

DESCRIPTION

OIL-BARRIER COMPOSITION

TECHNICAL FIELD

The present invention relates to a composition having an oil-barrier action and to a method of producing the composition. More specifically, the present invention relates to a composition having an oil-barrier action, the composition being intended for preventing oozing out of a lubricant used for a sliding portion of a precision instrument such as a clock, a motor, or a lens system of a single lens reflex camera and to a method of producing the composition. Furthermore, the present invention relates to a method of carrying out an oil-barrier processing with such a composition on the surface of a sliding component and the surface of another component adjacent to the sliding component.

BACKGROUND ART

For reducing frictional resistance, a lubricant such as a mineral oil is generally used for a sliding surface of a sliding portion of a precision instrument such as a clock, a motor, or a lens system of a single lens reflex camera. Such a lubricant is indispensable

for preventing the sliding surface of the component from wearing. However, the lubricant is generally in the form a fluid, so that the lubricant may be oozing out of the sliding surface to surrounding components. In the configuration of the above precision instruments, two or more components are typically arranged in a narrow area. Therefore, oozing of the lubricant may lead to adhesion of the lubricant on other components around the sliding component. Furthermore, a lubricant is a viscous material in general, so that the lubricant tends to accumulate dust or the like. Thus, the machine may break down when the lubricant oozes out of the desired area.

Furthermore, the oozing of the lubricant decreases the retaining time of the lubricant on the sliding surface, so that the need of reapplying the lubricant will be increased. For this reason, an oil-barrier composition is applied on the sliding component or components adjacent to the sliding component of the precision instrument to prevent the lubricant from oozing out.

The oil-barrier composition has been prepared by dissolving or dispersing a lipophobic compound in a medium and is used by being applied and dried on the components around the sliding surface of the sliding component so as to prevent the lubricant from oozing out and to keep the lubricant on a desired area for a long

period of time. The lipophobic compound may be a fluorinated polymer or a fluorinated phosphodiester compound having one or two or more perfluoroalkyl groups. In addition, the medium may be a fluorinated aromatic hydrocarbon compound such as chlorofluorocarbon (CFC), perfluorocarbon (PFC), or meta-xylene hexafluoride.

However, the fluorine regulation restricts the use of CFC because of its ozone-destroying action. In addition, PFC has a high global warming potential, so that the use of PFC will be a factor of environmental disruption. Besides, a fluorinated aromatic hydrocarbon compound has problems in toxicity, workability, and so on. Thus, an aqueous oil-barrier composition prepared using an aqueous medium, having no influence on the environment, has been demanded in the art. However, among the above lipophobic compounds, the fluorinated polymer, or the fluorinated compound having two or more perfluoroalkyl groups has poor solubility in water. Therefore, when an aqueous medium is used, an effective ingredient having the required amount for exerting enough oil barrier performance cannot be dissolved in the medium. In addition, the addition of a hydrocarbon surfactant for solubilization leads to problems in that the oil-barrier performance or durability falls. For instance, as a composition in which a fluorinated polymer

is dissolved in an aqueous medium, there is disclosed a composition for preventing oozing of a flux for soldering (JP 11-154783 A). However, the flux for soldering is constructed by dissolving a solid ingredient in a volatile solvent such as isopropyl alcohol even in a solid state or a liquid state at room temperature. Thus, the isopropyl alcohol in the flux can be vaporized by heat at the time of soldering, so that only the solid ingredient remains on the substrate of a product. Therefore, the flux does not require a high lipophobic property, compared with the oil-barrier action to the lubricant, which is an object of the present invention. In the above reference, as a surfactant, there is described that it is preferable to use a non-fluorochemical cationic surfactant having an alkyl group with six or more carbon atoms in its molecule or a non-fluorochemical anionic surfactant having an alkyl group with six or more carbon atoms in its molecule in addition to a fluorochemical surfactant. Furthermore, there is described that the amount of a non-fluorochemical surfactant contained in the surfactant is preferably from 50 to 80% by mass with respect to the sum of the amounts of fluorochemical surfactant and non-fluorochemical surfactant. In other words, there is described that it is preferable to contain the non-fluorochemical

surfactant more than the fluorochemical surfactant. The reasons for containing the non-fluorochemical surfactant more than the fluorochemical surfactant is that an emulsifying action at the time of manufacturing the composition is excellent and the handling nature of the resulting composition is excellent because of high dispersion stability of the lipophobic compound.

Furthermore, in many cases, structural components having their respective sliding surfaces to be treated with oil-barrier agents have a remaining oil content such as a press oil. That is, the oil content has been adhered on the sliding surface since the preceding steps including press processing. However, the conventional oil-barrier composition cannot form a coating film on the area having the remaining oil content. Therefore, for treating such an area with the conventional oil-barrier agent, there is a need for the step of removing the remaining oil content by washing the component to be treated with a halogen-based organic solvent such as trichlene in advance. For instance, as an aqueous oil-barrier composition, there is disclosed an oil-barrier composition in which a fluorinated phosphomonoester compound having one perfluoroalkyl group is dissolved in an aqueous medium (JP 2000-1669 A). In this case, the oil-barrier composition has excellent solubility in

water, but contains no fluorochemical surfactant. Thus, the composition keeps its surface tension enough to prevent the formation of a coating film on the oil content remaining on the surface. Therefore, there is a need for the step of removing the remaining oil content. Besides, the fluorinated phosphomonoester to be used has a phosphate moiety and a fluoroalkyl group moiety. At the time of applying on the component, the phosphate moiety is absorbed on a metallic component, allowing the fluoroalkyl group moiety to be in a free state. Therefore, the resulting coating film after drying has poor adhesiveness, compared with the oil barrier reagent using the fluorinated polymer.

