Abstract:
Segregated fluorinated esters are described that are useful as dielectric fluids in electrical devices and as heat transfer agents.
SEGREGATED FLUORINATED ESTERS

Field of the Invention

The present disclosure relates generally to the use of dielectric fluids in electrical devices such as capacitors, switchgear, transformers and electric cables or buses. The present disclosure further relates to heat transfer applications. In particular, the present disclosure pertains to the use of certain fluorinated esters as dielectric fluids in electrical devices and as heat transfer agents.

Background

In electrical devices such as capacitors, dielectric liquids are often used in place of air due to their low dielectric constant (K) and high dielectric strength (DS). Some capacitors of this type comprise alternate layers of metal foil conductors and solid dielectric sheets of paper or polymer film. Other capacitors are constructed by wrapping the metal foil conductor(s) and dielectric film(s) concentrically around a central core. This latter type of capacitor is referred to as a "film-wound" capacitor. Dielectric liquids are often used to impregnate dielectric film due to their low dielectric constant and high dielectric strength. Such dielectric liquids allow more energy to be stored within the capacitor (higher capacitance) as compared to air- or other gas-filled electrical devices.

Conventional dielectric liquids such as petroleum mineral oils have found wide application due to their low cost and availability. However, their use has been limited in many electrical devices because of their relative low chemical stability and their flammability. Chlorinated aromatic hydrocarbons, for example, polychlorinated biphenyls (PCBs), were developed as fire-resistant insulating liquids, have excellent chemical stability, and have a much lower dielectric constant than the mineral oils. Unfortunately, certain PCB isomers have a high resistance to biological degradation and problems of toxicity are now being encountered due to PCB spillage and leakage. A. C. M. Wilson, Insulating Liquids: Their Uses, Manufacture and Properties 6 (Peter Peregrinus Ltd 1980), notes the use of PCBs are likely to be phased out as other more environmentally safe liquids become available.
Presently various fluids are used for heat transfer. The suitability of the heat transfer fluid depends upon the application process. For example, some electronic applications require a heat transfer fluid that is inert, has a high dielectric strength, has low toxicity, has good environmental properties, and has good heat transfer properties over a wide temperature range. Other applications require precise temperature control and thus the heat transfer fluid is required to be a single phase over the entire process temperature range and the heat transfer fluid properties are required to be predictable, i.e., the composition remains relatively constant so that the viscosity, boiling point, etc., can be predicted so that a precise temperature can be maintained and so that the equipment can be appropriately designed.

In the semiconductor industry, there are numerous devices or processes that require a heat transfer fluid having select properties. These include testing the performance of semiconductor wafer chips, controlling temperature during reactive plasma etching, producing steppers, operating ashers, operating plasma enhanced chemical vapor deposition (PECVD) chambers, conducting thermal shock tests, and for constant temperature baths. The heat transfer fluid may be used to remove heat, add heat, or maintain a temperature.

Thus, Applicants recognize that there exists an ongoing need for fluorochemical esters compounds that can meet the performance requirements of a variety of different applications. For example, there is a continuing need for fluorochemical esters having a variety of different boiling ranges, thermal and/or hydrolytic stabilities, viscosity characteristics, and molecular weights.

The fluorochemical ester compounds described herein comprise a class of commercially valuable chemical compounds that exhibit a wide range of properties. The compounds as a class are neutral and, in some cases, are surprisingly inert, thermally stable, and hydrolytically stable. Such properties have made them useful as dielectric fluids in electronic or electric equipment.
Summary

Thus, we recognize that there exists an ongoing need for fluorochemical compounds that can meet the performance requirements of a variety of different applications. For example, there is a continuing need for fluorochemicals having a variety of different boiling ranges, thermal and/or hydrolytic stabilities, viscosity characteristics, and molecular weights.

A continuing need exists for heat transfer fluids that are inert, have high dielectric strength, low electrical conductivity, chemical inertness, thermal stability, effective heat transfer, are liquid over a wide temperature range, have good heat transfer properties over a wide range of temperatures, and also have shorter atmospheric lifetimes, and therefore have a lower global warming potential, than existing heat transfer fluids.

In one aspect, an apparatus is provided for heat transfer that includes a device and a mechanism for transferring heat to or from the device, the mechanism comprising a heat transfer fluid, wherein the heat transfer fluid comprises a fluorinated ester. In another aspect, a method is provided for transferring heat that includes providing a device and providing a mechanism for transferring heat to or from the device, the mechanism comprising a heat transfer fluid, wherein the heat transfer fluid comprises a partially fluorinated carbonate.

The fluorochemical ester compounds described herein comprise a class of commercially valuable chemical compounds that exhibit a wide range of properties. The compounds as a class are neutral and, in some cases, are surprisingly inert, thermally stable, and hydrolytically stable. Such properties have made them useful as dielectric fluids in electronic or electric equipment.

Briefly, in one aspect, this invention provides a fluorochemical ester compound comprising an a branched, perfluorinated acid portion, and a non-fluorinated alcohol portion. More particularly the present disclosure provides segregated fluorinated esters of the formula:

![Chemical Structure]

wherein,
each of $R_1^f$ and $R_2^f$ are independently a perfluorinated group;
the number of total perfluorinated carbon atoms is $\geq 4$ when $x$ is 1, and the number of
total perfluorinated carbon atoms is $\geq 3$ when $x$ is 2-4,

$R_1^f$ is a (hetero)hydrocarbyl group of valence $x$; and

$$x \text{ is lto } 4.$$  

By segregated, it is meant the ester is derived from a perfluorinated acyl fluoride
(or equivalent) and a non-fluorinated alcohol.

Each of $R_1^f$ and $R_2^f$ are independently a linear or branched, cyclic or acrylic
perfluoroalkyl group, which may optionally contain one or more in-chain oxygen or
nitrogen atoms. When cyclic, each of $R_1^f$ and $R_2^f$ may be selected from perfluorinated
cyclobutyl, cyclopentyl, cyclohexyl or tetrahydrofuran rings as well as piperazine,
piperidine, morpholine or pyrroldine rings, each with or without attached perfluoroalkyl
groups.

In some embodiments, the $R_1^f$ and $R_2^f$ are taken together to form a perfluorinated
ring, which may further contain one or more in-chain oxygen or nitrogen atoms, i.e. $R_1^f$-$CF(-)-R_2^f$ may form a ring. $R_1^f$ and $R_2^f$, taken together, may be selected from linear or
branched, cyclic or acyclic perfluoroalkylene. For example, $R_1^f$ and $R_2^f$, taken together
with the "CF" of Formula I, may form perfluorinated cyclobutyl, cyclopentyl, cyclohexyl
or tetrahydrofuran rings as well as piperazine, piperidine, morpholine or pyrroldine rings.
each with or without attached alkyl groups.

