

Description

OIL-REPELLENT COMPOSITION AND OIL-REPELLENT FILM

TECHNICAL FIELD

[0001]

The present invention relates to an oil-repellent composition and an oil-repellent film.

BACKGROUND ART

[0002]

As oil sealing agents for preventing oozing of oil at fluid bearing portions of motors in electronic equipment and the like, there have been used oil-repellent agents containing fluorine-containing polymers. For example, in a fluid bearing portion of a cooling fan motor for a microprocessor, an optical disk rotating device, a computer hard disk or the like, end faces of the bearing or a sleeve are provided with an oil-repellent film comprising the oil-repellent agent containing a fluorine-containing polymer, in order to prevent oozing of oil filled in the bearing as a lubricant (for example, see patent document 1). Further, as a fluorine-containing copolymer having oil repellency, there has been known a

polymer having fluorine-containing aliphatic ring structure (for example, see patent document 2).

However, the oil of the fluid bearing portion is elevated in temperature by heat generation from a motor portion, so that the oil-repellent film is exposed to the high-temperature oil, so that the oil may sometimes penetrates the oil-repellent film. Accordingly, the oil-repellent film is swelled, or adhesion of the oil-repellent film to the bearing or sleeve is decreased, thereby decreasing oil repellency of the oil-repellent film to cause a problem of impairing the function of preventing the oil from oozing.

[0003]

As a fluorine-containing resin composition excellent in adhesion to a base material, there has been proposed a composition comprising a fluorine-containing resin having a fluorine-containing ring structure and a fluorine-containing compound having a functional group with polarity and being soluble in a fluorine-based solvent (see patent document 3). However, the fluorine-containing resin having a fluorine-containing ring structure has an ether bond in its ring structure, so that it is amorphous. Accordingly, it does not develop a surface polarity, and hence oil repellency is insufficient, resulting in a fear of failing to repel oil.

Further, as an oil-repellent agent, there has been known a composition comprising a polymer having a polymerization unit derived from a polyfluoroalkyl group-containing (meth)acrylate (for example, see patent document 4).

However, the composition is excellent in initial oil repellency as an oil sealing agent, but it has a problem of poor oil repellency characteristics.

Further, an ordinary oil sealing agent is clear and colorless, and visual confirmation of a film thereof is difficult, so that a coated state of the oil sealing agent can not be evaluated, which causes a problem that it is difficult to secure stable quality. To this problem, there has been proposed a technique of mixing a coloring material characterized by vaporization on heating at 90°C to 150°C, and performing inspection before heating (see patent document 5).

However, in the case of patent document 5, the degree of coloring decreases by vaporization after heating, resulting in failure to visually confirm the coated state of the oil-repellent film. When dropped off or separated during heating, it is difficult to evaluate a final state of the oil-repellent film. Further, when parts coated with no oil sealing agent are mixed therein, there is a problem that selection is impossible.

Patent Document 1: JP-A-2000-297818

Patent Document 2: JP-A-63-238111

Patent Document 3: JP-A-2004-115622

Patent Document 4: JP-A-2000-160148

Patent Document 5: JP-A-2004-211851

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0004]

An object of the invention is to provide a oil-repellent composition enabling to obtain an oil-repellent film which is excellent in oil repellency, does not decrease in adhesion to a base material even when exposed to high-temperature oil for a long period of time, and is excellent in oil repellency durability, and an oil-repellent film excellent in oil repellency and durability thereof.

Further, another object of the invention is to provide a oil-repellent composition enabling to obtain an oil-repellent film excellent in visual confirmation properties, and an oil-repellent film excellent in visual confirmation properties.

MEANS FOR SOLVING THE PROBLEM

[0005]

The oil-repellent composition of the invention is characterized in that it comprises: a copolymer (A) having a polymerization unit derived from a polyfluoroalkyl group-containing (meth)acrylate (a1), a polymerization unit derived from a blocked isocyanate group-containing (meth)acrylate (a2) and a polymerization unit derived from a hydroxyl group-containing (meth)acrylate (a3-1) or (meth)acrylic acid (a3-2); and a solvent.

The above-mentioned copolymer (A) may further have a polymerization unit derived from an alkyl group-containing (meth)acrylate (a4).

The ratio of polymerization units derived from a (meth)acrylate (a1) in the above-mentioned copolymer (A) is preferably from 70 to 98% by mass of the total polymerization units (100% by mass).

It is preferred that the above-mentioned oil-repellent composition further comprises at least one kind of coloring material.

The above-mentioned coloring material is preferably a fluorescent coloring material.

[0006]

The oil-repellent film of the invention is characterized in that it comprises a copolymer (A) having a polymerization unit derived from a polyfluoroalkyl group-containing (meth)acrylate (a1), a polymerization

unit derived from a blocked isocyanate group-containing (meth)acrylate (a2) and a polymerization unit derived from a hydroxyl group-containing (meth)acrylate (a3-1) or (meth)acrylic acid (a3-2).

The above-mentioned copolymer (A) may further have a polymerization unit derived from an alkyl group-containing (meth)acrylate (a4).

The ratio of polymerization units derived from a (meth)acrylate (a1) in the above-mentioned copolymer (A) is preferably from 70 to 98% by mass of the total polymerization units (100% by mass).

It is preferred that the above-mentioned oil-repellent composition further comprises at least one kind of coloring material.

The above-mentioned coloring material is preferably a fluorescent coloring material.

ADVANTAGE OF THE INVENTION

[0007]

According to the oil-repellent composition of the invention, the oil-repellent film can be obtained which is excellent in oil repellency, does not decrease in adhesion to a base material even when exposed to high-temperature oil for a long period of time, and is excellent in oil repellency durability.

The oil-repellent film of the invention is excellent in oil repellency and durability thereof, and excellent in visual confirmation properties.