As described above, it is an object of the present invention is to provide an aqueous oil-barrier composition using an aqueous medium, which is free of environmental impact. When such an oil-barrier composition is applied around the sliding surface of a precision instrument such as a clock, a motor, or a lens system of a single lens reflex camera, the oil-barrier composition effectively prevents a lubricant from oozing out. Such an oil-barrier composition exerts an excellent oil-barrier effect even though a component having the remaining oil content such as press oil being attached from the previous step is directly treated with the oil-

barrier composition.

DISCLOSURE OF THE INVENTION

The present invention has been made for solving the above-mentioned problem, and an object of the present invention is to provide an emulsion type oil-barrier composition, including: a polymer (A) containing a polymer unit (a^1); a surfactant (B) containing 50% by mass or more of fluorochemical surfactant (B^1) with respect to the total mass of the surfactant (B); and an aqueous medium (C);

polymer unit (a^1): a polymer unit of an unsaturated ester containing a polyfluoroalkyl group, or a polymer unit of an unsaturated ester containing a polyfluoroalkyl group having an etheric oxygen atom inserted in a carbon-carbon bond.

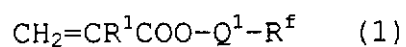
In the oil-barrier composition according to the present invention, it is preferable that the polymer (A) contain the polymer unit (a^1) at a ratio of 90% by mass or more.

In the oil-barrier composition according to the present invention, it is preferable that the polymer (A) be constituted by polymer units, all of which are the polymer unit (a^1).

In the oil-barrier composition according to the

present invention, it is preferable that the surfactant (B) be composed of the fluorochemical surfactant (B^1) only.

In the oil-barrier composition according to the present invention, it is preferable that the polymer unit (a^1) be a polymer unit of a compound represented by the following formula (1):



wherein Q^1 , R^1 , and R^f have the following meanings.

Q^1 : A single bond or bivalent connecting group.

R^1 : A hydrogen atom or a methyl group.

R^f : A polyfluoroalkyl group, or a polyfluoroalkyl group having an etheric oxygen atom inserted in a carbon-carbon bond.

In the oil-barrier composition according to the present invention, it is preferable that the aqueous medium (C) be water or a mixture of water and a water-soluble organic solvent having a boiling point of 40 to 200°C.

In the oil-barrier composition according to the present invention, it is preferable that the surface tension of the composition be 30 mN/m or less at room temperature (25°C).

In the oil-barrier composition according to the present invention, it is preferable that the accumulated

mean diameter of the emulsion of the polymer (A) in the composition be 10 μm or less.

Further, according to the present invention, there is provided a method of manufacturing an oil-barrier composition characterized by including: synthesizing a polymer (A) by emulsion polymerization in the presence of an emulsifier; and adding a fluorochemical surfactant (B^1) to the obtained polymer (A).

In the method of manufacturing an oil-barrier composition according to the present invention, it is preferable that the polymer (A) be synthesized by emulsion polymerization in the aqueous medium (C) in the presence of the fluorochemical surfactant (B^1).

According to the present invention, there is provided a method of subjecting the surface of a sliding component or a component adjacent to the sliding component to an oil-barrier treatment, the method including: applying an oil-barrier composition according to the present invention on the surface of a component, followed by drying or subjecting to a heat treatment.

Further, according to the present invention, there is provided a component, which is a sliding component or a component adjacent to the sliding component, obtained by a method of subjecting to an oil-barrier treatment according to the present invention, the surface of the

component being subjected to an oil-barrier treatment.

BEST MODE FOR CARRYING OUT THE INVENTION

The polymer (A) in the present invention is a polymer containing specific constituting units i.e. polymer units (a^1). Note that, in the following, a polyfluoroalkyl group and a polyfluoroalkyl group having an etheric oxygen atom inserted in the carbon-carbon bond will be generically referred to as a " R^f group". An alkyl group and an alkyl group having an etheric oxygen atom inserted in the carbon-carbon bond will be generically referred to as an "alkyl group which may contain an etheric oxygen atom". An acrylate and a methacrylate will be generically referred to as a (meth)acrylate, and the same applies to other (meth)acrylic acids.

The polymer units (a^1) are polymer units of an unsaturated ester containing an R^f group. The R^f group represents a group having at least two hydrogen atoms of an alkyl group, which may contain an etheric oxygen atom, substituted by fluorine atoms. When represented by $[(\text{the number of fluorine atoms in the } R^f \text{ group}) / (\text{the number of hydrogen atoms contained in the alkyl group, which may contain an etheric oxygen atom, having a structure corresponding to the } R^f \text{ group})] \times 100\%$, the number of

fluorine atoms in the R^f group is preferably at least 60% and particularly preferably at least 80%, as the oil-barrier performance can be easily developed.