The segregated fluorinated esters as a dielectric fluids advantageously have a broad
range of operating temperatures and pressures, are thermally, and chemically stable, have
a higher dielectric strength and heat transfer efficiency than conventional dielectric fluids,
have a lower global warming potential (GWP) than many dielectric fluids. The
fluorinated esters generally have a dielectric strength $\geq 30$ kV at 0.1 inches.

Advantageously, the dielectric fluid of the present disclosure has a high electrical
strength, also described as high breakdown voltage. "Breakdown voltage," as used in this
application means (at a specific frequency) the highest voltage applied to a fluid that
induces catastrophic failure of the fluid dielectric allowing electrical current to conduct
through the gas. Thus the fluid dielectric of the present invention can function under high
voltages. The fluid dielectric can also exhibit a low loss factor, that is, the amount of
electrical energy that is lost as heat from an electrical device such as a capacitor.
In addition, the fluorochemical esters are thermally and hydrolytically stable when compared to fluorochemical esters lacking the branching alpha to the carbonyl. The compounds generally exhibit a liquid phase over a wide temperature range. For example, the compounds are generally liquid at least about -50°C and have boiling points ≥ 100°C, preferably ≥ 120°C and more preferably > 140°C. Generally, the viscosity of the compounds in the liquid phase is less than 10 centistokes at 25°C.

The hydrofluoroether compounds of the present invention additionally have low global warming potential values (GWP), calculated as between 100 and 400. GWP is determined using a calculated value for atmospheric lifetime and an experimentally determined infrared absorbance data integrated over the spectral region of interest, typically 500 to 2500 cm⁻¹.

"GWP" is a relative measure of the warming potential of a compound based on the structure of the compound. The GWP of a compound, as defined by the intergovernmental Panel on Climate Change (IPCC) in 1990 and updated in 2007, is calculated as the warming due to the release of 1 kilogram of a compound relative to the warming due to the release of 1 kilogram of CO₂ over a specified integration time horizon (ITH).

\[
GWP_i(t') = \frac{\int_0^{\infty} a_i C(t') dt}{\int_0^{\infty} a_i C(t) dt} = \frac{\int_0^{\infty} a_i e^{-\tau t} dt}{\int_0^{\infty} a_i C(t) dt}
\]

In this equation \(a_i\) is the radiative forcing per unit mass increase of a compound in the atmosphere (the change in the flux of radiation through the atmosphere due to the IR absorbance of that compound), \(C\) is the atmospheric concentration of a compound, \(\tau\) is the atmospheric lifetime of a compound, \(t\) is time and \(i\) is the compound of interest.

The commonly accepted ITH is 100 years representing a compromise between short-term effects (20 years) and longer-term effects (500 years or longer). The concentration of an organic compound, \(i\), in the atmosphere is assumed to follow pseudo first order kinetics (i.e., exponential decay). The concentration of CO₂ over that same
time interval incorporates a more complex model for the exchange and removal of CO2 from the atmosphere (the Bern carbon cycle model).

The very short lifetimes of the fluorinated esters lead to very low GWPs. A measured IR cross-section may used to calculate the radiative forcing value for the instant fluorinated esters using the method of Pinnock, et al. (J. Geophys. Res., 100, 23227, 1995). The perfluoro esters of the disclosure typically have a GWP less than about 100, and preferably less than 10.

As a result of their rapid degradation in the lower atmosphere, the fluorinated esters have short lifetimes and would not be expected to contribute significantly to global warming. The low GWP of the fluorinated esters, in addition to the dielectric performance characteristics and stability, make them well suited for use as a dielectric fluid. In the present disclosure:

"alkyl" includes straight-chained, branched, and cycloalkyl groups and includes both unsubstituted and substituted alkyl groups. Unless otherwise indicated, the alkyl groups typically contain from 1 to 20 carbon atoms. Examples of "alkyl" as used herein include, but are not limited to, methyl, ethyl, n-propyl, n-butyl, n-pentyl, isobutyl, t-butyl, isopropyl, n-octyl, n-heptyl, ethylhexyl, cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, and norbornyl, and the like. Unless otherwise noted, alkyl groups may be mono- or polyvalent, i.e. monovalent alkyl or polyvalent alkyene.

"heteroalkyl" includes both straight-chained, branched, and cyclic alkyl groups with one or more heteroatoms independently selected from S, O, and N with both unsubstituted and substituted alkyl groups. Unless otherwise indicated, the heteroalkyl groups typically contain from 1 to 20 carbon atoms. "Heteroalkyl" is a subset of "hydrocarbyl containing one or more S, N, O, or P, or Si atoms" described below. Examples of "heteroalkyl" as used herein include, but are not limited to, methoxy, ethoxy, propoxy, 3,6-dioxaheptyl, 3-(trimethylsilyl)-propyl, 4-dimethylaminobutyl, and the like. Unless otherwise noted, heteroalkyl groups may be mono- or polyvalent, i.e. monovalent heteroalkyl or polyvalent heteroalkylene.

"aryl" is an aromatic group containing 5-18 ring atoms and can contain optional fused rings, which may be saturated, unsaturated, or aromatic. Examples of aryl groups include phenyl, naphthyl, biphenyl, phenanthryl, and anthracyl. Heteroaryl is aryl
containing 1-3 heteroatoms such as nitrogen, oxygen, or sulfur and can contain fused rings. Some examples of heteroaryl groups are pyridyl, furanyl, pyrrolyl, thienyl, thiazolyl, oxazolyl, imidazolyl, indolyl, benzofuranyl, and benzthiazolyl. Unless otherwise noted, aryl and heteroaryl groups may be mono- or polyvalent, i.e. monovalent aryl or polyvalent arylene.

"(hetero)hydrocarbyl" is inclusive of hydrocarbyl alkyl and aryl groups, and heterohydrocarbyl heteroalkyl and heteroaryl groups, the latter comprising one or more catenary (in-chain) oxygen heteroatoms such as ether or amino groups. Heterohydrocarbyl may optionally contain one or more catenary (in-chain) functional groups including ester, amide, urea, urethane, and carbonate functional groups. Unless otherwise indicated, the non-polymeric (hetero)hydrocarbyl groups typically contain from 1 to 60 carbon atoms. Some examples of such heterohydrocarbys as used herein include, but are not limited to, methoxy, ethoxy, propoxy, 4-diphenylaminobutyl, 2-(2'-phenoxyethoxy)ethyl, 3,6-dioxaheptyl, 3,6-dioxahexyl-6-phenyl, in addition to those described for "alkyl", "heteroalkyl", "aryl", and "heteroaryl" supra.