BEST MODE FOR CARRYING OUT THE INVENTION

[0008]

(Copolymer (A))

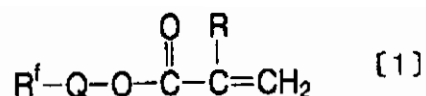
The copolymer (A) contains a polymerization unit derived from a polyfluoroalkyl group-containing (meth)acrylate (hereinafter described as a1), a polymerization unit derived from a blocked isocyanate group-containing (meth)acrylate (hereinafter described as a2) and a polymerization unit derived from a hydroxyl group-containing (meth)acrylate (hereinafter described as a3-1) or (meth)acrylic acid (hereinafter described as a3-2). The term "(meth)acrylate" in the invention means an acrylate or a methacrylate, and the term "(meth)acrylic acid means acrylic acid or methacrylic acid.

[0009]

As a1, a compound represented by the following formula [1] is preferred, wherein R^f represents a polyfluoroalkyl group, Q represents a divalent organic group, and R represents a hydrogen atom or a methyl group.

[0010]

[KA 1]



[0011]

R^f is preferably an alkyl group in which two or more hydrogen atoms are substituted by fluorine atoms. The number of carbon atoms of R^f is preferably from 2 to 20, and more preferably from 4 to 16. R^f may have either a straight-chain structure or a branched structure, and preferably a straight-chain structure. In the case of a branched structure, it is preferred that a branched portion exists at a terminal portion of R^f , and that it is a short chain having about 1 to 4 carbon atoms. R^f may contain an ethereal oxygen atom or a thioethereal sulfur atom. The structures of the terminal portions of R^f include $\text{CF}_3\text{CF}_2\text{-}$, $(\text{CF}_3)_2\text{CF-}$, $\text{CF}_2\text{H-}$, $\text{CFH}_2\text{-}$ and the like, and $\text{CF}_3\text{CF}_2\text{-}$ is preferred.

[0012]

The number of fluorine atoms in R^f is preferably 60% or more, more preferably 80% or more and most preferably 100%, when it is expressed by $[(\text{the number of fluorine atoms in Rf})/(\text{the number of hydrogen atoms contained in an alkyl group having the same number of carbon atoms as R}^f)] \times 100$. R^f in the case of 100% is called a

perfluoroalkyl group (hereinafter also described as an R^F group).

The number of carbon atoms of the R^F group is preferably from 2 to 20, and more preferably from 4 to 16. When the number of carbon atoms of the R^F group is within that range, polymerizability and solution stability after polymerization of al are good, and the oil-repellent composition is excellent in initial oil repellency and oil repellency durability.

[0013]

Specific examples of R^F include the following groups (including structural isomeric groups) and the like:

C_4F_9 -: $F(CF_2)_4$ -, $(CF_3)_2CF CF_2$ -, $(CF_3)_3C$ -, $CF_3CF_2(CF_3)CF$ - and the like;

C_5F_{11} -: $F(CF_2)_5$ - and the like;

C_6F_{13} -: $F(CF_2)_6$ - and the like;

C_7F_{15} -: $F(CF_2)_7$ -, $(CF_3)_2CF(CF_2)_4$ - and the like;

C_8F_{17} -: $F(CF_2)_8$ - and the like;

C_9F_{19} -: $F(CF_2)_9$ -, $(CF_3)_2CF(CF_2)_6$ - and the like;

$C_{10}F_{21}$ -: $F(CF_2)_{10}$ - and the like;

$C_{12}F_{25}$ -: $F(CF_2)_{12}$ - and the like;

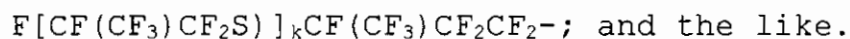
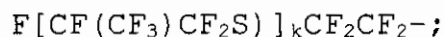
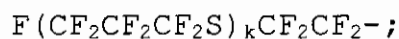
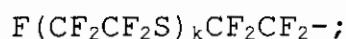
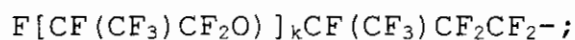
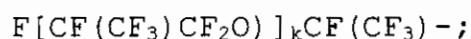
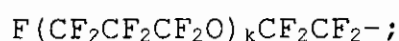
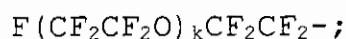
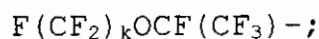
$C_{13}F_{27}$ -: $(CF_3)_2CF(CF_2)_8$ - and the like;

$C_{14}F_{29}$ -: $F(CF_2)_{14}$ - and the like; and

$C_{16}F_{33}$ -: $F(CF_2)_{16}$ - and the like.

[0014]

Specific examples in the case where R^f has an ethereal oxygen atom or a thioethereal sulfur atom include the following groups, wherein k represents an integer of 1 to 5:

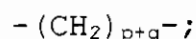


[0015]

As R^f , a straight-chain RF group is more preferred, and specifically, $F(CF_2)_4-$, $F(CF_2)_5-$, $F(CF_2)_6-$, $F(CF_2)_7-$, $F(CF_2)_8-$, $F(CF_2)_9-$, $F(CF_2)_{10}-$, $F(CF_2)_{11}-$ and $F(CF_2)_{12}-$ are particularly preferred.

[0016]

Q includes the following groups, wherein R^a represents a hydrogen atom or an alkyl group, p and q each independently represents an integer of 0 or 1 or more, and p+q is an integer of 1 to 22:



$-(CH_2)_pCONR^a(CH_2)_q-$;
 $-(CH_2)_pOCONR^a(CH_2)_q-$;
 $-(CH_2)_pSO_2NR^a(CH_2)_q-$;
 $-(CH_2)_pNHCONH(CH_2)_q-$;
 $-(CH_2)_pCH(OH)(CH_2)_q-$;
 $-(CH_2)_pCH(OCOR^a)(CH_2)_q-$; and the like.

[0017]

As Q, $-(CH_2)_{p+q}-$, $-(CH_2)_pCONR^a(CH_2)_q-$ or $-(CH_2)_pSO_2NR^a(CH_2)_q-$ (p represents an integer of 0 or 1 or more, q represents an integer of 2 or more, and p+q is from 2 to 6) is more preferred, and an ethylene group, a propylene group, a butylene group, a pentamethylene group or a hexamethylene group is most preferred.

