DESCRIPTION

OIL RETENTION TREATMENT AGENT, OIL RETENTION TREATMENT METHOD USING THE SAME, AND WATCH HAVING BEEN OIL RETENTION TREATED BY THE OIL RETENTION TREATMENT METHOD

FIELD OF THE INVENTION

The present invention relates to an oil retention treatment agent used in precision instruments such as a watch, namely, a watch oil diffusion-inhibiting agent, and a watch using the same. More particularly, the invention relates to an oil retention treatment agent used in oil retention treatment performed for bottom plates, receivers and gears of a watch.

BACKGROUND OF THE INVENTION

As watches, there are two types of mechanical watches which operate by the use of power of a mainspring and electronic watches which operate by electric power of buttery loaded therein. Each of the mechanical watches and the electronic watches has a train wheel portion to transmit a driving force from the driving source. The train wheel portion is constituted of gear, receiver, etc.

In the mechanical watches, a great driving force is continuously applied to its parts, so that metal parts have been mainly employed. In the electronic watches, metal parts have been conventionally employed, but a great driving force is not continuously applied to the parts, so that plastic (e.g., engineering plastic) parts also came to be employed.

Watches are usually desired to operate over a long period of time in view of its nature. On this account, a lubricating oil for watches (watch lubricating oil) is poured into the slide portion to prevent deterioration due to frictional wear and thereby inhibit deterioration of the slide portion with time.

However, even if the watch lubricating oil is poured into the slide portion, the lubricating oil is liable to spread out from the slide portion because wristwatch is used on a wrist and vibrated very frequently. If the lubricating oil spreads out, prevention of frictional wear becomes infeasible, and deterioration of the slide portion with time is promoted to finally cause stoppage of watch.

Therefore, in order to inhibit deterioration of the slide portion with time, it is necessary to subject the place where a watch lubricating oil is poured to oil

retention treatment so as to prevent diffusion of the lubricating oil from the slide portion.

As a method to prevent diffusion of a lubricating oil from the portion where the lubricating oil has been poured, an oil repellent treatment method using an oil repellent agent is generally known. The method is, for example, one wherein surfaces of other portions than the portion where a lubricating oil has been pored (portion where a lubricating oil is retained) are treated with a fluorine compound or the like to allow said portions to have oil repellency and thereby inhibit diffusion (spreading-out) of the lubricating oil (Japanese Patent Laid-Open Publication No. 288452/2001).

In the precision instruments such as watches, however, each part is small, so that it is very difficult to perform the oil repellent treatment method. Then, in the conventional oil retention treatment method for a watch, a fluorine type surface-active agent (e.g., Fluorad™ 722 available from 3M Co.) of high concentration is dissolved in a large amount of a low-boiling fluorine type solvent to prepare an oil retention treatment agent of low concentration, and in this solution a part having a metal or plastic slide portion is immersed to perform surface treatment and thereby allow the fluorine type surface-

active agent to adhere to the surface of the part, whereby the lubricating oil is retained.

In this method, however, the lubricating oil is retained by means of surface tension between the surface having been treated with the fluorine type surface-active agent and the lubricating oil, and the resistance to frictional wear in the sliding process (acting process of lubricating oil) and the interaction between the fluorine type surface-active agent and the lubricating oil are rarely taken into account, so that sufficient oil retention properties are not obtained. Further, with regard to the conventional fluorine type surface-active agent, a treatment solution is prepared by the use of a fluorine type solvent as a diluent. Therefore, plastic materials and metal materials cannot be treated with the same treatment solution, and hence it is necessary to appropriately prepare the suitable treatment solution. In the surface treatment using such a fluorine type surface-active agent, furthermore, there resides another problem that a stain remains on the surface.

Moreover, because the fluorine type solvent is high in the unit cost and is used in a large amount, there is brought about an economical problem that the cost of the treatment solution becomes high or an environmental

problem that a harmful gas is generated when the treatment solution is heated to remove the solvent or the fluorine type surface-active agent is hardly decomposed.

In order to solve such problems, solid lubrication by means of nickel composite plating for which prevention of oil diffusion is unnecessary has been proposed (Japanese Patent No. 3269090). In this method, however, there is a problem that the color of the part(s) changes to black or the treatment takes much time.

OBJECT OF THE INVENTION

It is an object of the present invention to provide an oil retention treatment agent exhibiting excellent oil retentivity in precision instruments such as a watch. It is another object of the present invention to provide an oil retention treatment agent employable for both of a metal part and a plastic part without using a fluorine type solvent, and a watch using the oil retention treatment agent.

DISCLOSURE OF THE INVENTION

The present inventor has earnestly studied to solve the above problems and has found that lubricants such as grease and lubricating oils can be more stably retained by

subjecting the parts of precision instruments such as a watch to surface treatment using an oil retention treatment agent comprising a fluorine compound having phosphorus atom or the like which exhibits high affinity for metal and plastic. Based on the finding, the present invention has been accomplished.

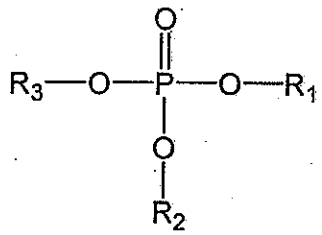
A oil retention treatment agent according to the invention contains, in a solvent, at least one organic fluorine compound (a) selected from fluorine compounds having in a molecule:

one atom selected from phosphorus, nitrogen and sulfur, and

a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group with a fluorine atom.

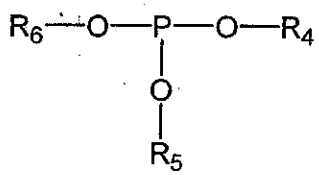
It is preferable that the hydrocarbon group is a hydrocarbon group of 1 to 20 carbon atoms and comprises a chain or branched aliphatic hydrocarbon group and/or an aromatic ring.

The organic fluorine compound (a) is preferably at least one organic fluorine compound selected from phosphorus-containing fluorine compounds represented by any one of the following formulas (1) to (3):



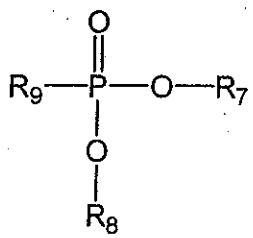
(1)

wherein R_1, R_2 and R_3 are each independently a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 1 to 12 carbon atoms and/or an aromatic ring, with a fluorine atom,



(2)

wherein R_4, R_5 and R_6 are each independently a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 1 to 12 carbon atoms and/or an aromatic ring, with a fluorine atom,



(3)

wherein R_7 and R_8 are each independently a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group comprising a chain or branched aliphatic

hydrocarbon group of 1 to 12 carbon atoms and/or an aromatic ring, with a fluorine atom, and R_9 is an acetyl group or a methoxycarbonylmethyl group.

The oil retention treatment agent according to the invention preferably further contains at least one organic fluorine compound (b) selected from fluorine compounds having in a molecule:

a functional group selected from a carbonyl group, a hydroxyl group, an ester group and an ether group, and

a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group with a fluorine atom.

It is preferable that the hydrocarbon group in the organic fluorine compound (b) is a hydrocarbon group of 1 to 20 carbon atoms and comprises a chain or branched aliphatic hydrocarbon group and/or an aromatic ring.