"fluorinated" refers to hydrocarbon compounds that have one or more C–H bonds replaced by C–F bonds;

"fluoroalkyl has essentially the meaning as "alkyl" except that one or more of the hydrogen atoms of the alkyl radical are replaced by fluorine atoms.

"fluoroalkylene has essentially the meaning as "alkylene" except that one or more of the hydrogen atoms of the alkyl radical are replaced by fluorine atoms.

"Perfluoroalkyl" has essentially the meaning as "alkyl" except that all or essentially all of the hydrogen atoms of the alkyl radical are replaced by fluorine atoms, e.g. perfluoropropyl, perfluorobutyl, perfluorooctyl, and the like.

"Perfluoroalkylene" has essentially the meaning as "alkylene" except that all or essentially all of the hydrogen atoms of the alkylene radical are replaced by fluorine atoms, e.g., perfluoropropylene, perfluorobutylene, perfluoroctylene, and the like.

"Perfluorinated" or the prefix "perfluoro" means an organic group wherein all or essentially all of the carbon bonded hydrogen atoms are replaced with fluorine atoms, e.g. Perfluoroalkyl and the like.
Detailed Description

The present disclosure provides segregated fluorinated esters of the formula:

Each $R^1$ and $R^2$ are independently selected from a perfluoroalkyl or perfluoroheteroalkyl group having from 1 to about 12 perfluorinated carbon atoms, preferably 1 to 8 carbon atoms, more preferably having from about 1 to about 5 carbon atoms. The total number of perfluorinated carbon atoms, i.e. from $R^1$ to $R^2$, is $\geq 4$ when $x$ is 1, and the number of total perfluorinated carbon atoms is $\geq 3$ when $x$ is 2-4. Preferably one or both of $R^1$ and $R^2$ is $\geq 4$.

$R^1$ and $R^2$ can contain linear or branched, acyclic or cyclic perfluorinated alkyl groups or combinations thereof. $R^1$ and $R^2$ are preferably free of polymerizable olefinic unsaturation and can optionally contain one or more in-chain heteroatoms such as oxygen, divalent or hexavalent sulfur, or nitrogen.

$R^1$ and $R^2$ can be taken together to form a perfluorinated ring, such as perfluorocyclopentyl or perfluorocyclohexyl. Such rings may further contain one or more in-chain heteroatoms such as oxygen, divalent or hexavalent sulfur, or nitrogen, such as perfluorinated piperazine, piperidine, morpholine or pyrrolidine rings. Such rings may further contain perfluorinated alkyl groups.

The $R^1$ group is a linear, branched or cyclic alkyne group having from 1 to about 8 carbon atoms and at least 3 hydrogen atoms for $x=1$ and 2 to 8 carbon atoms for $x=2-4$. $R^1$ can optionally contain one or more in-chain oxygen heteroatoms. $R^1$ may optionally have one or more pendant hydroxyl group.

In certain preferred embodiments, the segregated ester is of the formula:

wherein each of $R^3$, $R^4$ and $R^5$ are independently a perfluorinated group,
y is 1-4; and

\( R^1 \) is a (hetero)hydrocarbyl group of valence \( y \) as previously described.

Each of \( R^3 \), \( R^4 \) and \( R^5 \) are independently selected from a perfluoroalkyl or perfluoroheteroalkyl group having from 1 to about 12 perfluorinated carbon atoms, preferably 1 to 8 carbon atoms, more preferably having from about 1 to about 5 carbon atoms. Each of \( R^3 \), \( R^4 \) and \( R^5 \) can contain linear or branched chain, acyclic or cyclic perfluorinated alkyl groups or combinations thereof. \( R^3 \), \( R^4 \) and \( R^5 \) are preferably free of polymerizable olefinic unsaturation and can optionally contain one or more in-chain heteroatoms such as oxygen, divalent or hexavalent sulfur, or nitrogen.

When cyclic, each of \( R^3 \), \( R^4 \) and \( R^5 \) may be selected from perfluorinated cyclobutyl, cyclopentyl, cyclohexyl or tetrahydrofuran rings as well as piperazine, piperidine, morpholine or pyrrolidine rings, each with or without attached perfluoroalkyl groups.

In some embodiments, the \( R^3 \) and \( R^5 \) are taken together to form a perfluorinated ring, which may further contain one or more in-chain oxygen or nitrogen atoms, i.e. \( R^3 \cdot N(-)\cdot R^5 \) may form a ring. \( R^3 \) and \( R^5 \), taken together, may be selected from linear or branched, cyclic or acyclic perfluoroalkylene to produce perfluorinate piperazine, piperidine, morpholine or pyrrolidine rings, each with or without attached perfluoro alkyl groups.

Such compounds are prepared by esterification of the perfluorinated acid fluoride as previously described. The perfluorinated acid fluoride may be prepared by Michael addition of a secondary amine to a substituted acrylate, such as a methacrylate and fluorinated by electrochemical fluorination.

In another embodiment, the segregated ester is of the formula:

![Chemical Structure](image)

wherein each of \( R^3 \), \( R^4 \) and \( R^5 \) are independently a perfluorinated group, y is 1-4; and

\( R^1 \) is a (hetero)hydrocarbyl group of valence \( y \).
Regarding Formula III, each of Rf3, Rf4 and Rf5 are independently selected from represents a perfluoroalkyl or perfluoroheteroalkyl group having from 1 to about 12 perfluorinated carbon atoms, preferably 1 to 8 carbon atoms, more preferably having from about 1 to about 5 carbon atoms. Each of Rf3, Rf4 and Rf5 can contain linear or branched chain, acyclic or cyclic perfluorinated alkyl groups or combinations thereof. Rf3, Rf4 and Rf5 are preferably free of polymerizable olefmic unsaturation and can optionally contain one or more in-chain heteroatoms such as oxygen, divalent or hexavalent sulfur, or nitrogen.

When cyclic, each of Rf3, Rf4 and Rf5 may be selected from perfluorinated cyclobutyl, cyclopentyl, cyclohexyl or tetrahydrofuran rings as well as piperazine, piperidine, morpholine or pyrroldine rings, each with or without attached perfluoroalkyl groups.

In some embodiments, the Rf4 and Rf5 are taken together to form a perfluorinated ring, which may further contain one or more in-chain oxygen or nitrogen atoms, i.e. Rf4-N(-)-Rf5 may form a ring. Rf4 and Rf5, taken together, may be selected from linear or branched, cyclic or acyclic perfluoroalkylene to produce perfluorinate piperazine, piperidine, morpholine or pyrroldine rings, each with or without attached perfluoro alkyl groups.

Such compounds are prepared by the reaction of a non-fluorinated alpha-halo ester and a secondary amine, followed by electrochemical fluorination and esterification to provide the Rf1 group.