[0018]

As a1, preferred are the following compounds, wherein R represents a hydrogen atom or a methyl group:

$F(CF_2)_4CH_2OCOCR=CH_2$ [1-1];
 $F(CF_2)_5CH_2OCOCR=CH_2$ [1-2];
 $H(CF_2)_4CH_2OCOCR=CH_2$ [1-3];
 $H(CF_2)_6CH_2OCOCR=CH_2$ [1-4];
 $H(CF_2)_8CH_2OCOCR=CH_2$ [1-5];
 $H(CF_2)_{10}CH_2OCOCR=CH_2$ [1-6];
 $H(CF_2)_8CH_2CH_2OCOCR=CH_2$ [1-7];
 $F(CF_2)_4CH_2CH_2OCOCR=CH_2$ [1-8];
 $F(CF_2)_6CH_2CH_2OCOCR=CH_2$ [1-9];

$\text{F}(\text{CF}_2)_8\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-10];
 $\text{F}(\text{CF}_2)_9\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-11];
 $\text{F}(\text{CF}_2)_{10}\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-12];
 $\text{F}(\text{CF}_2)_{12}\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-13];
 $\text{F}(\text{CF}_2)_{14}\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-14];
 $\text{F}(\text{CF}_2)_{16}\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-15];
 $\text{F}(\text{CF}_2)_8(\text{CH}_2)_3\text{OCOCR}=\text{CH}_2$ [1-16];
 $\text{F}(\text{CF}_2)_8(\text{CH}_2)_4\text{OCOCR}=\text{CH}_2$ [1-17];
 $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_4\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-18];
 $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-19];
 $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_8\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-20];
 $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_5(\text{CH}_2)_3\text{OCOCR}=\text{CH}_2$ [1-21];
 $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_5\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-22];
 $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_7\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-23];
 $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_5\text{CH}_2\text{CH}(\text{OCOCH}_3)\text{OCOCR}=\text{CH}_2$ [1-24];
 $\text{F}(\text{CF}_2)_8\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-25];
 $\text{F}(\text{CF}_2)_8\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-26];
 $\text{F}(\text{CF}_2)_8\text{SO}_2\text{N}(\text{C}_3\text{H}_7)\text{CH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-27]; and
 $\text{F}(\text{CF}_2)_8\text{CONHCH}_2\text{CH}_2\text{OCOCR}=\text{CH}_2$ [1-28].

[0019]

As a1, of [1-1] to [1-28], [1-3] to [1-15] are more preferred, and [1-8] to [1-13] are most preferred.

[0020]

a2 is a compound obtained by reacting an isocyanate group-containing (meth)acrylate with a blocking agent.

The isocyanate group-containing (meth)acrylates include 2-isocyanateethyl (meth)acrylate, 1,3,3-trimethyl-4-isocyanatocyclohexylmethyamidooxyethyl (meth)acrylate and the like.

[0021]

The blocking agents include 2-butanoneoxime, cyclohexanoneoxime, ϵ -caprolactam, ethyl acetoacetate, acetylacetone, phenol, methanol, diethyl malonate, a bisulfite, pyrazole, 3-methylpyrazole, 3,5-dimethylpyrazole, indazole and the like. Of these blocking agents, 2-butanoneoxime, diethyl malonate, pyrazole, 3-methylpyrazole and 3,5-dimethylpyrazole are more preferred, and 2-butanoneoxime, 3-methylpyrazole and 3,5-dimethylpyrazole are most preferred, because their excellent stability and excellent reactivity.

[0022]

a3-1 includes 2-hydroxyethyl (meth)acrylate, 2--hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 1,4-cyclohexanedimethanol mono(meth)acrylate, 2-acryloyloxyethyl-2-hydroxyethylphthalic acid, 3-chloro-2-hydroxypropyl (meth)acrylate, a polyoxyalkylene mono(meth)acrylate, polyoxyethylene mono(meth)acrylate, polyoxypropylene mono(meth)acrylate, polyoxyethylene/polyoxypropylene mono(meth)acrylate and the like.

[0023]

By using a2 and a3-1 or a3-2 (a3-1 and a3-2 are hereinafter also collectively described as a3), the (meth)acrylate of a1 and the (meth)acrylate of a2 or a3 undergo copolymerization to allow an increase in the molecular weight of the copolymer (A) to proceed. Further, when the oil-repellent film is formed, the (meth)acrylate of a2 and the hydroxyl group of a3-1 or the carboxylic acid group of a3-2 react with each other to form a urethane bond, thereby forming a three-dimensionally crosslinked product. The oil-repellent film using such a high-molecular weight copolymer (A) and formed into the three-dimensionally crosslinked product exhibits good oil repellency durability without swelling or separation even when immersed in high-temperature oil.

[0024]

The copolymer (A) may further have a polymerization unit derived from an alkyl group-containing (meth)acrylate (hereinafter described as a4). When the number of carbon atoms of the R^F group of a1 exceeds 8, it is preferred to have the polymerization unit derived from a4.

[0025]

a4 includes methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl

(meth)acrylate, n-hexyl (meth)acrylate, 3-ethoxyethyl (meth)acrylate, 3-benzoyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, octadecyl (meth)acrylate, isobornyl (meth)acrylate, n-lauryl (meth)acrylate, tridecyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, benzyl (meth)acrylate, phenoxyethyl (meth)acrylate, isobonyl (meth)acrylate and the like. Of these (meth)acrylates of a4, ethyl (meth)acrylate, propyl (meth)acrylate and cyclohexyl (meth)acrylate are preferred. [0026]

By using a4 having a molecular weight of 200 or less, the (meth)acrylate of a1 and the (meth)acrylate of a4 undergo copolymerization to allow an increase in the molecular weight of the copolymer (A) to proceed. Further, the alkyl group of the polymerization unit derived from a4 suppresses crystallinity of the R^F group of the polymerization unit based a1 to inhibit precipitation of the copolymer (A) in the oil-repellent composition. Thus, the oil-repellent composition becomes a homogeneous solution to improve storage stability. Further, by having the polymerization unit derived from a4, film forming properties of the oil-repellent composition is improved to be able to obtain the uniform film. Furthermore, the use of a4 having a molecular weight of 200 or less increase

crystallinity of the oil-repellent film and improves dynamic wettability such as a sweepback contact angle, resulting in easy rolling of the oil to be capable of enforcing enclosing of the oil.