The organic fluorine compound (b) is preferably at least one organic fluorine compound selected from ether compounds represented by the following formula (4) or (5):

$$R_{10}\text{—}(\text{O—}R_{11})_n\text{—OH} \qquad (4)$$

wherein R_{10} is a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 3 to 12 carbon atoms and/or an aromatic ring, with a

fluorine atom, R_{11} is an alkylene group of 1 to 3 carbon atoms, and n is a number of 1 to 5,

$$R_{12}-(O-R_{14})_n-O-R_{13} \qquad (5)$$

wherein R_{12} and R_{13} are each independently a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 3 to 12 carbon atoms and/or an aromatic ring, with fluorine atom, R_{14} is an alkylene group of 1 to 3 carbon atoms, and n is a number of 1 to 5.

A watch according to the invention has at least one watch part having been subjected to oil retention treatment using any one of the above-mentioned oil retention treatment agents.

The watch according to the invention is preferably assembled by the use of at least one watch part having been subjected to oil retention treatment using an oil retention treatment agent comprising a sulfur-containing organic fluorine compound (a), and a lubricating oil comprising a sulfur type anti-wear agent, or is preferably assembled by the use of at least one watch part having been subjected to oil retention treatment using an oil retention treatment agent comprising a phosphorus-containing organic fluorine compound (a), and a

lubricating oil comprising a phosphorus type anti-wear agent.

The oil retention treatment method according to the invention comprises subjecting a portion where a lubricating oil is to be retained to oil retention treatment using any one of the above-mentioned oil retention treatment agents to allow at least the organic fluorine compound (a) to adhere to the surface of the portion.

The oil retention treatment method according to the invention preferably comprises (I) a step of immersing at least one precision instrument part in the oil retention treatment agent to allow the oil retention treatment agent to adhere to the surface of the part, and (II) a step of warm-air drying the precision instrument part obtained after the immersion step to remove the solvent. In the step (I), it is preferable that the precision instrument part is immersed with subjecting the part to ultrasonic treatment.

In the oil retention treatment method according to the invention, it is preferable that after the step (I), a step (III) of immersing the precision instrument part in a solvent to remove an excess oil retention treatment agent having adhered to the surface of the part is performed,

and thereafter the step (II) is performed. In the step (III), it is more preferable that the precision instrument part having been immersed in the solvent is oscillated in the solvent.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing changes of contact angles with time.

PREFERRED EMBODIMENTS OF THE INVENTION

<Oil retention treatment agent>

The oil retention treatment agent of the invention contains, in a solvent, at least one organic fluorine compound (a) selected from fluorine compounds having in a molecule:

one atom selected from phosphorus, nitrogen and sulfur, and

a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group with a fluorine atom.

<Organic fluorine compound (a)>

The organic fluorine compound (a) is adsorbed on the surface of a metal part or a plastic part by the action of its polarity. Particularly, a phosphorus atom, a nitrogen

atom and a sulfur atom have strong interaction with metals, and they are selectively adsorbed on the metal surface.

Of the organic fluorine compounds, organic fluorine compounds having a phosphorus atom or a nitrogen atom in a molecule are more preferable, and organic fluorine compounds having a phosphorus atom in a molecule are particularly preferable. The organic fluorine compounds having a phosphorus atom or a nitrogen atom in a molecule hardly cause corrosion of parts and can retain a lubricating oil for a longer period of time. The organic fluorine compounds having a phosphorus atom in a molecule are particularly excellent in the affinity for metals, and by the use of such compounds, the oil retention properties (oil retentivity) can be remarkably enhanced, the lubricating oil is hardly changed in its quality, and the resistance to frictional wear can be improved.

It is preferable that the hydrocarbon group of the organic fluorine compound (a) is a hydrocarbon group of 1 to 20 carbon atoms and comprises a chain or branched aliphatic hydrocarbon group and/or an aromatic ring. As such a hydrocarbon group, particularly preferable is a chain or branched alkyl group. The organic fluorine compound having a group derived from a chain or branched

alkyl group is well dissolved in the after-mentioned solvent and exhibits excellent oil retention properties.

The molar ratio (F/H) of fluorine to hydrogen contained in the group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group with a fluorine atom is not specifically restricted provided that the resulting oil retention treatment agent exhibits oil retention properties, but the molar ratio is preferably not less than 1. If the F/H ratio is markedly decreased, the lubricating oil is liable to spread out, and the oil retention properties are sometimes lowered.

Examples of the organic fluorine compounds (a) for use in the invention are given below.

(Organic fluorine compound having sulfur atom in molecule)

The organic fluorine compound having a sulfur atom in a molecule that is used in the invention is, for example, a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of a sulfone compound with a fluorine atom.

Examples of the sulfone compounds include sulfones represented by the following formula (6):

$$R_{21}—SO_2—R_{22} \qquad (6)$$

wherein R_{21} and R_{22} are each independently a hydrocarbon group containing a chain or branched aliphatic hydrocarbon group of 1 to 12 carbon atoms and/or an aromatic ring.

Of such compounds, preferable is a sulfone compound wherein R_{21} and R_{22} in the formula (6) are each independently a pentyl group or an octyl group.

The organic fluorine compound (a) for use in the invention is preferably a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of such a sulfone compound with a fluorine atom.

More specifically, there is preferably employed:

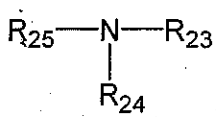
$(CF_2H(CFH)_3CF_2)_2SO_2$, or

$(CF_3(CF_2)_6CH_2)_2SO_2$.

(Organic fluorine compound having nitrogen atom in molecule)

The organic fluorine compound having a nitrogen atom in a molecule that is used in the invention is, for example, a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of an amine compound with a fluorine atom.

Examples of the amine compounds include amines represented by the following formula (7):



(7)

wherein R_{23}, R_{24} and R_{25} are each independently a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 1 to 12 carbon atoms and/or an aromatic ring.

Of such compounds, preferable is an amine compound wherein R_{23}, R_{24} and R_{25} in the formula (7) are each independently an ethyl group, a butyl group, an isobutyl group, a hexyl group, an isoheptyl group, an octyl group, a tridecyl group, a phenyl group, a tolyl group, a dimethylphenyl group or a nonylphenyl group.

Examples of amine compounds other than the amine compounds represented by the formula (7) include aniline, diethylaniline, bis(diethylphenyl)amine and tetra(tridecyl)-4,4'-isopropylidenediphenyldiamine.

The organic fluorine compound (a) for use in the invention is preferably a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of such an amine compound with a fluorine atom.

More specifically, there is preferably employed:

$\{(CF_3)_3C\}_3N$,

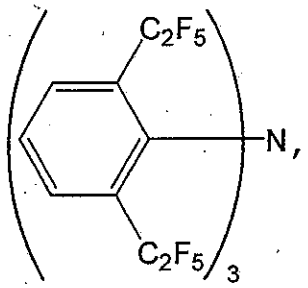
$(CHF_2CF_2CHFCF_2)_3N$,

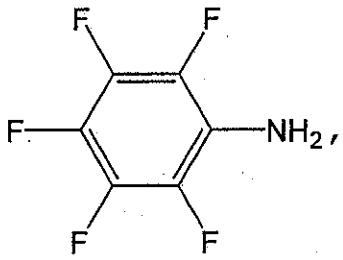
$(C_6F_{13})_3N$,

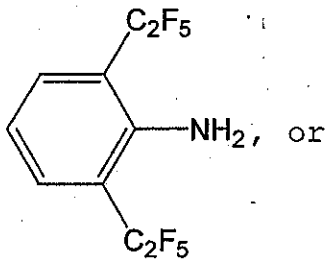
$\{CH_3CH_2(CF_2)_4\}_3N$,

$\{(CF_3)_3C(CF_2)_2CH\}_3N$,

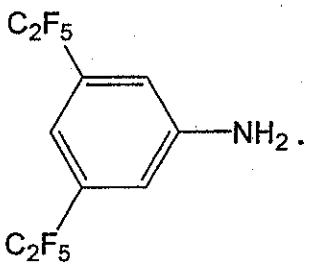
$(C_6F_5)_3N$;







or



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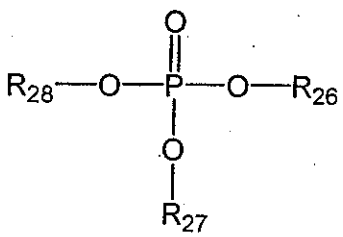
The organic fluorine compound having a nitrogen atom in a molecule is preferably used in combination with a lubricating oil having sufficient resistance to frictional wear or an anti-wear agent.