The segregated esters are desirably non-flammable. A useful indicator is the following formula:

\[(# \text{C-F} + # \text{S-F}) / (\#\text{C-F} + \#\text{C-H} + \#\text{C-C} + \# \text{C-N} + \# \text{C-S}) \times 100 \geq 40\]

More particularly, the segregated esters are non-flammable when tested according to ASTM D 7236-06. For a given perfluorinated acryl fluoride, the hydroxy-functional compound is selected such that the above calculation is met.

The segregated ester of Formula I may be prepared by esterification of perfluorinated acyl fluorides with mono- or polyfunctional alcohol, for example mono-dii- and tetrahydroxy compounds, using a metal fluoride ion, preferably an alkali or alkali-earth fluoride. The perfluorinated acyl fluorides are prepared, in turn, by electrochemical
fluorination of the corresponding non-fluorinated acids or esters, as is known in the art. It will be understood that the electrochemical fluorination process can produce isomers other than that corresponding to the starting material. Such isomers, e.g. unbranched isomer, are desirably less than 10% by weight. In many instances, undesirable isomers may be removed by distillation.

The alcohol used in the esterification of the perfluorinated acyl fluoride include aromatic and aliphatic mono- di- tri- and tetrahydroxy compounds and is of the formula \( R^1(Z)_X \) where \( R^1 \) is a non-polymeric aliphatic, cycloaliphatic, aromatic or alkyl-substituted aromatic moiety having from 1 to 30 carbon atoms and includes aliphatic and aromatic polyols. The carbon chain may include one or more in-chain heteroatoms.

Useful alcohols of the formula \( R^X Z H \) include aliphatic and aromatic monoalcohols and polyols. Useful monoalcohols include methanol, ethanol, propanol, isopropanol, butanol, sec-butanol, isobutanol, allyl alcohol, 1-methoxyethanol and 3-pentanol.

Example of useful polyols (where \( x \) is 2, 3 or 4) include ethylene glycol, propylene glycol, 1,2-propanediol, 2 methyl 1,3-propanediol, 1,2-, 1,3 and 1,4-butanediols, 1,32-pentane diol, glycerol, 1,5- and 2,4-pentanediol, 1,2-, 1,6 and 2,5-hexanediol, 1,2- and 1,8-octanediol. neopenty1 alcohol, and meso-erythritol. trimethylol ethane, trimethylol propane, trimethyl aminomethane, ethylene glycol, 2-butene-1,4-diol, pentaerythritol, dipentaerythritol, 1,2-, 1,3- and 1,4-cyclohexane diol, and tripentaerythritol.

The dielectric fluids of the present disclosure may be useful in a number of other applications that use dielectric fluids. Examples of such other applications are described in U.S. Pat. Nos. 4,899,249 (Reilly et al); 3,184,533 (Eiseman Jr.); UK Patent No. 1242 180 (Siemens) and such descriptions are incorporated in their entirety herein by reference.

In various embodiments, minor amounts (< 50 weight percent) of the fluorinated esters may be blended with other fluorinated fluids. The optional fluorinated, inert fluids can be one or a mixture of fluoroalkyl compounds having 5 to 18 carbon atoms or more, optionally, containing one or more catenary heteroatoms, such as divalent oxygen, hexavalent sulfur, or trivalent nitrogen and having a hydrogen content of less than 5 percent by weight or less than 1 percent by weight.

Suitable fluorinated, inert fluids useful of the present disclosure include, for example, perfluoroalkanes or perfluorocycloalkanes, such as, perfluoropentane, perfluorohexane, perfluoroheptane, perfluorooctane, perfluoro- 1,2-
bis(trifluoromethyl)hexafluorocyclobutane, perfluorotetradecahydrophenanthrene, and perfluorodecalin; perfluoroamines, such as, perfluorotributyl amine, perfluorotriethyl amine, perfluorotripropyl amine, perfluorotriamyl amine, perfluoro-N-methyl morpholine, perfluoro-N-ethyl morpholine, and perfluoro-N-isopropyl morpholine; perfluoroethers, such as perfluorobutyl tetrahydrofuran, perfluorodibutyl ether, perfluorobutoxyethoxy formal, perfluorohexyl formal, and perfluoroocetyl formal; perfluoropolyethers; hydrofluorocarbons, such as pentadecafluorohydroheptane, 1, 1,2,2-tetrafluorocyclobutane, 1-trifluoromethyl- 1,2,2-trifluorocyclobutane and 2-hydro-3-oxaheptadecafluoroctane.

In liquid-filled capacitors, it is advantageous to match the dielectric constant of the dielectric liquid with that of the dielectric film, that is, the dielectric constants of the two components should be approximately the same. In devices such as film-wound capacitors, the dielectric constant \( (K_{\text{totai}}) \) of the device is a function of the following equation, wherein \( (d_{\text{totai}}) \) represents the total thickness of the dielectric film(s) and of the dielectric liquid layer(s).

\[
d_{\text{totai}}/K_{\text{totai}} = (d_{\text{film}}/K_{\text{film}}) + K_{\text{film}} + (d_{\text{fluid}}/K_{\text{fluid}})
\]

In view of the above equation, the dielectric constant of the device \( (K_{\text{totai}}) \) is approximately that of the component having the lowest dielectric constant. For example, if the dielectric constant of the dielectric fluid is much lower than that of the dielectric film, the dielectric constant of the device is approximately that of the dielectric fluid. It is desirable for the dielectric constant of the film and fluid to match, that is, be the same or substantially the same. Furthermore, such a dielectric liquid displays other desirable properties such as nonflammability, dielectric strength, chemical stability, or surface tension.

Semiconductor processes can incorporate a device or a work-piece that has heat removed from it or has heat added to it. The heat transfer associated with either the heat removal or addition can take place over a wide temperature range. In each case a heat transfer fluid is preferably used which has attributes such as low toxicity and low flammability.

Heat transfer fluids that are presently used in semiconductor applications include perfluorocarbons (PFCs), perfluoropolyethers (PFPEs), perfluoroamines (PFAs), perfluoroethers (PFEs), water/glycol mixtures, deionized water, silicone oils and
hydrocarbon oils. PFCs, PFPEs, PFAs and PFEs can exhibit atmospheric lifetime values of greater than 500 years, and up to 5,000 years. At low temperatures water/glycol mixtures also exhibit relatively high viscosity. The high viscosity at low temperature yields high pumping power. Deionized water has a low temperature limit of 0 degrees centigrade. Silicone oils and hydrocarbon oils are typically flammable.

Provided is an apparatus and a method for heat transfer using fluorinated esters of Formulas I-III as a heat transfer fluid. The provided apparatus comprises a device and a mechanism for transferring heat to or from the device wherein the mechanism includes a heat transfer fluid.