Further, examples of the R^f group having an etheric oxygen atom may include, an R^f group containing an oxypolyfluoroalkylene moiety such as oxypolyfluoroethylene or oxypolyfluoropropylene. The carbon number of the R^f group is preferably from 4 to 14, particularly preferably from 6 to 12. When the carbon number of the R^f group is within the above ranges, the oil-barrier performance is sufficient, and polymer units (a^1) are easily obtained. Although the R^f group may be of a straight chain structure or a branched structure, a straight chain structure is more preferred. When the R^f group is of a branched structure, it is preferred that the branched moiety is present at a terminal portion of the R^f group and is a short chain with from 1 to 3 carbon atoms. Further, a chlorine atom may be present instead of the fluorine atom at the terminal portion in the R^f group. Examples of the structure of the terminal portion of the R^f group in which the fluorine atom may be present as described above may include a structure such as CF_3CF_2- , CF_2H- , CF_2Cl- or $(CF_3)_2CF-$.

The R^f group in the present invention is preferably a perfluoroalkyl group (hereinafter referred to as a R^F

group) which may contain an etheric oxygen atom, having substantially all hydrogen atoms of an alkyl group, which may contain an etheric oxygen atom, substituted by fluorine atoms as the oil-barrier performance is easily developed. The carbon number of the R^F group is preferably from 4 to 14, particularly preferably from 6 to 12. When the carbon number of the R^F group is within the above ranges, the oil-barrier performance is sufficient, and the polymer units (a^1) are easily obtained. Further, although the R^F group may be of a straight chain structure or a branched structure, from the viewpoint of the oil-barrier performance, a group of a straight chain structure is preferred. The R^F group is preferably a group having substantially all hydrogen atoms of an alkyl group substituted by fluorine atoms (i.e. a group containing no etheric oxygen atom), particularly preferably a straight chain group represented by $F(CF_2)_n-$ [wherein n is an integer of from 6 to 12].

Specific examples of the R^f group may include the following structures, but are not limited thereto. Further, in the following specific examples, groups corresponding to structurally isomeric groups are also included.

Examples of the R^f group containing no etheric

oxygen atom include the followings.

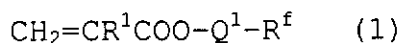
C_2F_5- , C_3F_7- [including both $F(CF_2)_3-$ and $(CF_3)_2CF-$], C_4F_9- [including $F(CF_2)_4-$, $(CF_3)_2CF CF_2-$, $(CF_3)_3C-$ and $F(CF_2)_2CF(CF_3)-$], $C_5F_{11}-$ [including structurally isomeric groups such as $F(CF_2)_5-$, $(CF_3)_2CF(CF_2)_2-$, $(CF_3)_3CCF_2-$, and $F(CF_2)_2CF(CF_3)CF_2-$], $C_6F_{13}-$ [including structurally isomeric groups such as $F(CF_2)_3(CF_3)_2-$], $C_8F_{17}-$, $C_{10}F_{21}-$, $C_{12}F_{25}-$, $C_{15}F_{31}-$, $HC_tF_{2t}-$ (wherein t is an integer of from 1 to 18), and $(CF_3)_2CFC_sF_{2s}-$ (wherein s is an integer of from 1 to 15).

Examples of the R^f group containing an etheric oxygen atom include the followings.

$F(CF_2)_5OCF(CF_3)-$, $F[CF(CF_3)CF_2O]_sCF(CF_3)CF_2CF_2-$,
 $F[CF(CF_3)CF_2O]_tCF(CF_3)-$, $F[CF(CF_3)CF_2O]_uCF_2CF_2-$,
 $F(CF_2CF_2CF_2O)_vCF_2CF_2-$, $F(CF_2CF_2O)_wCF_2CF_2-$ (wherein s and t are independently an integer of from 1 to 10, and preferably an integer of from 1 to 3 as the polymer units (a^1) are easily obtained. Reference symbol "u" is an integer of from 2 to 6. Reference symbol "v" is an integer of from 1 to 11, and preferably an integer of from 1 to 4 as the polymer units (a^1) are easily obtained. Reference symbol "w" is an integer of from 1 to 11, and preferably an integer of from 1 to 6) as the polymer units (a^1) are easily obtained.

As the polymer units (a^1) are easily obtained, the

polymer units (a^1) in the present invention are preferably polymer units of a R^f group-containing (meth)acrylate represented by the following formula (1):



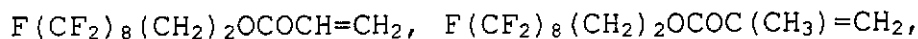
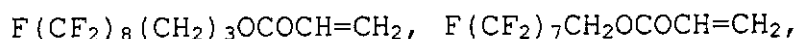
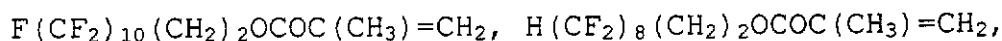
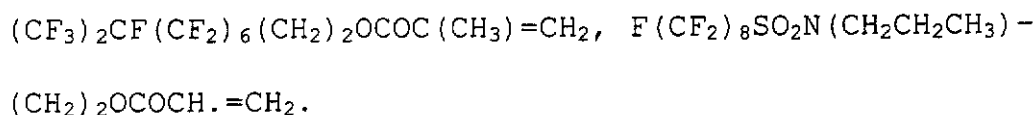
wherein the symbols in the formula (1) have the following meanings.

Q^1 : A single bond or bivalent connecting group.

R^1 : A hydrogen atom or a methyl group.

R^f : An R^f group.