[0027]

The copolymer (A) may have a polymerization unit derived from a polymerizable monomer (hereinafter described as a5) other than a1, a2, a3 and a4. When it has the polymerization unit derived from a5, it is excellent in adhesion to a base material. a5 includes glycidyl (meth)acrylate, aziridinyl (meth)acrylate, a polydimethylsiloxane group-containing (meth)acrylate, triallyl cyanurate, a dialkyl maleate, an N-substituted aminoalkyl (meth)acrylate, polyoxyalkylene glycol (meth)acrylate and the like.

[0028]

In the copolymer (A), the polymerization unit derived from a1, the polymerization unit derived from a2, the polymerization unit derived from a3 and the polymerization unit derived from a4 may each be used either alone or as two or more kinds thereof. When two or more kinds of polymerization units derived from a1 are contained, the numbers of carbon atoms of R^f of the respective a1 are preferably different from each other. Further, when two or more kinds of polymerization units

derived from a1 different in the number of carbons of R^f , the number of carbon atoms of R^f of a1 is indicated as an average value.

[0029]

The ratio of the polymerization unit derived from a1 in the copolymer (A) is preferably from 70 to 98% by mass, more preferably from 80 to 98% by mass, and most preferably from 85 to 98% by mass, of the total polymerization units (100% by mass). When the polymerization unit derived from a1 is within that range, oil repellency of the oil-repellent film is excellent.

[0030]

The ratio of the polymerization unit derived from a2 in the copolymer (A) is preferably from 0.5 to 10% by mass, more preferably from 1 to 8% by mass, and most preferably from 1 to 5% by mass, of the total polymerization units (100% by mass).

The ratio of the polymerization unit derived from a3 in the copolymer (A) is preferably from 0.5 to 10% by mass, more preferably from 1 to 8% by mass, and most preferably from 1 to 5% by mass, of the total polymerization units (100% by mass).

When the polymerization unit derived from a2 and the polymerization unit derived from a3 are within those ranges, a three-dimensionally crosslinked product is

sufficiently formed while maintaining oil repellency of the resulting oil-repellent film, and adhesion is sufficiently exhibited, resulting in excellent oil repellency durability.

[0031]

The ratio of the polymerization unit derived from a4 in the copolymer (A) is preferably 20% by mass or less. However, when the number of carbon atoms of the R^f group of a1 exceeds 8, the ratio of the polymerization unit derived from a4 in the copolymer (A) is preferably from 0.5 to 20% by mass, more preferably from 1 to 20% by mass, and most preferably from 1.5 to 15% by mass, of the total polymerization units (100% by mass). When a4 is within that range, the oil-repellent composition is excellent in storage stability and film forming properties.

The ratio of the polymerization unit derived from a5 in the copolymer (A) is preferably 10% by mass or less.

[0032]

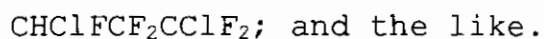
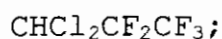
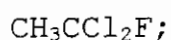
(Solvent)

The solvents include a halogen compound, a hydrocarbon, a ketone, an ester, an ether, a nitrogen compound, a sulfur compound, an inorganic solvent, an organic acid and the like.

The halogen compounds include a halogenated hydrocarbon, a halogenated ether and the like.

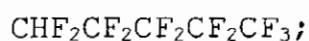
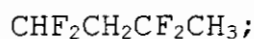
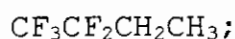
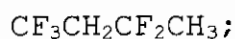
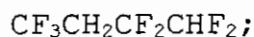
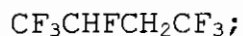
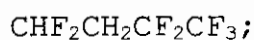
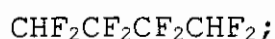
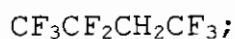
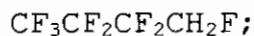
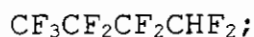
The halogenated hydrocarbons include a hydrochloro-fluorocarbon, a hydrofluorocarbon, a hydrobromocarbon, a fluorine-containing alcohol and the like.

The hydrochlorofluorocarbons include the following compounds:



[0033]

The hydrofluorocarbons include the following compounds:



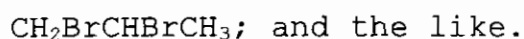
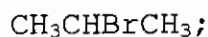
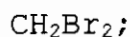
$\text{CF}_3\text{CF}_2\text{CF}_2\text{CHF}\text{CF}_3;$
 $\text{CHF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CHF}_2;$
 $\text{CF}_3\text{CHFCHFCF}_2\text{CF}_3;$
 $\text{CF}_3\text{CHFCF}_2\text{CH}_2\text{CF}_3;$
 $\text{CF}_3\text{CF}(\text{CF}_3)\text{CH}_2\text{CHF}_2;$
 $\text{CF}_3\text{CH}(\text{CF}_3)\text{CH}_2\text{CF}_3;$
 $\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_3;$
 $\text{CHF}_2\text{CHFCF}_2\text{CHFCHF}_2;$
 $\text{CHF}_2\text{CF}_2\text{CF}_2\text{CHFCH}_3;$
 $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}_3;$
 $\text{CHF}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CHF}_2;$
 $\text{CF}_3(\text{CF}_2)_4\text{CHF}_2;$
 $\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{F};$
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CF}_3;$
 $\text{CHF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CHF}_2;$
 $\text{CF}_3\text{CH}(\text{CF}_3)\text{CHFCF}_2\text{CF}_3;$
 $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}(\text{CF}_3)\text{CF}_3;$
 $\text{CF}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CF}_3;$
 $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_3;$
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_3;$
 $\text{CF}_3\text{CH}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{CF}_3;$
 $\text{CHF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CHF}_2;$
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CH}_3;$ and the like.

[0034]

The fluorine-containing alcohols include trifluoroethanol, 2,2,3,3,3-pentafluoro-1-propanol, 2-(pentafluorobutyl)ethanol, 2-(perfluoroexysil)ethanol, 2-(perfluorohexyl)ethanol, 2-(perfluorodecyl)ethanol, 2-(perfluoro-3-methylbutyl)ethanol, 1H,1H,3H-tetrafluoro-1-propanol, 1H,1H,5H-octafluoro-1-heptanol, 1H,1H,9H-hexadecafluoro-1-nonanol, 2H-hexafluoro-2-2-propanol, 1H,1H,3H-hexafluoro-2-butanol and the like.