Examples of the provided apparatus include, but are not limited to, a test head used in automated test equipment for testing the performance of semiconductor dice, a wafer chuck used to hold silicon wafers in asher, steppers, etchers, PECVD tools, a constant temperature bath, and a thermal shock test bath.

The provided apparatus comprises a device. The device is a component, work-piece, assembly, etc. to be cooled, heated or maintained at a selected temperature. Such devices include electrical components, mechanical components and optical components. Examples of suitable devices of the provided apparatus include, but are not limited to a microprocessor, a wafer used to manufacture semiconductor devices, a power control semiconductor, an electrochemical cell (including a lithium-ion cell), an electrical distribution switch gear, power transformer, a circuit board, a multi-chip module, a packaged or unpackaged semiconductor device, a fuel cell, and a laser.

In certain embodiments, the apparatus includes a heat transfer mechanism. The heat transfer mechanism, when placed in thermal contact with the device, can remove heat from the device or provide heat to the device, or maintain the device at a selected temperature by removing or providing heat as necessary. By thermal contact it is meant that device and the thermal-transfer fluid are in close enough proximity to enable heat to flow between them. The direction of heat flow (from device or to device) is determined by the relative temperature difference between the device and the heat transfer mechanism. The heat transfer mechanism can include the whole system that is involved in heat transfer exclusive of the device. The system can include facilities for managing the heat transfer fluid. These facilities can include containers, pumps, conduits, thermostats, stirrers, heating means, cooling means, and all other peripheral devices excepting the heat
transfer fluid that can be used to control the temperature of a device. The heating means
and/or cooling means are well known by those of ordinary skill in the art and include, for
example, heating coils or wires or cooling coils. The heat transfer mechanism includes the
heat transfer fluid of the provided apparatus. In some embodiments, the heat transfer
mechanism can maintain the device at a selected temperature by transferring heat to or
from the device as needed to maintain the temperature of the device.

In some embodiments the heat transfer mechanism can include facilities for
managing the heat transfer fluid, including, e.g., pumps, valves, fluid containment
systems, pressure control systems, condensers, heat exchangers, heat sources, heat sinks,
refrigeration systems, active temperature control systems, and passive temperature control
systems. Examples of suitable heat transfer mechanisms include, but are not limited to, a
system for cooling wafer chucks in plasma-enhanced chemical vapor deposition (PECVD)
tools, a system for controlling temperature in test heads for die performance testing, a
system for controlling temperatures within semiconductor process equipment, a thermal
management system for electrochemical cells such as lithium-ion cells, a system for
thermal shock testing of an electronic device, and a system for maintaining constant
temperature of an electronic device.

In one aspect, the apparatus includes a device, that can be an electronic device,
requiring heat transfer and a mechanism for transferring heat to or from the device, the
mechanism comprising a heat transfer fluid, wherein the heat transfer fluid includes a
fluorinated ester of Formulas I to III.

The fluorinated esters of Formulas I to III can be used alone or in admixture with
each other or with other commonly-used solvents (for example, alcohols, ethers, alkanes,
alkenes, perfluorocarbons, perfluorinated tertiary amines, perfluoroethers, cycloalkanes,
esters, ketones, aromatics, siloxanes, chlorinated alkanes, chlorinated alkenes, carbonates,
fluorinated ketones, fluorinated alkenes, hydrochlorocarbons, hydrochlorofluorocarbons,
hydrofluorocarbons, hydrofluoroethers, hydrofluoropolyethers, ionic liquids, and the like,
and mixtures thereof). Such co-solvents can be chosen to modify or enhance the
properties of a composition for a particular use and can be utilized in ratios (of co-
solvent(s) to hydrofluorocarbonate(s)) such that the resulting composition preferably has
no flash point. If desired, the fluorinated esters can be used in combination with other
compounds that are very similar in properties relative to a particular use to form compositions that include the provided fluorinated esters

Minor amounts of optional components can be added to the compounds to impart particular desired properties for particular uses. Useful compositions can comprise conventional additives such as, for example, surfactants, coloring agents, lubricants, stabilizers, anti-oxidants, flame retardants, and the like, and mixtures thereof.

In another aspect, a method is provided for transferring heat that includes providing a device and providing a mechanism for transferring heat to or from the device, comprising a heat transfer fluid, wherein the heat transfer fluid comprises a fluorinated ester of Formulas I to III.

In certain embodiments, the processes described in, for example, U.S. Re. Pat. No. 37,119 E (Sherwood) and U.S. Pat. No. 6,374,907 (Tousignant et al.) can be used for heat transfer. In carrying out these processes, heat can be transferred between a heat source (for example, a silicon wafer or a component of a flat panel display) and a heat sink through the use of a heat transfer agent comprising at least one hydrofluoroether compound of the invention. The device can be a heat source or a heat sink depending upon the direction of heat flow (e.g., to or from the device).

The fluorinated esters used herein are generally monodisperse (that is, of a narrow molecular weight range). This means that their physical properties remain relatively constant over time, thereby avoiding significant heat transfer performance deterioration. In addition, the fluorinated esters exhibit a wide liquid range, useful viscosity over that range, and relatively high thermal stability at end use temperatures, making them well-suited for use as heat transfer fluids.

The fluorinated esters can have high heat capacities. Additionally, heat transfer fluids made with the fluorinated esters can also have high heat capacities. Specific heat capacities (measured at 20 degrees centigrade) of the provided heat transfer fluids can be greater than 1.200 J/gK, greater than 1.225 J/gK, greater than 1.250 J/gK, or even greater than 1.260 J/gK.

Objects and advantages of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as
well as other conditions and details, should not be construed to unduly limit this
disclosure.

EXAMPLES

Unless otherwise noted, all solvents and reagents were available from Aldrich
Chemical Co. of Milwaukee, WI.

**Test Methods**

**Boiling Point**

Boiling point of a test sample was measured according to ASTM D120-94
"Standard Test Method for Boiling Point of Engine Coolants". The method used a 50-mL
glass round-bottom flask. Vacuum was measured and controlled using a J-KEM vacuum
controller (J-KEM Scientific, St. Louis, MO). The pressure transducer was calibrated on
the day of measurement by comparison with full vacuum and with an electronic barometer
located in the same laboratory, Analytical Instrument no. 1061. The test sample was
slowly heated, then vacuum was applied until boiling occurred and a steady dropwise
reflux rate was established. Pot temperature and pressure reading were recorded, then the
vacuum controller was set for a higher absolute pressure and the material was heated
further until a new reflux point was established. The pressure level was raised in ~100
mmHg (~13 kPa) increments until the vapor pressure curve was obtained up to the
atmospheric boiling point.