(Organic fluorine compound having phosphorus atom in molecule)

The organic fluorine compound having a phosphorus atom in a molecule that is used in the invention is, for example, a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of a phosphoric ester, such as an acid phosphate, an acid phosphite, a neutral phosphate, a neutral phosphite or phosphonate, with a fluorine atom.

Of such compounds, particularly preferable is a phosphorus-containing organic fluorine compound obtained from a neutral phosphate, a neutral phosphite or phosphonate. The oil retention treatment agent containing such a phosphorus-containing organic fluorine compound is excellent in oil retentivity over a long period of time.

Examples of the neutral phosphates include phosphoric esters represented by the following formula (8):



(8)

wherein R_{26}, R_{27} and R_{28} are each independently a hydrocarbon group comprising a chain or branched aliphatic

hydrocarbon group of 1 to 12 carbon atoms and/or an aromatic ring.

Of such compounds, preferable is a neutral phosphate wherein R_{26}, R_{27} and R_{28} in the formula (8) are each independently an ethyl group, a pentyl group, an octyl group, a decyl group, a tridecyl group, a stearyl group, a phenyl group, a tolyl group, a dimethylphenyl group, a di-t-butylphenyl group or a nonylphenyl group.

Examples of neutral phosphates other than the neutral phosphates represented by the formula (8) include trimethylol phosphate, tetraphenyldipropylene glycol diphosphate, tetraphenyltetra(tridecyl)pentaerythritol tetraphosphate, tetra(tridecyl)-4,4'-isopropylidene diphenylphosphate, bis(tridecyl)pentaerythritol diphosphate, bis(nonylphenyl)pentaerythritol diphosphate, distearyl pentaerythritol diphosphate and tris(2,4-di-t-butylphenyl) phosphate.

The organic fluorine compound (a) for use in the invention is preferably a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of such a neutral phosphate with a fluorine atom.

More specifically, there is preferably employed:

$(CF_3CH_2O)_3P{=}O$,

$\{CHF_2(CF_2)_3CH_2O\}_3P{=}O$,

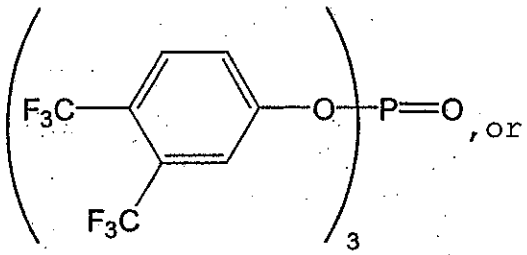
$(CHF_2CF_2CH_2CF_2CH_2O)_3P{=}O$,

$\{CF_3(CF_2)_2CHF(CF_2)_3CH_2O\}_3P{=}O$,

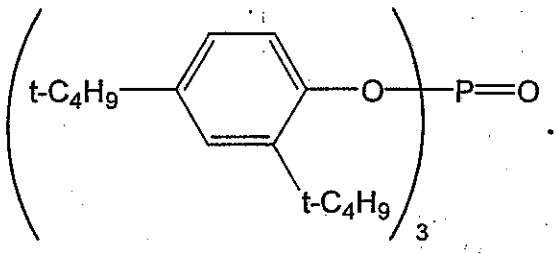
$(C_8F_{17}O)_3P{=}O$,

$\{CF_3(CF_2)_6CH_2CF_2CHFO\}_3P{=}O$,

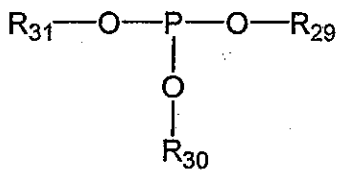
$(C_{18}F_{37}O)_3P{=}O$,



, or



Examples of the neutral phosphites include phosphoric esters represented by the following formula (9):



(9)

wherein R_{29}, R_{30} and R_{31} are each independently a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 1 to 12 carbon atoms and/or an aromatic ring.

Of such compounds, preferable is a neutral phosphite wherein R_{29}, R_{30} and R_{31} in the formula (9) are each

independently an ethyl group, a decyl group, an octyl group, a tridecyl group, an oleyl group, a stearyl group, a phenyl group, a tolyl group, a dimethylphenyl group, a di-t-butylphenyl group or a nonylphenyl group.

Examples of neutral phosphites other than the neutral phosphites represented by the formula (9) include trimethylol phosphite, tetraphenyldipropylene glycol diphosphite, tetraphenyltetra(tridecyl)pentaerythritol tetraphosphite, tetra(tridecyl)-4,4'-isopropylidene diphenylphosphite, bis(tridecyl)pentaerythritol diphosphite, bis(nonylphenyl)pentaerythritol diphosphite, distearyl pentaerythritol diphosphite and tris(2,4-di-t-butylphenyl) phosphite.

The organic fluorine compound (a) for use in the invention is preferably a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of such a neutral phosphite with a fluorine atom.

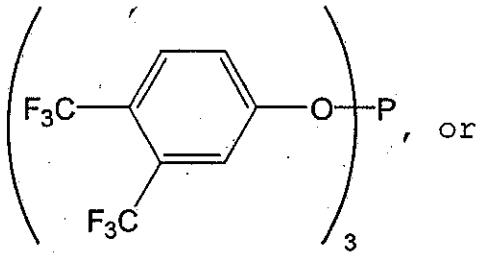
More specifically, there is preferably employed:

$(CF_3CH_2O)_3P$,

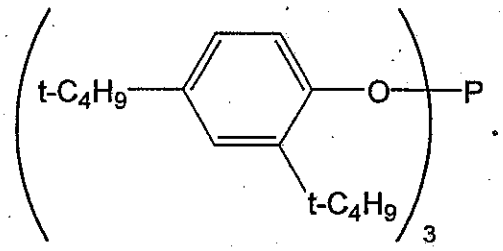
$(C_8F_{17}O)_3P$,

$\{CF_3(CF_2)_6CH_2CF_2CHFO\}_3P$,

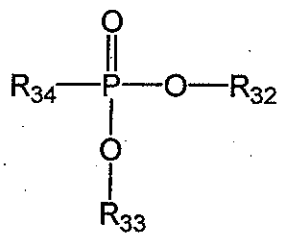
$(C_{18}F_{37}O)_3P$,



, or



Examples of the phosphonates include phosphoric esters represented by the following formula (10):



(10)

wherein R_{32} and R_{33} are each independently a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 1 to 12 carbon atoms and/or an aromatic ring, and R_{34} is an acetyl group or a methoxycarbonylmethyl group.

Of such compounds, preferable is a phosphonate wherein R_{32} and R_{33} in the formula (10) are each independently an ethyl group or a phenyl group.

The organic fluorine compound (a) for use in the invention is preferably a compound which is obtained by

replacing a part or all of hydrogen atoms in a hydrocarbon group of such a phosphonate with a fluorine atom.