[0035]

The hydrobromocarbons include the following compounds:

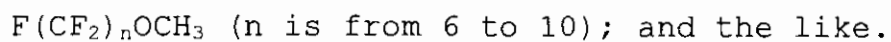
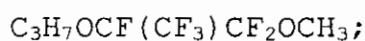
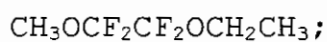
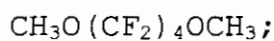
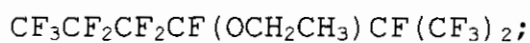
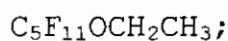
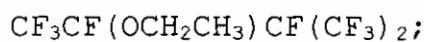
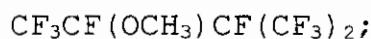
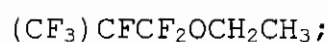
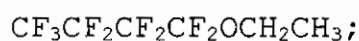
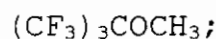
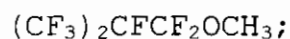
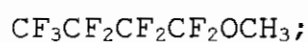
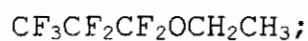
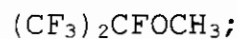
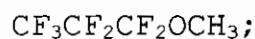


The halogenated ethers include a hydrofluoroether.

The hydrofluoroethers include a separation type hydrofluoroether and a non-separation type hydrofluoroether. The separation type hydrofluoroether is a compound in which a perfluoroalkyl group or a perfluoroalkylene group and an alkyl group or an alkylene group are linked to each other through an ethereal oxygen atom. The non-separation type hydrofluoroether is a hydrofluoroether containing a partially fluorinated alkyl group or alkylene group.

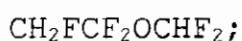
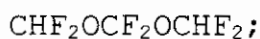
[0036]

The separation type hydrofluoroethers include the following compounds:



[0037]

The non-separation type hydrofluoroethers include the following compounds:



$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_2\text{F};$
 $\text{CF}_3\text{CF}_2\text{OCH}_2\text{CHF}_2;$
 $\text{CHF}_2\text{CF}_2\text{OCH}_2\text{CF}_3;$
 $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_3;$
 $\text{CF}_3\text{CF}_2\text{CH}_2\text{OCHF}_2;$
 $\text{CHF}_2\text{CF}_2\text{OCH}_2\text{CHF}_2;$
 $\text{CF}_3\text{CH}_2\text{OCF}_2\text{CH}_2\text{F};$
 $\text{CF}_3\text{CH}_2\text{OCF}_2\text{CHF}_2;$
 $\text{CHF}_2\text{CF}_2\text{CF}_2\text{OCH}_3;$
 $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCH}_3;$
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_2\text{CF}_3;$
 $\text{CF}_3\text{CF}_2\text{CH}_2\text{OCF}_2\text{CF}_3;$
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_2\text{CHF}_2;$
 $\text{CF}_3\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHF}_2;$
 $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CF}_3;$
 $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_2\text{CHF}_2;$
 $\text{CF}_3\text{CHF}\text{CF}_2\text{CH}_2\text{OCF}_3;$
 $\text{CF}_3\text{CHF}\text{CF}_2\text{CH}_2\text{OCHF}_2;$
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OCH}_3;$
 $(\text{CF}_3)_2\text{CHCF}_2\text{OCH}_3;$
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_2\text{CF}_2\text{CF}_3;$
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_2\text{CF}_2\text{CHF}_2;$
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}_2\text{CHF}_2;$
 $\text{CF}_3(\text{CF}_2)_5\text{OCHF}_2;$
 $\text{CHF}_2\text{OCF}_2\text{CF}_2\text{OCHF}_2;$

$\text{CHF}_2\text{OCF}_2\text{OCF}_2\text{CF}_2\text{OCHF}_2$;

$\text{CHF}_2\text{OCF}_2\text{OCF}_2\text{OCF}_2\text{OCHF}_2$; and the like.

[0038]

The hydrocarbons include an aliphatic hydrocarbon, an alicyclic hydrocarbon, an aromatic hydrocarbon and the like.

The aliphatic hydrocarbons include pentane, 2-methylbutane, 3-methylpentane, hexane, 2,2-dimethylbutane, 2,3-dimethylbutane, heptane, octane, 2,2,4-trimethylpentane, 2,2,3-trimethylhexane, decane, undecane, dodecane, 2,2,4,6,6-pentamethylheptane, tridecane, tetradecane, hexadecane and the like.

The alicyclic hydrocarbons include cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, ethylcyclohexane and the like.

The aromatic hydrocarbons include benzene, toluene, xylene and the like.

The ketones include acetone, methyl ethyl ketone, 2-pentanone, 2-hexanone, methyl isobutyl ketone and the like.

[0039]

The esters include methyl acetate, ethyl acetate, butyl acetate, methyl propionate, methyl lactate, ethyl lactate, pentyl lactate and the like.

The ethers include diisopropyl ether, dioxane, tetrahydrofuran and the like.

The nitrogen compounds include pyridine, N,N--dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone and the like.

The sulfur compounds include dimethyl sulfoxide, sulfolane and the like.

The inorganic solvents include liquid carbon dioxide and the like.

The organic acids include acetic acid, propionic acid, malic acid, lactic acid and the like.