Q^1 in the formula is preferably a bivalent organic connecting group, particularly preferably those to be mentioned in the following specific examples. R^f in the formula is preferably a polyfluoroalkyl group containing no etheric oxygen atom, particularly preferably a perfluoroalkyl group containing no etheric oxygen atom. The following compounds may be given as specific examples of the R^f group-containing (meth)acrylate represented by the formula (1).



The polymer units (a^1) in the polymer (A) may include one type only, or of two or more types. The

polymer (A) may contain polymer units other than the polymer units (a^1). The polymer units other than the polymer units (a^1) are not particularly limited, as long as they are polymer units of a monomer having a polymerizable unsaturated group and no R^f group (hereinafter referred to as other monomers). Such other monomers may be employed from known or well known compounds, and one or more types of such compounds may be used.

Such other monomers are preferably selected from the group consisting of polyolefin unsaturated esters such as acrylic acid esters, unsaturated esters having epoxy groups, compounds having vinyl groups, compounds having amino groups and polymerizable unsaturated groups, compounds having silicon and polymerizable unsaturated groups, and compounds having substituted amino groups and polymerizable unsaturated groups.

When the polymer (A) is a copolymer containing a polymer unit other than the polymer unit (a^1), the ratio of the polymer unit (a^1) in the polymer (A) is preferably 80% by mass or more, particularly preferably 90% by mass or more. If the ratio of the polymer unit (a^1) in the polymer (A) is within the above range, the oil-barrier performance of the oil-barrier composition is favorable.

The fluorine content in the polymer (A) of the

present invention is preferably 30% by mass or over, particularly preferably from 45 to 95% by mass. If the fluorine content in the polymer (A) is within the above range, the oil barrier performance of the oil-barrier composition is favorable.

The mass average molecular weight of the polymer (A) is preferably from 1×10^3 to 1×10^7 , particularly preferably from 1×10^4 to 1×10^5 . In addition, if the polymer (A) is a polymer containing two or more polymer units, each kind of the polymer units may be linked in either of a block fashion or a random fashion, particularly preferably linked in a random fashion.

In addition, the accumulated mean diameter of the emulsion of the polymer (A) in the composition is preferably 10 μm or less, more preferably 6 μm or less, still more preferably 1 μm or less, especially preferably 0.1 μm or less. If the accumulated mean diameter of the emulsion of the polymer (A) is 10 μm or less, the polymer is excellent in dispersion stability as an emulsion. In this case, therefore, there is no possibility of requiring an additional operation such as re-stirring at the time of application. In addition, the polymer excels in the homogeneity of a coating film after the application process, and there is no possibility that the oil barrier performance may fall.

Here, in the present invention, the accumulated mean diameter refers to a particle diameter at a point where an accumulation curve reaches 50%. The accumulation curve is determined as follows. One group of particles is assumed, and its particle size distribution is determined. Then, the total volume of the group of particles is set to be 100% to determine the accumulation curve.

The composition of the present invention contains a surfactant (B) and an aqueous medium (C) in addition to the aforementioned polymer (A). The polymer (A) in the composition is preferably dispersed as particles in the aqueous medium (C) described below. The concentration of the polymer (A) in the composition of the present invention is preferably from 0.01 to 10% by mass, particularly preferably from 0.1 to 5% by mass. If the concentration of the polymer (A) is within the above range, the oil-barrier performance of the oil-barrier composition is favorable and the composition is also favorable in the cost when the oil-barrier treatment is performed using the composition of the present invention.

In the present invention, the surfactant (B) mainly contains a fluorochemical surfactant (B^1), where the fluorochemical surfactant (B^1) amount is 50% by mass or more with respect to the total mass of the surfactant

(B). As far as the fluorochemical surfactant content is within the above range, the surfactant may contain a non-fluorochemical surfactant (B^2). The surfactant (B) preferably contains the fluorochemical surfactant (B^1) in an amount of 90% by mass or more with respect to its total mass. More preferably, the whole part of surfactant (B) is the fluorochemical surfactant (B^1).

If the fluorochemical surfactant (B^1) content is less than 50% by mass with respect to the total mass of the surfactant (B), the desired oil barrier performance cannot be obtained, and the resulting oil-barrier composition is useless because of its poor durability.

Examples of the fluorochemical surfactant (B^1) of the present invention may include, an ionic surfactant having fluorine atoms, or a nonionic surfactant having fluorine atoms. Further, the fluorochemical surfactant (B^1) may be any of an anionic fluorochemical surfactant having R^f groups and anionic groups in combination, a cationic fluorochemical surfactant having R^f groups and cationic groups in combination, an amphoteric surfactant having R^f groups and cationic and anionic groups in combination, and a nonionic surfactant having R^f groups and hydrophilic groups in combination.

