1 to 6;

where Q is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof;

wherein A is a (meth)acryl functional group having the chemical formula: $(-XC(O)C(R_2)=CH_2)$, where R_2 is a lower alkyl of 1 to 4 carbon atoms or H or F;

where G is selected from the group consisting of an alkyl, an aryl, an alkaryl and an aralkyl, wherein G optionally contains heteroatoms such as O, N, and S and optionally has heteroatom-containing functional groups such as carbonyl and sulfonyl and combinations of heteroatoms and heteroatom-containing functional groups; and G optionally contains pendant or terminal reactive groups selected from the group consisting of (meth)acryl groups, vinyl groups, allyl groups and $-Si(OR_3)_3$ groups, where R_3 is a lower alkyl of 1 to 4 carbon atoms; wherein G also optionally has fluoroalkyl or perfluoroalkyl groups;

wherein D is selected from the group consisting of an alkylene, an arylene, an alkarylene, a fluoroalkylene, a

perfluoroalkylene and an aralkylene and optionally contains heteroatoms such as O, N, and S;

wherein D_1 is selected from the group consisting of an alkyl, an aryl, an alkaryl, a fluoroalkyl, a perfluoroalkyl and an aralkyl group and optionally contains heteroatoms such as O, N, and S;

where Q_1 is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof;

where m or z is at least 1;

where n or v is at least 1;

where o, s, v, and w are 0 or greater;

where $(m+n+o+[(u+1)s]+2v+w)=cN_{NCO}$, where N_{NCO} is the number of isocyanate groups originally appended to R_i ; the quantity $(m+n+o+[(u+1)s]+2v)/(cN_{NCO})$ is greater than or equal to least 0.75, p is 2 to 6, t is 1 to 6, and u is independently 1 to 3, and in which each unit referred to by the subscripts m, n, o, s, v and w is attached to an R_i unit.

9. A hardcoat composition comprising:

a hardcoat-compatible, monovalent perfluoropolyether moiety-containing urethane multi-(meth)acryl additive; a hydrocarbon hardcoat composition; and

optionally a plurality of surface modified inorganic nanoparticles.

10. The hardcoat composition of claim 9 comprising the additive of claim 1.

11. The hardcoat composition of claim 9 comprising the additive of claim 3.

12. The hardcoat composition of claim 9 comprising the additive of claim 7.

13. The hardcoat composition of claim 9 comprising the additive of claim 8.

14. The hard coating composition of claim 9, wherein said plurality of surface modified inorganic nanoparticles comprises a plurality of modified silica particles.

15. The hard coating composition of claim 9, wherein said hydrocarbon-based hard coat formulation comprises an acrylate-based hard coating formulation.

16. The hard coating composition of claim 9 further comprising a particulate matting agent.

17. The hard coating composition of claim 9, wherein said additive comprises between about 0.01% and 10% of the total solids of said hard coating composition.

18. The hard coating composition of claim 9 further comprising a compatibilizer selected from

a) a free radically reactive fluoroalkyl group-containing material having the chemical formula: $R_{ff}Q_3(X_1)_{n1}$;

where R_{ff} is a fluoroalkyl;

where Q_3 is a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene group, a straight or branched chain or cycle-

containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof;

where X_1 is a free-radically reactive group selected from (meth)acryl, —SH, allyl, or vinyl groups; and

where n1 is independently 1 to 3;

b) a free radically reactive fluoroalkylene group having the chemical formula: $(X_1)_{n1}Q_3R_{ff2}Q_3(X_1)_{n1}$;

where R_{ff2} is a fluoroalkylene;

where Q_3 is a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene group, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof;

where X_1 is a free-radically reactive group selected from (meth)acryl, —SH, allyl, or vinyl groups; and

where n1 is independently 1 to 3;

c) a fluoroalkyl- or fluoroalkylene-substituted thiol or polythiol selected from the group consisting of $C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)CH_2SH$, $C_4F_9SO_2N(CH_3)CH_2CH_2OC(O)CH_2CH_2SH$, $C_4F_9SO_2N(CH_3)CH_2CH_2SH$, and $C_4F_9SO_2N(CH_3)CH(OC(O)CH_2SH)CH_2OC(O)CH_2SH$;

and combinations of a), b) or c).

19. An optical display comprising:

an optical substrate; and a cured hardcoat composition disposed on the substrate wherein the hardcoat comprising the composition of claim 9.

20. An optical display comprising:

an optical substrate;

a first hardcoat layer disposed on the substrate; and

a second hardcoat surface layer disposed on the first hardcoat layer wherein the second hardcoat surface layer comprises the composition of claim 9.

21. A fluorocarbon- and urethane-acrylate-containing additive comprising one or more perfluoropolyether urethanes with multi-meth(acryl) groups having the chemical formula: $(R_i)_c—(NHC(O)XQR_{ff})_m$, $—(NHC(O)OQ(A)_p)_n$, $—(NHC(O)XQG)_o$, $—(NHC(O)XQ-R_{ff}(QXC(O)NH))_r$, $—NHC(O)XQ-D(QXC(O)NH)_s$, $—D_1(QXC(O)NH)_y$, $—NHC(O)OQ(A)_tQ_1Q(A)_tOC(O)NH)_v$, $—(NCO)_w$;

wherein R_i is the residue of a multi-isocyanate;

where c is 1 to 50;

where X is O, S or NR, where R is H or lower alkyl;

where R_{ff} is a monovalent perfluoropolyether moiety composed of groups comprising the formula: $F(R_{fc}O)_x C_d F_{2d}$, each R_{fc} independently represents a fluorinated alkylene group having from 1 to 6 carbon atoms and each x independently represents an integer greater than or equal to 2 and wherein d is an integer from 1 to 6;