[0040]

As the solvents, preferred are the hydrochlorofluorocarbons, the hydrofluorocarbons, the hydrofluoroethers and the perfluorocarbons, and more preferred are $\text{CH}_3\text{CCl}_2\text{F}$, $\text{CHCl}_2\text{CF}_2\text{CF}_3$, $\text{CHClFCF}_2\text{CClF}_2$, $\text{CH}_2\text{FCF}_2\text{OCHF}_2$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCH}_2\text{F}$, $\text{CF}_3\text{CF}_2\text{OCH}_2\text{CHF}_2$, $\text{CHF}_2\text{CF}_2\text{OCH}_2\text{CF}_3$, $\text{CHF}_2\text{CF}_2\text{CH}_2\text{OCF}_3$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{OCHF}_2$, $\text{CHF}_2\text{CF}_2\text{OCH}_2\text{CHF}_2$, $\text{CF}_3\text{CH}_2\text{OCF}_2\text{CH}_2\text{F}$, $\text{CF}_3\text{CH}_2\text{OCF}_2\text{CHF}_2$, $\text{CHF}_2\text{CF}_2\text{CF}_2\text{OCH}_3$, $\text{CF}_3(\text{CF}_2)_4\text{CHF}_2$, $\text{CF}_3(\text{CF}_2)_4\text{CH}_2\text{F}$ and $\text{CF}_3(\text{CF}_2)_5\text{OCH}_3$, in terms of solubility. These solvents are excellent in solubility for the polymer and storage stability in the solution state.

The solvents may be used either alone or as a mixture of two or more thereof.

[0041]

(Oil-Repellent Composition)

The oil-repellent composition of the invention is a composition containing the polymer (A) and the solvent.

The content of the polymer (A) in the oil-repellent composition is preferably from 0.1 to 20% by mass, and more preferably from 0.1 to 10% by mass, in the oil-repellent composition (100% by mass). When the content is within that range, the oil-repellent composition is excellent in oil repellency and oil repellency durability.

The content of the solvent in the oil-repellent composition is preferably from 80 to 99.9% by mass, and more preferably from 90 to 99.9% by mass, in the oil-repellent composition (100% by mass). When the content is within that range, the oil-repellent composition is excellent in oil repellency durability, and the oil-repellent film can be formed by one coating.

[0042]

In order to improve adhesion of the oil-repellent film to a base material, a silane coupling agent, a primer or the like may be added to the oil-repellent composition of the invention to such a degree that oil repellency of the oil-repellent film and storage stability of the oil-repellent composition are not impaired.

In order to increase oil repellency and oil repellency durability of the oil-repellent film, a fluoropolymer free from the polymerization unit derived

from the polyfluoroalkyl group-containing (meth)acrylate may be added to the oil-repellent composition of the invention. The fluorine-containing polymers include a polymer having a fluorine-containing aliphatic ring structure on a main chain thereof as described in JP-A-63-238111, a perfluoropolyether, a tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer and the like.

[0043]

(Coloring Material)

A coloring material such as a dye or a pigment is preferably added to the oil-repellent composition of the invention. When the coloring material is mixed, the presence or absence of the oil-repellent film becomes easily viewable, resulting in excellent visibility.

When the coloring material is added, it may be directly added to the oil-repellent composition or may be added after the coloring material has been mixed with a solvent compatible with the oil-repellent composition and the coloring material, when it is insoluble in oil-repellent composition.

The coloring material is preferably one which develops a color different from that of the base material and has high absorbance, and more preferably a fluorescent coloring material which emits light when irradiated with

an ultraviolet ray, even when the base material is black, thereby being capable of visually confirming the oil-repellent film. The fluorescent coloring material provides stronger light emission when irradiated with a light ray having a fluorescent maximum wavelength of that coloring material, which makes it easy to visually confirm the oil-repellent film. Preferred is a coloring material which can be distinguished even after the oil-repellent composition has been heated, more preferred is a coloring material whose color is liable to remain even at a heat curing temperature of the oil-repellent composition, and most preferred is a coloring material whose color is liable to remain even when heated at 80°C or more.

The coloring materials include coumarin, stilbene, thiophene, xanthene, naphthaloid, pyrazoline, oxazole, naphthalimide, indigo, acridine and the like. Stilbene, xanthene and naphthaloid are preferred in terms of heat resistance. Two or more kinds of coloring materials may be mixed.

The amount of the coloring material added is preferably from 0.1 to 30% by mass, and more preferably from 1 to 10% by mass, in the oil-repellent film (100% by mass). When it is 0.1% by mass or more, the oil-repellent film is excellent in color development, and the oil-repellent film can be visually confirmed. Further, 30% by

mass or less results in no deposition of the coloring material from the oil-repellent film, and no layer separation occurs.

[0044]

(Oil-Repellent Film)

The oil-repellent film of the invention is a film containing the above-mentioned copolymer (A).

The oil-repellent film of the invention is formed, for example by applying the oil-repellent composition of the invention to the base material, and completely evaporating the solvent. Coating methods include spraying, dipping, brush coating, potting, spin coating and the like.

The base materials include resin, metal, fiber and the like. The base material may be subjected to pretreatment, primer treatment or the like such as corona treatment or UV ozone treatment. That treatment improves adhesion of the oil-repellent film to the base material.

[0045]

The oil-repellent film of the invention is a film formed by crosslinking of the oil-repellent composition, and crosslinking improves adhesion to the base material. Method for crosslinking the oil-repellent composition include heat curing, photocuring by UV irradiation, electron beam curing by electromagnetic wave irradiation or electron beam irradiation, and the like. Of these,

preferred is heat curing which requires only a small capital investment and generates no harmful light ray. It is preferred that the temperature of heat curing is high in order to promote curing of functional groups, chemical bonding to the base material and anchor bonding, and heating up to a temperature at which the base material can resist is preferred. The heating temperature is preferably from 100 to 200°C, and more preferably from 100 to 150°C. The heating time is preferably 30 minutes or longer. Within that temperature range and that time range, the oil-repellent film is well cured to obtain an oil-repellent film excellent in oil repellency.

[0046]

In the oil-repellent film of the invention, it is conceivable that the isocyanate group of the copolymer (A) react with the hydroxyl group or the carboxylic acid group to increase the molecular weight of the copolymer (A). Further, it is conceivable that the oil-repellent film decreases in solubility for oil by the existence of the urethane bond (crosslinked structure) of the isocyanate group and the hydroxyl group or the carboxylic acid group. Furthermore, the oil-repellent film is excellent in oil repellency because of the R^f groups existing in large amounts, so that even when exposed to oil of 100°C or higher for a long period of time, it is not decomposed or

dissolved, excellent in adhesion to the base material, and can be maintained for a long period of time without largely impairing initial oil repellency.