Examples of tradenames of fluorochemical cationic surfactants may include, "SURFLON (Registered Trademark)

S-121", manufactured by SEIMI CHEMICAL Co., Ltd., "Fluorade FC-134", manufactured by 3M Co., and "Megafac F-150", manufactured by Dainippon Ink & Chemicals Inc. Examples of tradenames of fluorochemical anionic surfactants may include, "SURFLON (Registered Trademark) S-111", manufactured by SEIMI CHEMICAL Co., Ltd., "Fluorade (Registered Trademark) FC-143", manufactured by 3M Co., and "Megafac (Registered Trademark) F-120", manufactured by Dainippon Ink & Chemicals Inc. Examples of tradenames of fluorochemical amphoteric surfactants may include, "SURFLON (Registered Trademark) S-132", "SURFLON (Registered Trademark) S-131", manufactured by SEIMI CHEMICAL Co., Ltd., "Fluorade (Registered Trademark) FX-172", manufactured by 3M Co., and "Megafac (Registered Trademark) F-120", manufactured by Dainippon Ink & Chemicals Inc. Examples of tradenames of fluorochemical nonionic surfactants may include, "SURFLON (Registered Trademark) S-145", manufactured by SEIMI CHEMICAL Co., Ltd., "Fluorade (Registered Trademark) FC-170", manufactured by 3M Co., and "Megafac (Registered Trademark) F-141", manufactured by Dainippon Ink & Chemicals Inc.

As the non-fluorochemical surfactant (B^2) which may be included in the surfactant (B), a non-fluorochemical non-ionic surfactant having a HLB value of at least 7, a

non-fluorochemical cationic surfactant having an alkyl group having at least 6 carbon atoms in its molecule, or a non-fluorochemical anionic surfactant having an alkyl group having at least 6 carbon atoms in its molecule, is preferred.

As the non-fluorochemical non-ionic surfactant having a HLB value of at least 7, a known nonionic surfactant having at least 5 oxyalkylene units in its molecule is preferred. As the oxyalkylene units, oxyethylene or oxypropylene is preferred. Further, examples of the non-fluorochemical cationic surfactant having an alkyl group having at least 6 carbon atoms in its molecule may include an alkyl ammonium salt, and examples of the non-fluorochemical anionic surfactant having an alkyl group having at least 6 carbon atoms in its molecule may include an alkyl sulfate.

Specific examples of the non-fluorochemical surfactant (B^2) in the present invention will be given below. Polyoxyethylene lauryl ether (HLB=14.5, oxyethylene addition mols=9), polyoxyethylene polyoxypropylene cetyl ether (HLB=9.5, oxyethylene addition moles=1, oxypropylene addition mols=8), polyoxyethylene octyl phenyl ether (HLB=11.5, oxyethylene addition mols=10), polyoxyoxyethylene nonyl phenyl ether (HLB=8.0, oxyethylene addition mols=5), stearyl

trimethylammonium chloride, dioctyl dimethylammonium chloride, ammonium lauryl sulfate, sodium polyoxyethylene lauryl ether sulfate, dimethyl octadecylamine acetate. Among these, preferred examples of the non-fluorochemical surfactant (B²) include polyoxyethylene lauryl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene nonyl phenyl ether, or dimethyloctyldecylamine acetate.

The amount of the surfactant (B) in the composition is preferably from 0.001% by mass to 10% by mass, particularly preferably from 0.01% by mass to 5% by mass. If the amount of the surfactant (B) is less than 0.001% by mass, wettability of the composition to a substrate might be insufficient. On the other hand, if the amount is more than 10% by mass, there is a problem in that the adhesion of the resulting coating film to the substrate is decreased.

Further, the composition of the present invention contains an aqueous medium (C). Examples of the aqueous medium (C) may include, water, or a medium having a water-soluble organic solvent incorporated in water. Examples of the water-soluble organic solvent may include a ketone, an ester, a glycol, a glycol ether or an alcohol. When the aqueous medium (C) contains a water-soluble organic solvent, the proportion of water in the aqueous medium (C) is preferably from 50 to 95 wt %,

while the proportion of the water-soluble organic solvent is preferably from 5 to 50 wt %.

Further, from the viewpoint of drying efficiency, the water-soluble organic solvent is preferably one having a boiling point of from 40 to 200°C. Further, the aqueous medium (C) is preferably an organic solvent which has a solubility in water at 20°C of at least 1 wt %.

The surface tension of the oil-barrier composition of the present invention at room temperature (25°C) is preferably 30 mN/m or less, more preferably 20 mN/m or less. If the surface tension of the composition at room temperature (25°C) is 30 mN/m or less, the oil-barrier performance of the composition is favorable. In addition, the surface tension of the composition is lower than the surface tension of oil content such as higher fatty acid ester which is likely to adhere to the surface of a component in the preceding step like a press oil to be used at the time of press processing. Thus, the composition of the present invention shows excellent wettability and adhesiveness even on the surface being attached with oil content, so that the target surface can be treated with the composition without removing the oil content attaching to the target surface by washing.

For the composition of the present invention, when a coating film is formed on the target surface, a contact

angle of a lubricant to the surface of the coating film is 50° or more. In this case, the lubricant may be a hydrocarbon lubricant having 16 or more carbon atoms, specifically for example normal hexadecane. As far as the contact angle of the lubricant to the surface of the coating film on the composition is within the above range, the oil barrier performance is excellent.

In addition to those mentioned above, the compound of the present invention may contain other components within a range not to adversely affect the dispersion stability, oil-barrier characteristics, wettability on the substrate, the outer appearance, and the like. Specific examples of such other compounds may include, a pH regulator to prevent corrosion, a rust-preventing agent, a dye for controlling the concentration of the polymer in liquid, a stabilizer for the dye, a flame retardant, and an antistatic agent.