More specifically, there is preferably employed:

$(CH_3COOCH_2)P(O)(OCH_2CF_3)_2$, or

$(CH_3CO)P(O)\{OCH_2CHF(CF_2)_2CF_3)_2$.

<Organic fluorine compound (b)>

The oil retention treatment agent according to the invention preferably contains the organic fluorine compound (a) and an organic fluorine compound other than the above-mentioned organic fluorine compounds containing a sulfur atom, a nitrogen atom or a phosphorus atom.

As such an organic fluorine compound, more preferable is at least one organic compound (b) selected from fluorine compounds having in a molecule:

a functional group selected from a carbonyl group, a hydroxyl group, an ester group and an ether group, and

a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group with a fluorine atom.

The above organic fluorine compound is also adsorbed on the surface of a metal part or a plastic part by the action of its polarity. Particularly, many plastic parts have a functional group such as an ether bond or an ester bond. By virtue of the interaction between the functional

group of the organic fluorine compound (b), such as an ester group or an ether group, and the functional group of the plastic part, the oil retention treatment agent is more stably adsorbed on the surface of the plastic part. Moreover, some of the organic fluorine compounds having an ester group or an ether group in a molecule exhibit biodegradability.

It is preferable that the hydrocarbon group in the organic fluorine compound (b) is a hydrocarbon group of 1 to 20 carbon atoms and comprises a chain or branched aliphatic hydrocarbon group and/or an aromatic ring. As such a hydrocarbon group, particularly preferable is a chain or branched alkyl group. The organic fluorine compound having a group derived from a chain or branched alkyl group is well dissolved in the after-mentioned solvent and exhibits excellent oil retentivity.

The molar ratio (F/H) of fluorine to hydrogen contained in the group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group with a fluorine atom is not specifically restricted provided that the resulting oil retention treatment agent exhibits oil retention properties, but the molar ratio is preferably not less than 1. If the F/H ratio is markedly

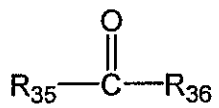
decreased, the lubricating oil is liable to spread out, and the oil retention properties are sometimes lowered.

Examples of the organic fluorine compounds (b) for use in the invention are given below.

(Organic fluorine compound having carbonyl group in molecule)

The organic fluorine compound having a carbonyl group in a molecule that is used in the invention is, for example, a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of a hydrocarbon compound having a carbonyl group with a fluorine atom.

Examples of the hydrocarbon compounds having a carbonyl group include carbonyl compounds represented by the following formula (11):



(11)

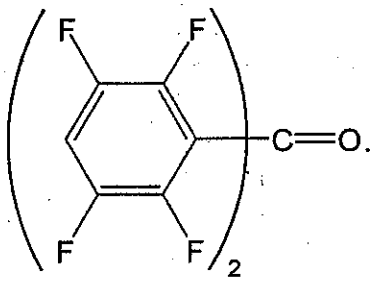
wherein R_{35} and R_{36} are each independently a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 3 to 12 carbon atoms and/or an aromatic ring.

Of such compounds, preferable is a carbonyl compound wherein R_{35} and R_{36} in the formula (11) are each independently an octyl group or a phenyl group.

The organic fluorine compound having a carbonyl group in a molecule that is used in the invention is preferably a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of such a carbonyl compound with a fluorine atom.

More specifically, there is preferably employed:

$(n\text{-}C_8F_{17})_2C{=}O$, or



(Organic fluorine compound having hydroxyl group in molecule)

The organic fluorine compound having a hydroxyl group in a molecule that is used in the invention is, for example, a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of a hydrocarbon compound having a hydroxyl group with a fluorine atom.

Examples of the hydrocarbon compounds having a hydroxyl group include hydroxyl group-containing hydrocarbon compounds represented by the following formula (12):

$$R_{37}{-}(R_{38})_k{-}OH \qquad (12)$$

wherein R_{37} is a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 3 to 12 carbon atoms and/or an aromatic ring, R_{38} is an alkylene group of 1 to 5 carbon atoms, and k is a number of 1 to 5.

Of such compounds, preferable is a hydrocarbon compound wherein R_{37} in the formula (12) is an octyl group or a nonyl group, and R_{38} in the formula (12) is an ethylene group or a butylene group.

The organic fluorine compound having a hydroxyl group in a molecule that is used in the invention is preferably a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of such a hydroxyl group-containing hydrocarbon compound with a fluorine atom.

More specifically, there is preferably employed:

$n\text{-}C_9F_{19}—(CH_2)_4—OH$, or

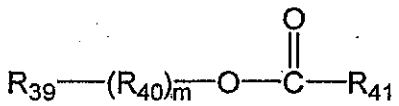
$n\text{-}C_8F_{17}—(CH_2)_2—OH$.

(Organic fluorine compound having ester group in molecule)

The organic fluorine compound having an ester group in a molecule that is used in the invention is, for example, a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of a hydrocarbon compound having an ester bond, with a fluorine atom. The hydrocarbon compound having an ester group

preferably contains an ether bond. Such a hydrocarbon compound having an ether linkage is adsorbed on a metal surface or a plastic surface, and the degree of adsorption can be controlled by changing the number of repeating units having the ether bond, such as alkyleneoxide.

Examples of the hydrocarbon compounds having an ester group include ester compounds represented by the following formula (13):



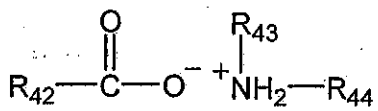
(13)

wherein R_{39} is a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 3 to 12 carbon atoms and/or an aromatic ring, R_{40} is an alkylene group of 1 to 5 carbon atoms or an alkyleneoxide group of 1 to 5 carbon atoms, R_{41} is an alkyl group of 1 to 5 carbon atoms, and m is a number of 1 to 5.

Of such compounds, preferable is a hydrocarbon compound wherein R_{39} in the formula (13) is an octyl group or a nonyl group, R_{40} in the formula (13) is a methylene group, an ethylene group, a propylene group or a butylene group, and R_{41} in the formula (13) is a methyl group.

Examples of hydrocarbon compounds having an ester group other than the ester compounds represented by the

formula (13), include ester group-containing ionic compounds represented by the following formula (14):



(14)

wherein R_{42}, R_{43} and R_{44} are each independently a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 3 to 12 carbon atoms and/or an aromatic ring.

Of such compounds, preferable is an ionic compound wherein R_{42} in the formula (14) is an octyl group or a nonyl group, and R_{43} and R_{44} in the formula (14) are each a butyl group.

The organic fluorine compound having an ester group in a molecule that is used in the invention is preferably a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of such an ester group-containing hydrocarbon compound with a fluorine atom.

More specifically, there is preferably employed:

$n\text{-}C_9F_{19}—O—(CH_2)_m—OCOCH_3$ (m=1 to 4),

$n\text{-}C_8F_{17}—O—(CH_2)_2—OCOCH_3$, or

$n\text{-}C_8F_{17}—COO^{-}{}^{+}NH_2\{(CH_2)_3CH_3\}_2$.

(Organic fluorine compound having ether group in molecule)

The organic fluorine compound having an ether group in a molecule that is used in the invention is, for example, a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of a hydrocarbon compound having an ether bond with a fluorine atom. The organic fluorine compound having an ether group in a molecule may contain a hydroxyl group.

Such a hydrocarbon compound having an ether bond is adsorbed on a metal surface or a plastic surface, and the degree of adsorption can be controlled by changing the number of repeating units having the ether bond, such as alkyleneoxide.