EXAMPLES

[0047]

The present invention will be illustrated with reference to specific examples (examples: Exs. 1 to 7, comparative examples: Exs. 8 to 10), but the invention should not be construed as being limited thereto.

Evaluations of oil repellency were performed according to methods shown below.

(Initial Oil Repellency)

About 1 μ L of n-hexadecane was dropped onto a test plate, and the contact angle thereof was measured. The oil sealing performance was evaluated by the contact angle of n-hexadecane. A contact angle of 50 degrees or more was judged to have the oil sealing property, and a contact angle of less than 50 degrees was judged to have no oil sealing property.

(Oil Repellency Durability)

A test plate was immersed in n-hexadecane of 120°C for 40 hours, and pulled up, followed by drying using an air gun. Then, the contact angle of n-hexadecane was measured in the same manner as described above.

(Contact Angle)

Measurement of the contact angle was made by the sessile drop method under conditions of 25°C by using CA-A, Kyowa Interface Science Co., Ltd.

[0048]

[Example 1]

In a 50-mL glass flask, 5.7 g of perfluorohexylethyl acrylate [$F(CF_2)_6CH_2CH_2OCOCH=CH_2$] (hereinafter described as C6FA), 0.12 g of 2-isocyanate ethyl methacrylate (hereinafter described as IS) in which an isocyanate group was blocked with 3,5-dimethylpyrazole, 0.09 g of 1,4-cyclohexanedimethanol monomethacrylate [$CH_2=CH(CH_3)COOCH_2C_6H_{10}CH_2OH$] (hereinafter described as CM), 0.09 g of 2,2'-azobis(2-methylbutyronitrile) (hereinafter described as AB1) and 13.5 g of $HCF_2CF_2OCH_2CF_3$ (hereinafter described as solvent Y) were placed.

The gas in the inside of the flask was replaced by nitrogen gas, followed by sealing. The flask was maintained in a hot water bath of 60°C for 15 hours with stirring the inside thereof to obtain a transparent solution containing a copolymer. Solid impurities were separated from the resulting solution by filtration using a 1 micron filter paper, and the resulting filtrate was diluted with solvent Y to prepare an oil-repellent solution having a polymer concentration of 2% by mass.

A SUS plate which had been washed was coated with the resulting oil-repellent solution by a spin coat method under conditions of 500 rpm for 20 seconds, and heat treated at 120°C for 60 minutes to obtain a test plate having an oil-repellent film. For this test plate, initial oil repellency and oil repellency durability were evaluated. The results thereof are shown in Table 1.

[0049]

[Example 2]

A test plate was obtained in the same manner as in Example 1 with the exception that 5.77 g of C6FA, 0.15 g of IS, 0.07 g of AB1 and 14 g of solvent Y were used, and that 0.08 g of 2-hydroxyethyl methacrylate [$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{OH}$] (hereinafter described as 2HEMA) was used in place of 0.09 g of CM. For this test plate, initial oil repellency and oil repellency durability were evaluated. The results thereof are shown in Table 1.

[0050]

[Example 3]

A test plate was obtained in the same manner as in Example 2 with the exception that 5.92 g of perfluorohexylethyl methacrylate (hereinafter described as C6FMA) was used in place of 5.7 g of C6FA. For this test plate, initial oil repellency and oil repellency

durability were evaluated. The results thereof are shown in Table 1.

[0051]

[Example 4]

In a 50-mL glass flask, 5.9 g of perfluoroalkylethyl acrylate [$F(CF_2)_nCH_2CH_2OCOCH=CH_2$] (a mixture of $n=6$ to $n=16$; $n=8$ or more is 80% by mass or more; the average value of n is 8, hereinafter described as CmFA), 0.09 g of IS, 0.05 g of 2HEMA, 0.29 g of ethyl acrylate [$CH_2=CHCOOCH_2C_5$] (hereinafter described as EA), 0.12 g of 2,2'-azobis(2,4-dimethylvaleronitrile) (hereinafter described as AB2) and 13.6 g of solvent Y were placed.

The gas in the inside of the flask was replaced by nitrogen gas, followed by sealing. The flask was maintained in a hot water bath of 60°C for 15 hours with stirring the inside thereof to obtain a transparent solution containing a copolymer. Then, a test plate was obtained in the same manner as in Example 1. For this test plate, initial oil repellency and oil repellency durability were evaluated. The results thereof are shown in Table 1.

[0052]

[Example 5]

A test plate was obtained in the same manner as in Example 4 with the exception that 5.6 g of CmFA, 0.09 g of

IS, 0.05 g of 2HEMA and 13.6 g of solvent Y were used, and that 0.12 g of cyclohexyl acrylate (hereinafter described as CHA) was used in place of 0.29 g of EA. For this test plate, initial oil repellency and oil repellency durability were evaluated. The results thereof are shown in Table 1.

[0053]

[Example 6]

A test plate was obtained in the same manner as in Example 4 with the exception that 5.6 g of CmFA, 0.09 g of IS, 0.05 g of 2HEMA and 0.29 g of EA were used, that 0.09 g of AB1 was used in place of AB2, that 13.6 g of $\text{CF}_3(\text{CF}_2)_4\text{CHF}_2$ was used in place of solvent Y, and a hot water bath of 70°C was used in place of the hot water bath of 60°C. For this test plate, initial oil repellency and oil repellency durability were evaluated. The results thereof are shown in Table 1.

[0054]

[Example 7]

To 99.75 g of methyl ethyl ketone, 0.25 g of a stilbene-based coloring material was added, followed by stirring to a homogeneous solution to obtain solution D. To 99.5 g of trifluoroethanol, 0.5 g of a xanthene-based coloring material was added, followed by stirring to a homogeneous solution to obtain solution E.

To 100 g of the copolymer solution (2% by mass) of Example 1, 10 g of solution D and 20 g of solution E were added, followed by stirring to a homogeneous state. Using this solution, a test plate was obtained in the same manner as in Example 4. Compared to Example 1, this test plate was colored pink at an oil-repellent film portion, and when irradiated with a light ray of 365 nm, the oil-repellent film portion emitted light, and the oil-repellent film could be visually confirmed.