The oil barrier composition of the present invention may be prepared by any method as far as the composition is obtained, which has the desired composition and physical properties as described above. Therefore, for example, the method may include: synthesizing a polymer (A) by performing solution polymerization of polymer units containing polymer units including the polymer unit (a¹) in a fluorinated solvent;

removing the fluorinated solvent; and dispersing the resulting polymer (A) in an aqueous solvent (C) in the presence of a fluorochemical surfactant (B¹). In this case, examples of the fluorinated solvent applicable to the composition of the present invention include: HFC such as 1,3-bis (trifluoromethyl)benzene, or 2,3-dihydrodecafluoro (n-)pentane; and HCFC such as C₃HF₅C₁₂ (trade name: "AK-225", manufactured by Asahi Glass Co., Ltd.). Because of directly obtaining the composition of the present invention, there is preferably a method in which a polymer (A) is synthesized by emulsion polymerization of monomers containing polymer units (a¹) and optionally other monomers in the presence of an emulsion solvent.

When the polymer (A) is synthesized by emulsion polymerization, it is preferably carried out by the following method 1 or 2.

Method 1: A method which includes emulsifying a monomer in the presence of a medium and an emulsifier, followed by polymerization with stirring.

Method 2: A method which includes emulsifying a monomer in the presence of a medium and an emulsifier by using a homomixer or high pressure emulsifying apparatus, prior to addition of a polymerization initiator, and then reacting a polymerization initiating source with the

emulsion for polymerization.

In either one of the above methods, when a monomer in the state of gas such as vinyl chloride is employed as the monomer, it may be continuously supplied under pressure by means of a pressure container.

The polymerization initiating source is not particularly limited, and a general polymerization initiator such as an organic peroxide, an azo compound, a persulfate; or ionizing radiation rays such as γ -rays, may be employed.

As the medium, the same medium as the aqueous medium (C) is preferably employed.

That is, when the composition of the present invention is manufactured by preparing the polymer (A) with emulsion polymerization, the polymer (A) is preferably synthesized by emulsion-polymerization of monomers containing polymer units (a^1), preferably those represented by the formula (1), and optionally other monomers in the aqueous medium (C) in the presence of the emulsion.

In all of the methods described above, an emulsifier may be the surfactant (B). In this case, furthermore, the emulsifier may be the fluorochemical surfactant (B^1) or the non-fluorochemical surfactant (B^2). However, using the fluorochemical surfactant (B^1)

is preferable because of directly obtaining the composition of the present invention. The surfactant (B) may be a combination of two or more surfactants having different ionicities. However, for using the surfactants having different ionicities, it is preferred to combine cationic and non-ionic, anionic and non-ionic, or non-ionic and amphoteric surfactants.

In the present invention, the constituents of the oil-barrier composition, specifically the mass average molecular weight of the polymer (A), the content of each of the polymer (A), the surfactant (B), and the aqueous medium (C) in the composition, the content of the fluorochemical surfactant (B^1) in the surfactant (B), and so on, and physical properties of the composition, specifically the surface tension of the composition, and so on, can be easily adjusted to within their favorable ranges described above. Therefore, the composition of the present invention is preferably prepared by adding the fluorochemical surfactant (B^1) after the emulsion polymerization.

According to the composition of this invention, depending on purpose or use, the surface of the sliding component or other components around the sliding component (hereinafter, also correctively referred to as a "target component"), which require oil-barrier

processing, can be subjected to an oil-barrier processing. As the processing method, a general covering-processing method is employable, for example a dip-coating method, a splay-coating method, or a method of coating with an aerosol can be filled with the composition of the present invention.

A coating film can be formed on the surface of the target component by applying the composition of the present invention to the surface and drying the composition. After applying and drying the composition, a heat treatment may be preferably applied. Such a heat treatment makes a coating film wherein is continuous and has no defect on the surface of the target component. Conditions of the drying and the heat treatment may be appropriately selected depending on the constituents of the composition to be applied, the coating area, or the like. For instance, in the examples described later, the composition is dried at 60°C for 15 minutes. For instance, in the examples described later, the composition is heated at 120°C for 10 minutes.

(Examples)

Hereinafter, the present invention will be described in more detail by way of the following examples, but the present invention is not limited thereto.

[Preparation Example of Polymer 1]

Charged into a 1 liter autoclave made of glass were 219 g of $F(CF_2)_8(CH_2)_2OCOCH=CH_2$, 64.4 g of a fluorochemical surfactant S-131 (a solid content concentration of 30%, manufactured by SEIMI CHEMICAL Co., Ltd.), 48.2 g of acetone, and 266 g of ion-exchanged water, and pre-emulsification was carried out in the mixture at 50°C. for 1 hour. Then, 2 g of 2,2'-azobis(2-methylpropionamidine) hydrochloride (V-50, manufactured by Wako Pure Chemical Industries, Ltd.) was added to the mixture, and the autoclave was flushed with nitrogen.

The temperature of the mixture was raised to 60°C while the mixture was being stirred with the stirring speed 200rpm (20L cylindrical vessel ($\phi = 26\text{cm}$), anchor wing ($\phi = 18\text{cm}$)) and polymerization was carried out for 18 hours. After cooling, the mixture was subjected to an analysis by gas chromatography (GC). As a result, the degree of conversion of $F(CF_2)_8(CH_2)_2OCOCH=CH_2$ was at least 99%, and thus, the polymerization reaction was found to have proceeded satisfactorily. Then, the mixture was subjected to filtration with a pore diameter of 6 μm to obtain a milky white emulsion. The solid content concentration of the emulsion was 36.0%.