where Q is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof;

wherein A is a (meth)acryl functional group having the chemical formula: $(-XC(O)C(R_2)=CH_2)$, where R_2 is a lower alkyl of 1 to 4 carbon atoms or H or F;

where G is selected from the group consisting of an alkyl, an aryl, an alkaryl and an aralkyl, wherein G optionally contains heteroatoms such as O, N, and S and optionally has heteroatom-containing functional groups such as carbonyl and sulfonyl and combinations of heteroatoms and heteroatom-containing functional groups; and G optionally contains pendant or terminal reactive groups selected from the group consisting of (meth)acryl groups, vinyl groups, allyl groups and $-Si(OR_3)_3$ groups, where R_3 is a lower alkyl of 1 to 4 carbon atoms; wherein G also optionally has fluoroalkyl or perfluoroalkyl groups;

where R_{f2} is a multi-valent perfluoropolyether moiety, R_{f2} is composed of groups comprising the formula: $Y((R_{fe1}O)_x C_{d1} F_{2d1})_b$, wherein each R_{fe1} is independently selected from: $-CF(CF_3)CF_2-$, $-CF_2CF_2CF_2-$, and $(CH_2C(CH_3)(CH_2OCH_2CF_3)CH_2-)$ _{aa} where aa is 2 or greater; each x independently represents an integer greater than or equal to 2, and d1 is an integer from 0 to 6; Y represents a polyvalent organic group or covalent bond having a valence of b, and b represents an integer greater than or equal to 2;

wherein D is selected from the group consisting of an alkylene, an arylene, an alkarylene, a fluoroalkylene, a perfluoroalkylene and an aralkylene group and optionally contains heteroatoms such as O, N, and S;

wherein D_1 is selected from the group consisting of an alkyl, an aryl, an alkaryl, a fluoroalkyl, a perfluoroalkyl and an aralkyl group and optionally contains heteroatoms such as O, N, and S;

where Q_1 is independently a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene, a straight or branched chain or cycle-containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof;

where r is at least 1;

where n or v is at least 1;

where m, o, s, v, and w are 0 or greater;

where $(m+n+o+[(u+1)r]+[(u+1)s]+2v+w)=cN_{NCO}$, where N_{NCO} is the number of isocyanate groups originally appended to R_i ; the quantity $(m+n+o+[(u+1)r]+[(u+1)s]+2v)/(cN_{NCO})$ is greater than or equal to least 0.75, p is 2 to 6, t is 1 to 6, and u is independently 1 to 3, and

in which each unit referred to by the subscripts m, n, o, r, s, v and w is attached to an R_i unit.

22. A hard coating composition having the fluorocarbon- and urethane-acrylate-containing additive of claim 21 and further comprising a hydrocarbon-based hard coat formulation.

23. An optical display comprising:

an optical substrate;

a first hardcoat layer disposed on the substrate; and

a second hardcoat surface layer disposed on the first hardcoat layer wherein the second hardcoat surface layer comprises the composition of claim 22.

24. A method for forming an optical display comprising:

(a) forming an additive comprising a perfluoropolyether urethane having a monovalent perfluoropolyether moiety and a multi-(meth)acryl terminal group by first reacting a polyisocyanate with a hydroxyl functional acrylate and further reacting the resultant compound with a perfluoropolyether-containing alcohol or thiol having a monovalent perfluoropolyether moiety, said additive having no free isocyanate groups;

(b) mixing said additive with a hydrocarbon-based hardcoat composition to form a hard coating composition;

(c) applying said hard coating composition to an optical substrate; and

(d) curing said hard coating composition to form a stain repellent optical hard coat on said optical substrate.

25. A method for forming an optical display comprising:

(a) forming an additive comprising a perfluoropolyether urethane having a monovalent perfluoropolyether moiety and a multi-(meth)acryl terminal group by first reacting a polyisocyanate with a perfluoropolyether-containing alcohol, thiol or amine having a monovalent perfluoropolyether moiety and further reacting the resultant compound with hydroxyl functional multiacrylate, said additive having no free isocyanate groups;

(b) mixing said additive with a hydrocarbon-based hardcoat composition to form a hard coating composition;

(c) applying said hard coating composition to an optical substrate; and

(d) curing said hard coating composition to form a stain repellent optical hard coat on said optical substrate.

26. A hard coating composition for optical displays comprising:

a hydrocarbon-based hard coating composition;

a compatibilizer selected from the group consisting of a free radically reactive fluoroalkyl group-containing compatibilizer, a free radically reactive fluoroalkylene group-containing compatibilizer, and a perfluoroalkyl substituted urethane mono or multi (meth)acrylate compatibilizer; and

a perfluoropolyether-substituted urethane acrylate having the chemical formula: $R_f-Q-(XC(O)NHQOC(O)C(R)=CH_2)_t$;

wherein R_f is a monovalent perfluoropolyether moiety composed of groups comprising the formula: $F(R_{fc}O)_x C_{d1} F_{2d1}-$, wherein each R_{fc} independently rep-

resents a fluorinated alkylene group having from 1 to 6 carbon atoms, each x independently represents an integer greater than or equal to 2, and wherein d is an integer from 1 to 6;

wherein a is 2-15;

wherein Q is a connecting group of valency at least 2 and is selected from the group consisting of a covalent bond, an alkylene, an arylene, an aralkylene, an alkarylene group, a straight or branched chain or cycle-

containing connecting group optionally containing heteroatoms such as O, N, and S and optionally a heteroatom-containing functional group such as carbonyl or sulfonyl, and combinations thereof;

wherein X is O or S; and

wherein f is 1-5.

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