As the hydrocarbon compound having an ether linkage, an ether compound represented by the following formula (15) is also employable.

$$R_{45}\text{—}(\text{O—}R_{46})_n\text{—OH} \qquad (15)$$

wherein R_{45} is a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 3 to 12 carbon atoms and/or an aromatic ring, R_{46} is an alkylene group of 1 to 3 carbon atoms, and n is a number of 1 to 5.

Of such compounds, preferable is an ether compound wherein R_{45} in the formula (15) is an octyl group or a

nonyl group, and R_{46} in the formula (15) is an ethylene group or a butylene group.

The organic fluorine compound having an ether group in a molecule that is used in the invention is preferably a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of such an ether group-containing hydrocarbon compound with a fluorine atom.

More specifically, there is preferably employed:

$n\text{-}C_9F_{19}—O—(CH_2)_4—OH$, or

$n\text{-}C_8F_{17}—O—(CH_2)_2—OH$.

As the hydrocarbon compound having an ether bond, an ether compound represented by the following formula (16) is also employable.

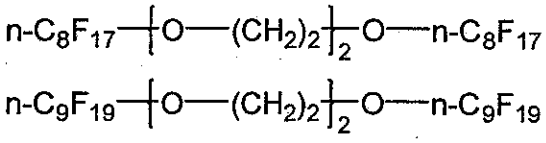
$$R_{47}—(O—R_{49})_n—O—R_{48} \qquad (16)$$

wherein R_{47} and R_{48} are each independently a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 3 to 12 carbon atoms and/or an aromatic ring, R_{49} is an alkylene group of 1 to 3 carbon atoms, and n is a number of 1 to 5.

Of such compounds, preferable is an ether compound wherein R_{47} and R_{48} in the formula (16) are each independently an octyl group or a nonyl group, and R_{49} in the formula (16) is an ethyl group.

The organic fluorine compound having an ether group in a molecule that is used in the invention is preferably a compound which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group of such an ether group-containing hydrocarbon compound with a fluorine atom.

More specifically, there is preferably employed:



<Solvent>

In the present invention, a fluorine type solvent is employable as the solvent, but the fluorine type solvent generates a toxic gas when heated, so that a non-fluorine type gas is preferably employed. Further, because the fluorine type gas is expensive, the cost for oil retention treatment becomes high, and hence a non-fluorine type solvent that is economically advantageous is preferably employed.

The non-fluorine type solvent preferably used in the invention is, for example, a non-fluorine type solvent having a site in a molecule, said site being capable of forming a polar group or a hydrogen bond, such as ketone, alcohol or ester.

Although the boiling point of the solvent is not specifically restricted, it is preferably not higher than

200°C. When a solvent having a boiling point of not higher than 200°C is used, a precision instrument such as a watch can be assembled by drying it without performing post-cleaning after the oil retention treatment. In order to dry the precision instrument at a low temperature for a short period of time, it is preferable to use a solvent having a low boiling point.

Examples of the non-fluorine type solvents include ketone solvents, such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohols, such as methanol, ethanol and IPA; and ester solvents, such as ethyl acetate and butyl acetate.

Of these solvents, a water-soluble solvent can be used after mixed with water. Therefore, oil retention treatment can be carried out cheaper.

When the part(s) of a precision instrument such as a watch is made of an acetal resin (POM), any of the above solvents is employable, but when the part(s) is made of a resin having low solvent resistance, such as polycarbonate (PC), it is preferable to use an alcohol. When the part(s) of a precision instrument such as a watch is made of a metal, any of the above solvents is employable.

Accordingly, the oil retention treatment agent of the invention can be used for any of metal and plastic parts for a precision instrument.

<Oil retention treatment agent>

The oil retention treatment agent of the present invention contains at least the organic fluorine compound (a) in the solvent. The organic fluorine compound (a) is used singly or in combination of two or more kinds. The concentration of the organic fluorine compound (a) is usually in the range of 0.1 to 10.0% by weight, preferably 0.1 to 5.0% by weight, more preferably 0.5 to 3.0% by weight. When the organic fluorine compounds (a) are used in combination of two or more kinds, it is preferable that the concentrations of them are each in the above range.

The oil retention treatment agent of the present invention further contains at least the organic fluorine compound (b). The organic fluorine compound (b) is used singly or in combination of two or more kinds. The concentration of the organic fluorine compound (b) is usually in the range of 0.1 to 10.0% by weight, preferably 0.1 to 5.0% by weight, more preferably 0.5 to 3.0% by weight. When the organic fluorine compounds (b) are used in combination of two or more kinds, it is preferable that the concentrations of them are each in the above range.

<Oil retention treatment method>

The oil retention treatment method according to the invention is a method wherein, of the surface of the part of a precision instrument such as a watch, a portion where a lubricating oil is to be retained is subjected to oil retention treatment using the above-mentioned oil retention treatment agent to allow at least the organic fluorine compound (a) to adhere to the surface of the portion.

First, the precision instrument part and the lubricating oil are described.

<Precision instrument part>

The part(s) of a precision instrument such as a watch for use in the invention is a part made of a metal or a plastic. Examples of materials of the metal part(s) for a precision instrument include various copper alloys, various iron alloys, and materials obtained by subjecting surfaces of these metal materials to nickel plating, gold plating, rhodium plating or the like.

The plastic part(s) for a precision instrument is, for example, a molded article obtained from a resin, such as an acetal resin (POM), polycarbonate (PC) or an alloy resin of polycarbonate and polybutylene terephthalate (PC/PBT), and an inorganic filler.

<Lubricating oil>

Examples of the lubricating oils employable in the invention include a polyalkylene glycol oil, an ester oil and a hydrocarbon oil (poly-α-olefin oil). When the precision instrument is a mechanical watch or an electronic watch (metal quartz watch) with a metallic plate, any of the above lubricating oils can be used because the slide portion is mainly made of a metal.

When the precision instrument is an electronic watch (plastic quartz watch) with a plastic plate, a lubricating oil having no compatibility with a plastic material is preferable because the slide portion is mainly made of a plastic, and a hydrocarbon oil (e.g., hydrocarbon lubricating oil described in International Publication WO01/59043) is preferably used.

The lubricating oil for the invention is preferably used after mixed with an anti-frictional wear agent, an antioxidant or a metal deactivator. Examples of the anti-frictional wear agents include phosphorus type anti-frictional wear agents, such as a neutral phosphite and a neutral phosphate, and sulfur type anti-frictional wear agents, such as zinc dithiophosphate.

<Oil retention treatment>

The oil retention treatment is specifically carried out in the following manner.

First, the precision instrument part(s) is immersed in the oil retention treatment agent. In order to perform oil retention treatment of the whole surface of the part(s) uniformly, it is preferable to immerse the part(s) with subjecting the part(s) to ultrasonic treatment. Alternatively, the part(s) may be oscillated. When the part(s) is small and in a complicated shape, it is preferable to perform ultrasonic treatment. By virtue of the ultrasonic treatment, the oil retention treatment agent can be allowed to adhere to every nook and corner of the part. Although the immersion time is not specifically restricted, it is preferably in the range of 30 seconds to 5 minutes.

Thereafter, the part(s) is taken out and subjected to warm-air drying to remove the solvent. The temperature of the warm-air drying can be appropriately determined according to the boiling point of the solvent. The drying time may be controlled.

When the precision instrument is assembled using the lubricating oil containing a sulfur type anti-wear agent in the oil retention treatment method of the invention, it

is preferable to use, as an oil retention treatment agent, the oil retention treatment agent containing the sulfur-containing organic fluorine compound (a). When the precision instrument is assembled using the lubricating oil containing a phosphorus type anti-wear agent, it is preferable to use, as an oil retention treatment agent, the oil retention treatment agent containing the phosphorus-containing organic fluorine compound (a).