[Preparation Example of Polymer 2]

Charged into a 1 liter autoclave made of glass were 217 g of $F(CF_2)_8(CH_2)_2OCOCH=CH_2$, 133 g of a 20 wt% aqueous solution of a hydrocarbon surfactant K-220 (manufactured by NOF corporation), 47.6 g of acetone, and 201 g of ion-exchanged water, and pre-emulsification was carried out in the mixture at 50°C. for 1 hour. Then, 1.9 g of 2,2'-azobis(2-methylpropionamidine) hydrochloride (V-50, manufactured by Wako Pure Chemical Industries, Ltd.) was added to the mixture, and the autoclave was flushed with nitrogen.

The temperature of the mixture was raised to 60°C while the mixture was being stirred at same condition with Polymer 1, and polymerization was carried out for 18 hours. After cooling, the mixture was subjected to an analysis by gas chromatography (GC). As a result, the degree of conversion of $F(CF_2)_8(CH_2)_2OCOCH=CH_2$ was at least 99%, and thus, the polymerization reaction was found to have proceeded satisfactorily. Then, the mixture was subjected to filtration with a pore diameter of 6 μm to obtain a milky white emulsion. The solid content concentration of the emulsion was 40.9%.

[Preparation of Composition 1]

SURFLON (registered trademark) S-111 (a solid content concentration of 30%, manufactured by SEIMI CHEMICAL Co, Ltd.) was diluted with a 20% ethanol aqueous

solution to prepare a solution (1) having a solid content concentration of 0.2%. Then, an emulsion (a solid content of 36%) synthesized in Synthesis Example of the polymer 1 was diluted with the prepared solution (1). Consequently, a composition 1 having the polymer 1 with a solid content concentration of 2% was prepared.

The accumulated mean diameter of the emulsion of the polymer 1 in the resulting composition was measured by a dynamic reflecting method using a particle size analyzer MICROTRAC UPA (MODEL: 9230, manufactured by Nikkiso Co., Ltd.). Consequently, the measured accumulated mean diameter was 0.0112 μm .

[Preparation of Composition 2]

A composition 2 containing the polymer 2 with a solid content of 2% was prepared. That is, the emulsion (a solid content concentration of 40%) prepared in Synthesis Example of the polymer 2 was diluted with the solution (1) prepared in Preparation of Composition 1.

The accumulated mean diameter of the emulsion of the polymer 2 in the resulting composition was measured as described in Preparation of Composition 1. Consequently, the measured accumulated mean diameter was 0.0689 μm .

[Preparation of Composition 3]

A composition 3 was prepared as follows. That is,

the emulsion (a solid content concentration of 36%) prepared in Synthesis Example of the polymer 1 was diluted with a 0.2 wt% aqueous solution of SURFLON (registered trademark) S-111 (a solid content of 30%, manufactured by SEIMI CHEMICAL Co, Ltd.) and ion-exchange water such that the solid content concentration of the polymer 1 would become 0.4%, while the solid content concentration of S-111 would become 0.04 %.

The accumulated mean diameter of the emulsion of the polymer 1 in the resulting composition was measured as described in Preparation of Composition 1. Consequently, the measured accumulated mean diameter was 0.0119 μm .

[Preparation of Composition 4]

A composition 4 was prepared as follows. That is, the emulsion (a solid content concentration of 36%) prepared as Synthesis Example of the polymer 1 with proviso that the stirring speed in the polymerization step was 120 rpm (20L cylindrical vessel ($\phi = 26\text{cm}$), anchor wing ($\phi = 18\text{cm}$) was diluted with a 0.2 wt% aqueous solution of SURFLON (registered trademark) S-111 (a solid content concentration of 30%, manufactured by SEIMI CHEMICAL Co, Ltd.) and ion-exchanged water such that the solid content concentration of the polymer would

become 0.4%, while the solid content concentration of S-111 would become 0.04 %.

The accumulated mean diameter of the emulsion of the polymer in the resulting composition was measured as described in Preparation of Composition 1. Consequently, the measured accumulated mean diameter was 0.3178 μm .

[Method of Evaluating the Performance and Evaluation Results]

(1) Wettability

To evaluate the wettability of each of the compositions 1 and 2, the surface tensions of the compositions at room temperature (25°C) were measured by using a Wilhelmy surface tension meter. The results (unit: mN/m) are shown in Table 1.

Table 1

Composition	Surface tension (mN/m)
Composition 1	18.9
Composition 2	18.7

(2) Evaluation of oil-barrier performance (Part 1)

Iron plates (10 cm x 10 cm x 1 mm) were immersed in the compositions 1 and 2 for one minute, respectively. Then, the iron plates were dried by heating at 120°C for 10 minutes to form a coating film on the surface of each

iron plate. After the formation of the coating film, the contact angle of normal hexadecane to the surface of iron plate was measured by using a liquid-droplet projecting type contact angle meter manufactured by KYOWA INTERFACE SCIENCE Co., Ltd. Subsequently, after leaving the iron plate whereupon the droplet of normal hexadecane is placed for a predetermined time at room temperature (25°C) or 90°C, The variation per time of the contact angle of normal hexadecane was measured. The average values of contact angles are shown in Table 2.