**Melting Point**

Melting point of a test sample was measured by placing a sealed glass sample vial
containing 3 mL of a test sample into a cold bath. The cold bath was a 250 mL Dewar
flask filled with n-pentane bath fluid. The cold bath was pre-cooled using liquid nitrogen.
Temperature was measured using an RTD thermometer probe immersed in the bath. The
sample vial was attached directly to the RTD probe. The sample was pre-frozen in liquid
nitrogen, and then placed in the cold bath. The bath was allowed to warm naturally,
checking the sample every 1°C and recording the temperature when the solid just began to
melt and when it was all liquid.
Pour Point

The pour point of test samples was determined by placing a sealed glass vial containing 3 mL of the fluid test sample into a stirred Dewar flask containing n-pentane bath fluid. The sealed glass vial was attached directly to a thermocouple probe. The n-pentane bath fluid was chilled by placing a plastic beaker of liquid nitrogen in contact with the bath fluid, and cooling until the test sample did not pour. Temperature was then allowed to increase in 1 °C increments until the test sample poured. Pouring was defined as visible movement of the material during a five second count, according to the criterion specified in ASTM D97-12.

Dielectric Strength

Dielectric strength was determined according to ASTM D877/877M-13.

Hydrolvtic Stability

Ten grams of the ester compound to be tested and 10 grams of DI water were added to a 1 inch (~2.5 cm) ID by 3.875 inch (~9.8 cm) long Monel tube with threaded Monel caps, available from Parr Instrument Company. The test mixture was heated at 100°C for 24 hours. After cooling, the phases were separated and analyzed by 19F-NMR for likely alcohol breakdown products. The percent decomposition was then determined by 19F-NMR integration or by fluoride electrode measurement of released fluoride in ppm fluoride per gram-hour (ppm F/gh).

Thermal Stability at Reflux

Thermal stability at reflux was determined by placing 50 grams of material into a 125 mL distillation flask, containing a thermal well and thermocouple, and water cooled condenser connected to a gas bubbler. Heat was applied to the heating mantle using a variable autotransformer to achieve a slight reflux in the condenser. The liquid temperature, color and clarity of the solution and any off gassing were recorded daily. The material was said to have good thermal stability over the test period if the following conditions were met: temperature remained constant, appearance and clarity did not
change, no off-gassing after the initial heat up, the GC of the input and final material remained the same, and > 99.5% of the starting material was recovered.

**Closed Cup Flammability**

Closed Cup Flammability was determined according to ASTM D 7236-06 "Standard Test Method for Flash Point by Small Scale Closed Cup Tester (Ramp Method)."

**Kinematic Viscosity**

Kinematic viscosity was measured using a SCHOTT AVS 350 VISCOSITY TIMER, Analytical Instrument No. 341. For temperatures below 0 °C, a LAWLER TEMPERATURE CONTROL BATH Analytical Instrument No. 320 was used. The viscometers used for all temperatures were 545-10, 20 and 23. Viscometers were also corrected using the Hagenbach correction.

**Preparatory Example 1 (PE-1): Preparation of heptafluoroisobutyryl fluoride.**

\[(\text{CF}_3)_2\text{CFCOF}\]

Heptafluoroisobutyryl fluoride was prepared by electrochemical fluorination of isobutyric anhydride in a Simons ECF cell as described in U.S. Pat. No. 2,713,593 (Brice et al.) and in R.E.Banks, Preparation, Properties, and Industrial Applications of Organofluorine Compounds, pages 19-43 (1982). The gaseous products from the cell were further purified by fractional distillation to yield heptafluoroisobutyryl fluoride of about 80% purity by \(^{19}\text{F-}{\text{NMR}}\) with the remainder being inert materials. This mixture was used in subsequent reactions without further purification. As used in the text of subsequent examples herein, the term "heptafluoroisobutyryl fluoride" refers to this mixture.
Example 1 (EX-1): Preparation of 3-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoyl]oxypropyl 2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoate

A clean, dry, 600 mL stainless steel Parr pressure reactor was charged with sodium fluoride (115.3 grams, 2.74 mol) and 1,3-propanediol (94.4 grams, 1.24 mol). The vessel was sealed, brought to a vacuum of about 20 mniHg (2.7 kPa) and isolated, cooled with a dry-ice acetone bath, charged with heptafluoroisobutyryl fluoride (670 grams, 2.5 mol), warmed to about 25 °C with high agitation and held for 16 hours. Methanol (32 grams, 1.0 mol) from a charge bomb was transferred to the reactor and stirred for 1 hour. The reactor pressure was vented and the contents was filtered using a Buchner funnel to afford 587 grams of material containing 90.5% of the desired 3-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoyl]oxypropyl 2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoate, according to GC analysis. The material was purified by vacuum fractionation using silver coated, vacuum jacketed, distillation column (28 mm plate diameter), packed with 12 inches (~30 cm) of 0.16 inch (~4 mm) Monel distillation packing (Ace-Glass Corporation product # 6624-09) to afford material of 99.9% purity by 19F-NMR. The product was confirmed by 19F-NMR.

Example 2 (EX-2): Preparation of 2-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoyl]oxyethyl 2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoate

A clean, dry, 600 ml stainless steel Parr pressure reactor was charged with sodium fluoride (42 grams, 1.0 mol) and ethylene glycol (31 grams, 0.50 mol). The vessel was
sealed, brought to a vacuum of about 20 mmHg (2.7 kPa) and isolated, cooled with a dry-

ice acetone bath, charged with heptafluoroisobutyryl fluoride (PE-1; 297 grams, 1.10 mol), warmed to about 25°C with high agitation and held for 16 hours. Methanol (32 grams, 1.0 mol) from a charge bomb was transferred to the reactor and stirred for 1 hour. The reactor pressure was vented and the contents was washed one time with one liter of water to afford 227.5 grams of material containing 81% of the desired 3-[2,3,3,3-
tetrafluoro-2-(trifluoromethyl)propanoyl]oxyethyl 2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoate. The material was combined with three other preps and purified by vacuum fractionation using the same system as described in EX-1 to afford 99.7 % purity by 19F-NMR. Product was confirmed by 19F-NMR.