It can be presumed that the part(s) having been subjected to oil retention treatment by the above method exhibits oil retentivity by the following mechanism.

The oil retention treatment agent according to the invention contains a compound having an atom that exhibits strong interaction with a metal, e.g., a phosphorus-containing organic fluorine compound. Therefore, when the metal part(s) is subjected to oil retention treatment using the oil retention treatment agent of the invention, the phosphorus-containing organic fluorine compound having high adsorbability on a metal is selectively adsorbed on the metal surface. Other organic fluorine compounds are adsorbed around the phosphorous-containing organic fluorine compound. Especially when the oil retention treatment agent contains an organic fluorine compound having a polar functional group in its molecular structure,

e.g., an organic fluorine compound having an ether bond, the organic fluorine compound is more strongly adsorbed. As a result, a film of the organic fluorine compound is formed on the metal surface, and because the fluorinated hydrocarbon group of the organic fluorine compound shows lipophilicity, oil retention properties appear.

On the other hand, in case of a plastic part, the organic fluorine compound is adsorbed on the surface of the plastic part mainly by the action of polarity of the plastic and the action of polarity of the organic fluorine compound, and a film of the organic fluorine compound is formed on the surface, whereby oil retention properties appear similarly to the above.

<Stain-proofing treatment>

In the present invention, it is preferable to carry out stain-proofing treatment prior to the warm-air drying (removal of solvent) of the oil retention treatment. In the oil retention treatment using a liquid, stain or tarnish is liable to occur, so that in case of parts whose appearance is thought to be important, e.g., parts of precision instruments such as a watch, the stain-proofing treatment is particularly preferably carried out.

The stain-proofing treatment is carried out by removing an excess oil retention treatment agent present

on the surface of the part by the use of a solvent, preferably a hydrocarbon solvent. Because the hydrocarbon solvent is non-polar, the excess oil retention treatment agent can be easily removed, but the oil retention treatment agent having adhered to the surface of the part by the oil retention treatment cannot be removed.

The hydrocarbon solvent is preferably a hydrocarbon having a boiling point of not higher than 180°C, such as n-decane, hexane, octane or nonane.

The stain-proofing treatment is specifically carried out in the following manner. The part(s) obtained after the immersion in the oil retention treatment agent is immersed, before evaporation of the solvent, in a hydrocarbon solvent and oscillated several times. Thus, unnecessary molecules other than the molecules having adhered to the surface of the part can be removed. Thereafter, the part(s) is taken out of the hydrocarbon solvent and subjected to hot-air drying, optionally in combination with suction drying or centrifugal separation, to remove the solvent and thereby dry the part(s).

The hot-air drying is carried out using hot air of preferably 120 to 150°C. By the use of hot air of such a temperature range, the hydrocarbon solvent having a

boiling point of not higher than 180°C can be removed within 30 minutes.

<Watch>

After the oil retention treatment of at least one watch part is carried out by the above method, the watch of the invention is assembled using the watch part and the aforesaid lubricating oil. In this watch, the lubricating oil is retained in the slide portion without spreading-out, so that the watch exhibits stable operating performance. Particularly in the watch having been subjected to oil retention treatment using the oil retention treatment agent containing a phosphorus-containing fluorine compound, oil retentivity is maintained over a long period of time, and the watch exhibits stable operating performance.

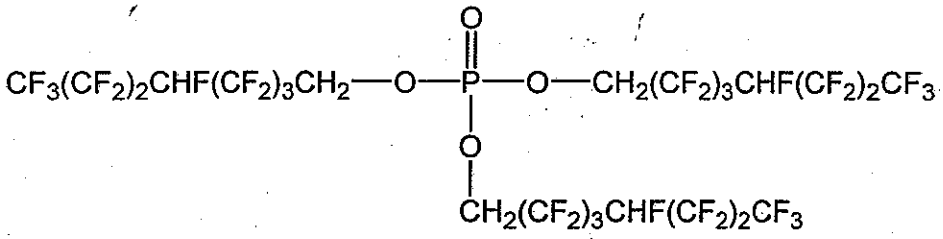
EXAMPLES

The present invention is further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

(Materials)

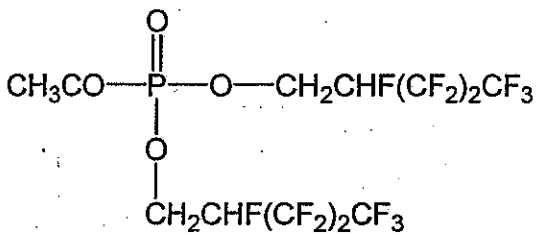
Alkyl fluoride compound (a-1):

Tris(1H,1H,5H-tetradecafluorooctyl) phosphate represented by the following formula:



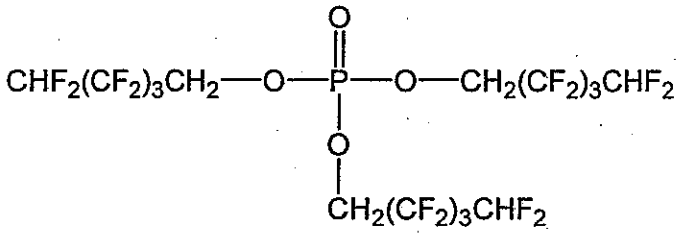
Alkyl fluoride compound (a-2):

Di(1H,1H,2H-octafluoropentyl)acetyl phosphonate represented by the following formula:



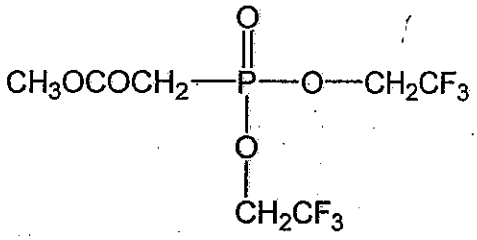
Alkyl fluoride compound (a-3):

Tris(1H,1H,5H-octafluoropentyl) phosphate represented by the following formula:



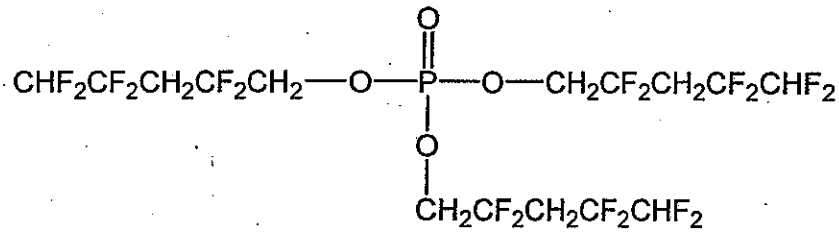
Alkyl fluoride compound (a-4):

Di(2,2,2-trifluoroethyl)methoxycarbonylmethyl phosphonate represented by the following formula:



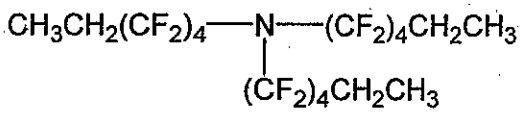
Alkyl fluoride compound (a-5):

Tris(1H,1H,3H,3H,5H-hexafluoropentyl) phosphate represented by the following formula:



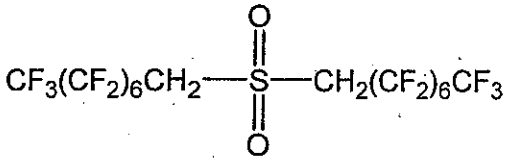
Alkyl fluoride compound (a-6):