Table 2

Composition	Contact angle of normal hexadecane (°)						
	Immediately after the treatment	Leaving at room temperature (25°C)			Leaving at 90°C		
		After 1 day	After 2 days	After 10 days	After 1 day	After 2 days	After 10 days
Untreated	10 or less	10 or less	10 or less	10 or less	10 or less	10 or less	10 or less
Composition 1	82	82	82	82	62	58	58
Composition 2	30	10 or less	10 or less	10 or less	10 or less	10 or less	10 or less

(3) Evaluation of oil-barrier performance (Part 2)

Iron plates used herein were similar to those of the above evaluation (2). The measurement of the contact angle of normal hexadecane to the surface of each iron plate was performed by using a liquid-droplet projecting type contact angle meter manufactured by KYOWA INTERFACE SCIENCE Co., ltd., just as in the case of the evaluation (2) except that oil used for press processing (AK-280, manufactured by COSMO OIL LUBRICANTS Co., Ltd.) was applied with a brush. The average values of contact angles are shown in Table 3.

(4) Evaluation of oil-barrier performance (Part 3)

After glass plates were immersed in press oil (AK-280, manufactured by COSMO OIL LUBRICANTS Co., Ltd.), the glass plates were dried overnight at room temperature. Then, the glass plates were immersed in the respective compositions 3 and 4 for one minute, followed by drying the glass plates for 15 minutes at 60°C. Then, a coating film was formed on the surface of the glass plate, and then the contact angle of normal hexadecane to the surface of each iron plate was measured by using a liquid-droplet projecting type contact angle meter (manufactured by KYOWA INTERFACE SCIENCE Co., Ltd.). The average values of contact angles are shown in Table 4.

Table 4

Composition	Contact angle of normal hexadecane (°)	Surface tension (mN/m)
Untreated	30 or less	
Composition 3	75	28.7
Composition 4	66	25.7

INDUSTRIAL APPLICABILITY

The oil-barrier composition of the present invention uses an aqueous medium, so that the composition exhibits excellent oil barrier performance while having no worries about ozone layer destruction and global warming. The composition of the present invention is

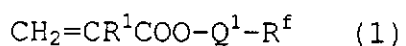
very advantageous in terms of a work environment because the composition has substantially no problem of bad smell. In addition, this composition can be processed as it is, even when the oil content adheres, which was used for the target component in the preceding step.

Therefore, the step of washing for removing the oil content can be skipped, so that the simplification of the process can be realized.

CLAIMS

1. An oil-barrier composition, comprising:
a polymer (A) containing a polymer unit (a^1); a surfactant (B) containing 50% by mass or more of a fluorochemical surfactant (B^1) with respect to a total mass of the surfactant (B); and an aqueous medium (C);
polymer unit (a^1): a polymer unit of an unsaturated ester containing a polyfluoroalkyl group, or a polymer unit of an unsaturated ester containing a polyfluoroalkyl group having an etheric oxygen atom inserted in a carbon-carbon bond.
2. The oil-barrier composition according to Claim 1, wherein the polymer (A) contains the polymer unit (a^1) at a ratio of 90% by mass or more.
3. The oil-barrier composition according to Claim 1 or 2, wherein the polymer (A) is constituted by polymer units, all of which are the polymer unit (a^1).
4. The oil-barrier composition according to any one of Claims 1 to 3, wherein the surfactant (B) is composed of the fluorochemical surfactant (B^1) only.

5. The oil-barrier composition according to any one of Claims 1 to 4, wherein the polymer unit (a^1) is a polymer unit of a compound represented by the following formula (1):



wherein Q^1 , R^1 , and R^f have the following meanings:

Q^1 : A single bond or bivalent connecting group,

R^1 : A hydrogen atom or a methyl group, and

R^f : A polyfluoroalkyl group, or a polyfluoroalkyl group having an etheric oxygen atom inserted in a carbon-carbon bond.

6. The oil-barrier composition according to any one of Claims 1 to 5, wherein the aqueous medium (C) is water or a mixture of water and a water-soluble organic solvent having a boiling point of 40 to 200°C.

7. The oil-barrier composition according to any one of Claims 1 to 6, which has a surface tension of 30 mN/m or less at room temperature (25°C).

8. The oil-barrier composition according to Claim 1, wherein the emulsion of the polymer (A) has an accumulated mean diameter of 10 μm or less.

9. A method of manufacturing an oil-barrier composition according to any one of Claims 1 to 8, comprising:

synthesizing a polymer (A) by emulsion polymerization in the presence of an emulsifier; and adding a fluorochemical surfactant (B¹) to the obtained polymer (A).

10. The method of manufacturing an oil-barrier composition according to Claim 9, comprising:

synthesizing the polymer (A) by emulsion polymerization in an aqueous medium (C) in the presence of the fluorochemical surfactant (B¹).

11. A method of subjecting a surface of a sliding component or a component adjacent to the sliding component to an oil-barrier treatment, comprising:

applying an oil-barrier composition according to any one of Claims 1 to 8 or an oil-barrier composition prepared by a method of manufacturing an oil-barrier composition according to Claim 9 or 10 on a surface of a component, followed by drying or subjecting to a heat treatment.

12. A component, which is a sliding component or a component adjacent to the sliding component, obtained by a method according to Claim 11, the component having a surface subjected to an oil-barrier treatment.