Example 3 (EX-3): Preparation of 4-[2,3,3,3-tetrafluoro-2-

(trifluoromethyl)propanoyl]oxybutyl 2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoate

A clean, dry 600 ml stainless steel Parr pressure reactor was charged with sodium fluoride (168 grams, 4.0 mol) and 1,4-butanediol (90 grams, 1.00 mol). The vessel was sealed, brought to a vacuum of about 20 mmHg (2.7 kPa) and isolated, cooled with a dry-

ice acetone bath, charged with heptafluoroisobutyryl fluoride (548 grams, 2.03 mol), heated to 50 °C with high agitation and held for 16 hours. The reactor was cooled to 25 C and methanol (32 grams, 1.0 mol) from a charge bomb was transferred to the reactor and stirred for 1 hour. The reactor pressure was vented and the contents was filtered using a Buchner funnel to afford 432 grams containing 88.3 % of the desired 3-[2,3,3,3-
tetrafluoro-2-(trifluoromethyl)propanoyl]oxybutyl 2,3,3,3-tetrafluoro-2-

(trifluoromethyl)propanoate. The material was vacuum fractionation using the same system as EX-1 to afford 99.3 % purity by GC. The product was confirmed by GC/MS.
Example 4 (EX-4): Preparation of [l-methyl-3-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoyl]oxy-butyl] 2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoate

A clean, dry 600 ml stainless steel Parr pressure reactor was charged with sodium fluoride (23.1 grams, 0.55 mol) and 2,4-pentanediol (26 grams, 0.25 mol). The vessel was sealed, brought to a vacuum of about 20 mmHg (2.7 kPa) and isolated, cooled with a dry-ice acetone bath, charged with heptafluoroisobutyryl fluoride (148.5 grams, 0.55 mol), heated slowly to 90°C with high agitation and held for 16 hours. The reactor was cooled to 25°C and the reactor pressure was vented and the contents were centrifuged for 30 minutes at 2200 rpm's to afford 82.5 grams containing 90.5% of the desired [l-methyl-3-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoyl]oxy-butyl] 2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoate. The material was combined with three other preps and purified by vacuum fractionation using the same system as described in EX-1 to afford 99.5% purity by GC. The product was confirmed by GC/MS.

Preparatory Example 2 (PE-2): Preparation of heptafluorobutyryl fluoride, C3F7COF

Heptafluorobutyryl fluoride was prepared by electrochemical fluorination of isobutyric anhydride in a Simons ECF cell as described in U.S. Pat. No. 2,713,593 (Brice et al.) and in R.E.Banks, Preparation, Properties, and Industrial Applications of Organofluorine Compounds 19-43 (1982). The gaseous products from the cell were purified by fractional distillation to yield about 80% purity heptafluorobutyryl fluoride with the remainder being mostly inert materials. The composition of heptafluorobutyryl fluoride consisted of 60%> 2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoyl fluoride, (CF₃)₂CFCOF, and 40% normal 2,2,3,3,4,4,4-heptafluorobutanoyl fluoride, CF₃CF₂CF₂COF, and was used in subsequent reaction without further purification. As used herein, the term "perfluorobutyryl fluorides" will refer to this mixture.
Example 5 (EX-5): Preparation of 2-(2,2,3,3,4,4,4-heptafluorobutanoyloxy)ethyl 2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoate

A clean, dry 2 liter stainless steel Parr pressure reactor was charged with sodium fluoride (186.7 grams, 4.44 mol) and ethylene glycol (114.7 grams, 1.85 mol). The vessel was sealed, brought to a vacuum of about 20 mmHg (2.7 kPa) and isolated, cooled with an internal water cooling loop, charged with perfluorobutyryl fluorides (PE-2; 1090 grams, 4.07 mol) over 4 hours and warmed to about 25 °C with high agitation and held for 64 hours. Methanol (128 grams, 4.0 mol) from a charge bomb was transferred to the reactor and stirred for 1 hour. The reactor pressure was vented and the contents was washed five times with water (1000 grams each wash) to afford 890 grams containing 87.8% of three isomers of the desired product. The material was vacuum fractionation using the same system as EX-1 to afford 99.7% purity. The product was confirmed by GC/MS and $^{19}$F-NMR. The normalized isomer ratio of the final product was as follows (percentages were determined by $^{19}$F-NMR):

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure1" /></td>
<td>30.3%</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure2" /></td>
<td>47.8%</td>
</tr>
</tbody>
</table>
Example 6 (EX-6): Preparation of [2-methyl-3-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoyloxy]-2-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoyloxymethyl]propyl] 2,3,3-tetrafluoro-2-(trifluoromethyl)propanoate

A clean, dry 600 ml stainless steel Parr pressure reactor was charged with sodium fluoride (96.6 grams, 2.30 mol), 1,1,1-tris(hydroxymethyl)ethane (94.4 grams, 0.73 mol), and methyl tert-butyl ether (20 grams). The vessel was sealed, cooled with a dry-ice acetone bath, charged with heptafluoroisobutyryl fluoride (PE-1; 621 grams, 2.3 mol), warmed to about 25 °C with high agitation, and held for 16 hours. Methanol (73.6 grams, 2.3 mol) from a charge bomb was transferred to the reactor and stirred for 1 hour. The reactor pressure was vented and the contents were washed three times water (1000 grams each wash) to afford 542 grams containing 65.2% of the desired [2-methyl-3-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoyloxy]-2-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoyloxymethyl]propyl] 2,3,3-tetrafluoro-2-(trifluoromethyl)propanoate, according to GC analysis. This material was combined with 2 other preps and purified by vacuum fractionation using the same system as described in EX-1 to afford material having 99.4% purity by GC. The product was confirmed by GC/MS.
Example 7 (EX-7): Preparation of 2,3-bis[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoylloxylpropyl 2,3,3,3-tetrafluoro-2-(trifluoromethyl)propanoate

\[
\begin{align*}
\text{F}_3\text{C} & \text{F} \\
\text{O} & \text{O} \\
\text{CF}_3 & \text{O} \\
\text{CF}_3 & \text{CF}_3 \\
\text{F}_3\text{C} & \text{F} \\
\text{CF}_3
\end{align*}
\]

A clean, dry 600 ml stainless steel Parr pressure reactor was charged with sodium fluoride (96.6 grams, 2.3 mol) and glycerol (55 grams, 0.60 mol). The vessel was sealed, brought to a vacuum of about 20 mmHg (2.7 kPa) and isolated, cooled with a dry-ice acetone bath, charged with heptafluoroisobutyryl fluoride (PE-1; 600 grams, 3.83 mol), slowly heated to 70°C with high agitation and held for 64 hours. The reactor was cooled to 25 °C and the pressure was vented. The reactor contents were washed several times with one liter of water to afford 456 grams containing 13.3 % of the desired triester and 76% diesters. This material was added back to a clean, dry, 600 ml, stainless steel, Parr, pressure reactor along with sodium fluoride (40 grams, 1.0 mol). The vessel was sealed, brought to a vacuum of about 20 mmHg (2.7 kPa) and isolated, cooled with a dry-ice acetone bath, charged with heptafluoroisobutyryl fluoride (PE-1; 230 grams, 0.65 mol), and slowly heated to 70°C with high agitation and held for 16 hours. The reactor was cooled to 25 °C and the pressure was vented. The reactor contents were washed several times with one liter of water to afford 465 grams containing 80% of the desired triester. The material was vacuum fractionated using the same system as described in EX-1 to afford material having 97.6% purity by GC. The product was confirmed by GC/MS.
Example 8 (EX-8): Preparation of \([3-\{2,3,3,3\text{-tetrafluor-2-}
\text{(trifluoromethyl)}\text{propanoyl}1\text{oxy-2,2-bisrr2,3,3,3\text{-tetrafluor-2-}}
\text{(trifluoromethyl)propanoylloxymethyl}lpropyl\} \text{2,3,3-tetrafluor-2-}
\text{(trifluoromethyDpropanoate}