Tris(5H,5H,6H,6H,6H-octafluorohexyl)amine represented by the following formula:



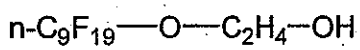
Alkyl fluoride compound (a-7):

Tris(1H,1H-pentadecafluorooctyl)sulfone represented by the following formula:



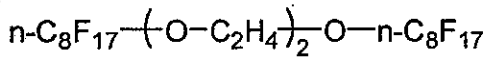
Alkyl fluoride compound (b-1):

Nonadecafluorononyl-oxy-ethanol represented by the following formula:



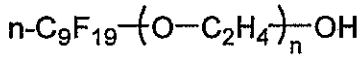
Alkyl fluoride compound (b-2):

Bis(heptadecafluorooctyloxyethyl) ether represented by the following formula:



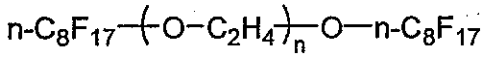
Alkyl fluoride compound (b-3):

Mixture of alkyl fluoride compounds represented by the following formula (n=1 to 3):



Alkyl fluoride compound (b-4):

Mixture of alkyl fluoride compounds represented by the following formula (n=1 and 2):



<Example 1>

The alkyl fluoride compounds (a-1), (a-2), (b-1) and (b-2) were mixed with isopropanol in each concentration of 0.5% by weight to prepare an oil retention treatment agent.

In the resulting oil retention treatment agent, a copper alloy substrate, a nickel-plated copper alloy substrate and a plastic substrate (POM substrate) were each immersed with performing ultrasonic treatment. Then, the copper alloy substrate, the nickel-plated copper alloy

substrate and the plastic substrate were taken out of the oil retention treatment agent and subjected to warm-air drying to remove the solvent. Thus, oil retention treatment of the surfaces of the copper alloy substrate, the nickel-plated copper alloy substrate and the plastic substrate (POM substrate) was carried out.

On the surface of each substrate, a lubricating oil (AO-3 available from Citizen Watch Co., Ltd.) was dropped, and the contact angle between the substrate surface having been subjected to the oil retention treatment and the lubricating oil was measured. Then, the substrates were stored at 80°C to measure change of the contact angle with time. The result regarding the nickel-plated copper alloy substrate is shown in Fig. 1. Other substrates had the same tendency as shown in Fig. 1.

Separately, using the oil retention treatment agent obtained, parts having slide portions of Watch Movement #20 (quartz watch mainly constituted of metal parts, manufactured by Citizen Watch Co., Ltd.), Watch Movement #82 (mechanical watch, manufactured by Citizen Watch Co., Ltd.) and Watch Movement #10 (quartz watch mainly constituted of plastic parts, manufactured by Citizen Watch Co., Ltd.) were each subjected to oil retention treatment, and using these parts and a hydrocarbon

lubricating oil (AO-2 available from Citizen Watch Co., Ltd.), watches were assembled.

The resulting watches were confirmed as to whether the lubricating oil spread out from the slide portion or not (oil retentivity). Then, confirmation of operations of these watches was carried out in the following manner. The results are set forth in Table 1.

Criteria for evaluation of oil retentivity:

A: In the vibrations caused by usual handling, the lubricating oil did not spread out from the slide portion.

B: In the vibrations caused by usual handling, the lubricating oil spread out from the slide portion.

(Method to confirm operation (accelerated test))

The watch assembled as above was placed in a constant temperature bath at 60°C, and the slide portion of the watch was controlled to cause the watch to operate for a given period of time at a rate of 8 times the usual rate (i.e., rate at which the watch gains, for 1 second, 8 seconds of the usual rate) in case of a mechanical watch and at a rate of 32 times the usual rate (i.e., rate at which the watch gains, for 1 second, 32 seconds of the usual rate) in case of a quartz watch.

Thereafter, the watch was taken out of the constant temperature bath and confirmed with regard to the

operating accuracy at room temperature, tarnish of the slide portion of the part and occurrence of wearing. Criteria for evaluation of operating performance:

AA: Even after a 10-years accelerated test was carried out, the operating accuracy was not changed, and the slide portion suffered neither tarnish nor wearing.

A: After a 3-years accelerated test, the operating accuracy was not changed, and the slide portion suffered neither tarnish nor wearing, but after a 5-years accelerated test, the slide portion suffered wearing.

B: After a 3-years accelerated test, the operating accuracy was not changed, and the slide portion suffered neither tarnish nor wearing, but after a 5-years accelerated test, the slide portion suffered tarnish.

C: Before the accelerated test, the operating accuracy was not changed, and the slide portion suffered neither tarnish nor wearing, but after a 3-years accelerated test, the slide portion suffered wearing.

<Example 2>

An oil retention treatment agent was prepared in the same manner as in Example 1, except that the alkyl fluoride compounds (a-3), (a-4), (b-3) and (b-4) were used instead of the alkyl fluoride compounds (a-1), (a-2), (b-1) and (b-2). Then, measurements of contact angles and

confirmation of operations of the watches were carried out. The results are set forth in Table 1 and Fig. 1.

<Example 3>

An oil retention treatment agent was prepared in the same manner as in Example 2, except that the alkyl fluoride compound (a-5) was used instead of the alkyl fluoride compound (a-3). Then, measurements of contact angles and confirmation of operations of the watches were carried out. The results are set forth in Table 1 and Fig. 1.

<Example 4>

An oil retention treatment agent was prepared in the same manner as in Example 2, except that the alkyl fluoride compound (a-6) was used instead of the alkyl fluoride compound (a-3). Then, measurements of contact angles and confirmation of operations of the watches were carried out. The results are set forth in Table 1 and Fig. 1.

<Example 5>

An oil retention treatment agent was prepared in the same manner as in Example 2, except that a mixed solvent of isopropanol (75%) and water (25%) was used instead of isopropanol. Then, measurements of contact angles and

confirmation of operations of the watches were carried out. The results are set forth in Table 1 and Fig. 1.

<Example 6>

An oil retention treatment agent was prepared in the same manner as in Example 2, except that a mixed solvent of ethanol (75%) and water (25%) was used instead of isopropanol. Then, measurements of contact angles and confirmation of operations of the watches were carried out. The results are set forth in Table 1 and Fig. 1.

<Example 7>

An oil retention treatment agent was prepared in the same manner as in Example 2, except that the alkyl fluoride compound (a-7) was used instead of the alkyl fluoride compound (a-3). Then, measurements of contact angles and confirmation of operations of the watches were carried out. The results are set forth in Table 1 and Fig. 1.

<Comparative Example 1>

The alkyl fluoride compounds (b-1) and (b-2) were dissolved in isopropanol in each concentration of 0.5% by weight to prepare an oil retention treatment agent.

Regarding the oil retention treatment agent, the contact angles were measured in the same manner as in Example 1. The result is shown in Fig 1.

Three watches were assembled in the same manner as in Example 1, and confirmation of operations of the watches was carried out. The results are set forth in Table 1.