[0055]

[Example 8]

In a 50-mL glass flask, 6 g of C6FA, 0.09 g of AB1 and 14 g of solvent Y were placed. The gas in the inside of the flask was replaced by nitrogen gas, followed by sealing. The flask was maintained in a hot water bath of 60°C for 20 hours with stirring the inside thereof to obtain a transparent solution containing a copolymer. Then, a test plate was obtained in the same manner as in Example 1. For this test plate, initial oil repellency and oil repellency durability were evaluated. The results thereof are shown in Table 1.

[0056]

[Example 9]

In a 50-mL glass flask, 6 g of CmFA, 0.09 g of AB2 and 14 g of solvent Y were placed. The gas in the inside

of the flask was replaced by nitrogen gas, followed by sealing. The flask was maintained in a hot water bath of 60°C for 20 hours with stirring the inside thereof to obtain a transparent solution containing a copolymer. Then, a test plate was obtained in the same manner as in Example 1. For this test plate, initial oil repellency and oil repellency durability were evaluated. The results thereof are shown in Table 1.

[0057]

[Example 10]

In a pressure-resistant glass autoclave, 100 g of $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}=\text{CF}_2$ (hereinafter described as CY), 0.5 g of CH_3OH as a chain transfer agent and 0.7 g of $((\text{CH}_3)_2\text{CHOC}(\text{O})\text{O})_2$ as a polymerization initiator were placed, followed by sealing. The inside of the autoclave was maintained at 40°C for 22 hours to conduct polymerization reaction, thereby obtaining a polymer. The intrinsic viscosity of the resulting polymer was 2 dL/g in perfluoro(2-butyltetrahydrofuran) of 30°C.

The resulting polymer was heat treated in a hot air cycling type oven under an atmospheric atmosphere at 300 °C for 1 hour, further immersed in ultrapure water at 110°C for 1 week, and then, vacuum dried at 100°C for 24 hours to obtain polymer G.

As a result of analysis of polymer G with IR spectra, a peak belonging to the carboxyl group was confirmed. Further, polymer G had a glass transition point of 108°C, was tough, transparent and glasslike at 25°C, and had a light transmittance of 95% or more. Furthermore, the 10% pyrolysis temperature of polymer G was 465°C. A solution was obtained by dissolving 2 g of polymer G in 99 g of perfluorooctane, and then, a test plate was obtained in the same manner as in Example 1. For this test plate, initial oil repellency and oil repellency durability were evaluated. The results thereof are shown in Table 1.

[0058]

[Table 1]

Polymerization Unit (% by mass)	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10
a1 C6FA	96.4	96.3	-	-	-	-	96.4	100	-	-
C6FMA	-	-	96.4	-	-	-	-	-	-	-
CmFA	-	-	-	93.2	95.6	93.2	-	-	100	-
a2 IS	2.0	2.5	2.4	1.4	1.5	1.4	2.0	-	-	-
a3 CM	1.5	-	-	-	-	-	1.5	-	-	-
2HEMA	-	1.2	1.1	0.8	0.9	0.8	-	-	-	-
a4 EA	-	-	-	4.6	-	-	-	-	-	-
CHA	-	-	-	-	2.0	4.6	-	-	-	-
CY	-	-	-	-	-	-	-	-	-	100
Initial Oil Repellency (degrees)	77.1	72.2	71.0	74.8	76.7	75.5	76.0	71.7	71.7	53.0
Oil Repellency Durability (degrees)	73.8	70.5	67.7	73.9	75.8	67.6	74.3	42.8	42.8	47.2

INDUSTRIAL APPLICABILITY

[0059]

The oil-repellent composition of the invention can be utilized for application as an oil sealing agent. Further, the oil-repellent composition of the invention is excellent not only in oil repellency but also in water repellency, so that it can be utilized for various protective films such as soil-resistant films, and the like. It can be utilized for water- and oil-repellent films for fiber, soil-resistant films for ink jet nozzles, water- and moisture-resistant films for semiconductors, protective films for semiconductor wafers, and the like.

[0060]

While the present invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to those skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

This application is based on Japanese Patent Application No. 2005-097043 filed on March 30, 2005 and Japanese Patent Application No. 2005-185577 filed on June 24, 2005, and the contents thereof are herein incorporated by reference.

Claims

1. An oil-repellent composition comprising:
a copolymer (A) having a polymerization unit derived from a polyfluoroalkyl group-containing (meth)acrylate (a1), a polymerization unit derived from a blocked isocyanate group-containing (meth)acrylate (a2) and a polymerization unit derived from a hydroxyl group-containing (meth)acrylate (a3-1) or (meth)acrylic acid (a3-2); and
a solvent.

2. The oil-repellent composition according to claim 1, wherein the copolymer (A) further has a polymerization unit derived from an alkyl group-containing (meth)acrylate (a4).

3. The oil-repellent composition according to claim 1 or 2, wherein the ratio of polymerization units derived from a (meth)acrylate (a1) in the copolymer (A) is from 70 to 98% by mass of the total polymerization units (100% by mass).

4. The oil-repellent composition according to claim 1, 2 or 3, wherein the oil-repellent composition further comprises at least one kind of coloring material.

5. The oil-repellent composition according to claim 4, wherein the coloring material is a fluorescent coloring material.

6. An oil-repellent film comprising a copolymer (A) having a polymerization unit derived from a polyfluoroalkyl group-containing (meth)acrylate (a1), a polymerization unit derived from a blocked isocyanate group-containing (meth)acrylate (a2) and a polymerization unit derived from a hydroxyl group-containing (meth)acrylate (a3-1) or (meth)acrylic acid (a3-2).

7. The oil-repellent film according to claim 6, wherein the copolymer (A) further has a polymerization unit derived from an alkyl group-containing (meth)acrylate (a4).

8. The oil-repellent film according to claim 6 or 7, wherein the ratio of polymerization units derived from a (meth)acrylate (a1) in the copolymer (A) is from 70 to 98% by mass of the total polymerization units (100% by mass).

9. The oil-repellent film according to claim 6, 7 or 8, wherein the oil-repellent composition further comprises at least one kind of coloring material.

10. The oil-repellent film according to claim 9, wherein the coloring material is a fluorescent coloring material.