Table 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Comp. Ex. 1
Alkyl fluoride compound (a)	a−1/a−2	a−3/a−4	a−5/a−4	a−6/a−4	a−3/a−4	a−3/a−4	a−7/a−4	a−1/a−2
Alkyl fluoride compound (b)	b−1/b−2	b−3/b−4	b−3/b−4	b−3/b−4	b−3/b−4	b−3/b−4	b−3/b−4	b−1/b−2
Solvent	IPA	IPA	IPA	IPA	IPA : 75% water : 25%	EtOH : 75% water : 25%	IPA	IPA
Quartz watch with metallic plate								
Oil retentivity	A	A	A	A	A	A	A	B
Operating performance	AA	AA	AA	A	AA	AA	B	C
Mechanical watch								
Oil retentivity	A	A	A	A	A	A	A	B
Operating performance	AA	AA	AA	A	AA	AA	B	C
Quartz watch with plastic plate								
Oil retentivity	A	A	A	A	A	A	A	B
Operating performance	AA	AA	AA	A	AA	AA	B	C

IPA: isopropanol, EtOH: ethanol

As shown in Fig. 1, whereas the contact angle decreased with time and the lubricating oil spread out by conducting oil retention treatment using the conventional oil retention treatment agent, the contact angle was not changed with time and the lubricating oil did not spread out by using the oil retention treatment agent of the invention.

As shown in Table 1, the oil retention treatment agent containing an alkyl fluoride phosphorus compound exhibited excellent oil retentivity. Further, even in the use of an organic solvent such as an alcohol, oil retention treatment could be carried out. Moreover, the watches using the oil retention treatment agent of the invention exhibited excellent operating performance compared with that using a conventional oil retention treatment agent. Of these, the watch using the phosphorus-containing oil retention treatment agent was particularly excellent in operating performance.

INDUSTRIAL APPLICABILITY

The oil retention treatment agent of the invention can improve oil retentivity of precision instruments such as watches. Further, the oil retention treatment agent of

the invention can be used for both of plastic parts and metal parts.

By conducting oil retention treatment using the oil retention treatment agent of the invention, precision instruments such as watches, which are free from spreading-out of the lubricating oil inside and have excellent oil retention properties and operating performance, can be obtained.

The precision instruments, such as watches, having excellent oil retention properties can be reduced in wearing of the driving portion (slide portion) and thereby remarkably improved in the durability. As a result, the precision instruments stably operate over a long period of time even if maintenance is not performed. Moreover, the precision instruments have extremely longer life than the conventional ones, and by conducting the oil retention treatment of the invention, discharge of new waste products can be inhibited.

What is claimed is:

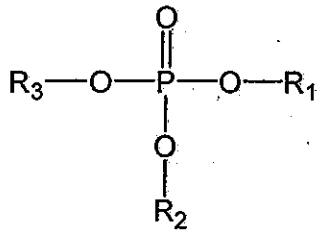
1. An oil retention treatment agent comprising, in a solvent, at least one organic fluorine compound (a) selected from fluorine compounds having in a molecule:

phosphorus atom, and

a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group with a fluorine atom.

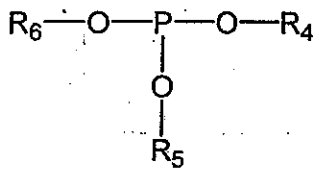
2. The oil retention treatment agent as claimed in claim 1, wherein the hydrocarbon group is a hydrocarbon group of 1 to 20 carbon atoms and comprises a chain or branched aliphatic hydrocarbon group and/or an aromatic ring.

3. The oil retention treatment agent as claimed in claim 2, wherein the organic fluorine compound (a) is at least one organic fluorine compound selected from phosphorus-containing fluorine compounds represented by any one of the following formulas (1) to (3):



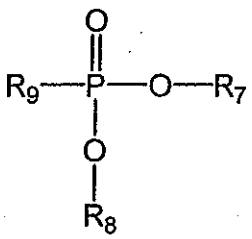
(1)

wherein R_1, R_2 and R_3 are each independently a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 1 to 12 carbon atoms and/or an aromatic ring, with a fluorine atom,



(2)

wherein R_4, R_5 and R_6 are each independently a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 1 to 12 carbon atoms and/or an aromatic ring, with a fluorine atom,



(3)

wherein R_7 and R_8 are each independently a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group comprising a chain or branched aliphatic

hydrocarbon group of 1 to 12 carbon atoms and/or an aromatic ring, with a fluorine atom, and R_9 is an acetyl group or a methoxycarbonylmethyl group.

4. The oil retention treatment agent as claimed in any one of claims 1 to 3, further comprising at least one organic fluorine compound (b) selected from fluorine compounds having in a molecule:

a functional group selected from a carbonyl group, a hydroxyl group, an ester group and an ether group, and

a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group with a fluorine atom.

5. The oil retention treatment agent as claimed in claim 4, wherein the hydrocarbon group in the organic fluorine compound (b) is a hydrocarbon group of 1 to 20 carbon atoms and comprises a chain or branched aliphatic hydrocarbon group and/or an aromatic ring.

6. The oil retention treatment agent as claimed in claim 5, wherein the organic fluorine compound (b) is at least one organic fluorine compound selected from ether compounds represented by the following formula (4) or (5):

$$R_{10}\text{—}(\text{O—}R_{11})_n\text{—OH} \qquad (4)$$

wherein R_{10} is a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 3 to 12 carbon atoms and/or an aromatic ring, with a fluorine atom, R_{11} is an alkylene group of 1 to 3 carbon atoms, and n is a number of 1 to 5,

$$R_{12}\text{—}(\text{O—}R_{14})_n\text{—O—}R_{13} \qquad (5)$$

wherein R_{12} and R_{13} are each independently a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group comprising a chain or branched aliphatic hydrocarbon group of 3 to 12 carbon atoms and/or an aromatic ring, with a fluorine atom, R_{14} is an alkylene group of 1 to 3 carbon atoms, and n is a number of 1 to 5.

7. A watch wherein at least one watch part has been subjected to oil retention treatment using the oil retention treatment agent of any one of claims 1 to 6.

8. The watch as claimed in claim 7, which is obtained by the use of at least one watch part having been subjected to oil retention treatment using an oil retention treatment agent comprising a phosphorus-containing organic fluorine compound (a), and a lubricating oil comprising a phosphorus type anti-wear agent.

9. An oil retention treatment method comprising subjecting a portion where a lubricating oil is to be retained to oil retention treatment using the oil retention treatment agent of any one of claims 1 to 6 to allow at least the organic fluorine compound (a) to adhere to the surface of the portion.

10. The oil retention treatment method as claimed in claim 9, comprising:

(I) a step of immersing at least one precision instrument part in the oil retention treatment agent to allow the oil retention treatment agent to adhere to the surface of the part, and

(II) a step of warm-air drying the precision instrument part obtained after the immersion step to remove the solvent.

11. The oil retention treatment method as claimed in claim 10, wherein in the step (I), the precision instrument part is immersed with subjecting the part to ultrasonic treatment.

12. The oil retention treatment method as claimed in claim 10 or 11, wherein after the step (I), a step (III) of immersing the precision instrument part in a solvent to remove an excess oil retention treatment agent having adhered to the surface of the part is performed, and thereafter the step (II) is performed.

13. The oil retention treatment method as claimed in claim 12, wherein in the step (III), the precision instrument part having been immersed in the solvent is oscillated in the solvent.

ABSTRACT

OIL RETENTION TREATMENT AGENT, OIL RETENTION TREATMENT METHOD USING THE SAME, AND WATCH HAVING BEEN OIL RETENTION TREATED BY THE OIL RETENTION TREATMENT METHOD

Disclosed is an oil retention treatment agent comprising, in a solvent, at least one organic fluorine compound (a) selected from fluorine compounds having, in a molecule, one atom selected from phosphorus, nitrogen and sulfur and a group which is obtained by replacing a part or all of hydrogen atoms in a hydrocarbon group with a fluorine atom. By performing oil retention treatment using the oil retention treatment agent, precision instruments, such as a watch, having excellent oil retention properties can be obtained. Further, this watch exhibits stable operating performance.

(FIG. 1)