A clean, dry 600 ml stainless steel Parr pressure reactor was charged with ethylene glycol dimethyl ether (62 grams) and pentaerythritol (50 grams, 0.37 mol). The vessel was sealed and cooled with a dry-ice acetone bath, charged with heptafluoroisobutyryl fluoride (PE-1; 423 grams, 1.57 mol), then slowly heated to 70 °C with high agitation and held for 64 hours. The reactor was cooled to 25 °C, pressure was vented, and the reactor contents were titrated with 45 wt.% aqueous KOH (135 ml) to bring the pH up to 6. The mixture was phase split to remove the aqueous phase and the bottom product phase was washed one time with 500 grams of water. The bottom product phase was centrifuged at 2,200 rpm for one hour. The bottom product phase was then removed and purified by vacuum fractionation using the same system as described in EX-1 to afford 208 grams at 95.1% purity by GC. The desired product was confirmed by GC/MS.

Preparatory Example 3 (PE-3): Preparation of intermediate heptafluorobutyryl fluoride, 

Heptafluorobutyryl fluoride was prepared by electrochemical fluorination of isobutyric anhydride in a Simons ECF cell as described in U.S. Pat. No. 2,713,593 (Brice et al.) and in R.E.Banks, Preparation, Properties, and Industrial Applications of 

Organofluorine Compounds 19-43 (1982). The gaseous products from the cell were
further purified by fractional distillation to yield material having 65.1% CF₃CF₂CF₂COF and 4.9% (CF₃)₂CFCOF (¹⁹F-NMR purity values) with the remainder being inert materials. This mixture was used in subsequent reactions without further purification. As used herein, the term "n-perfluorobutyryl fluoride" will refer to this mixture.

Comparative Example 1 (CE-1): Preparation of [3-(2,2,3,3,4,4,4-heptafluorobutanoyloxy)-2,2-bis(2,2,3,3,4,4,4-heptafluorobutanoyloxymethyl)propyl] 2,2,3,3,4,4,4-heptafluorobutanoate

A clean, dry, 600 ml, stainless steel, Parr, pressure reactor was charged with ethylene glycol dimethyl ether (62 grams) and pentaerythritol (50 grams, 0.37 mol). The vessel was sealed and cooled with a dry-ice acetone bath, charged with n-perfluorobutyryl fluoride (PE-3; 500 grams, 1.62 mol), slowly heated to 65 °C with high agitation and held for 16 hours. The reactor was cooled to 25 °C. Methanol (32 grams, 1.0 mol) from a charge bomb was transferred to the reactor and stirred for 1 hour. The reactor pressure was vented and the contents were washed two times with one liter of water used for each wash to afford 339 grams at 80% purity (by ¹⁹F-NMR) of the desired tetra ester. The mixture was purified by vacuum fractionation using the same system as described in EX-1.
Preparatory Example 4 (PE-4): Preparation of intermediate 2,3,3,4,4,4-hexafluoro-2-(1,1,2,2,2-pentafluoroethyl)butanoyl fluoride

![Chemical Structure](attachment:image.png)

The 2,3,3,4,4,4-hexafluoro-2-(1,1,2,2,2-pentafluoroethyl)butanoyl fluoride was prepared by electrochemical fluorination of ethyl 2-ethylbutyrate (purchased from TCI America, Montgomeryville, PA) in a Simons ECF cell as described in U.S. Pat. No. 2,713,593 (Brice et al.) and in R.E.Banks, Preparation, Properties, and Industrial Applications of Organofluorine Compounds 19-43 (1982). The gaseous products from the cell were further purified by fractional distillation to yield 2,3,3,4,4,4-hexafluoro-2-(1,1,2,2,2-pentafluoroethyl)butanoyl fluoride having a purity of about 48% (by $^{19}$F-NMR), with the remainder being mostly inert. As used herein, the term "perfluoro-2-ethylbutyryl fluoride" will refer to this mixture.

Example 9 (EX-9): Preparation of methyl 2,3,3,4,4,4-hexafluoro-2-(1,1,2,2,2-pentafluoroethyl)butanoate

![Chemical Structure](attachment:image.png)

A one liter poly-bottle was charged with anhydrous methanol (96 grams, 3.0 mol), capped, cooled with a dry-ice acetone bath, charged with perfluoro-2-ethylbutyryl fluoride (PE-4; 658 grams, 1.0 mol), in about 150 gram increments, mixed by shaking, then cooled in the dry-ice acetone batch before adding the next increment. Once the final charge had been added and the heat removed, the sample was allowed to sit for two hours. The reaction mixture was washed three times with water (500 grams per wash) to afford 649 grams at 49.1% purity (by GC) of the desired ester. The ester was purified by vacuum
fractionation using silver coated, vacuum jacketed, 10 perforated plate, internal bellows, distillation column, available from Ace Glass Incorporated, Vineland, NJ. The desired product was confirmed by GC/MS.

Example 10 (EX-10): Preparation of ethyl 2,3,3,4,4,4-hexafluoro-2-(T,1,2,2,2-pentafluoroethoxy)butanoate

\[
\begin{align*}
\text{CF}_3\text{CF}_2\text{F} & \quad \text{O} \\
\text{OCH}_2\text{CH}_3 & \quad \text{CF}_2\text{CF}_3
\end{align*}
\]

The preparation and purification was completed essentially the same as for EX-10, except that instead of using anhydrous methanol, 200 proof ethanol (138 grams, 3 mol, dried over 3A molecular sieves for 3 days) was used. This procedure recovered 657 grams containing 50.5% (by GC) of the desired ester. The product was confirmed by GC/MS.

Example 11 (EX-11): Preparation of isopropyl 2,3,3,4,4,4-hexafluoro-2-(l,1,2,2,2-pentafluoroethoxy)butanoate

\[
\begin{align*}
\text{CF}_3\text{CF}_2\text{F} & \quad \text{O} \\
\text{OCH(CH}_3)_2 & \quad \text{CF}_2\text{CF}_3
\end{align*}
\]

The preparation and purification was completed essentially the same as EX-9, except instead of using anhydrous methanol, anhydrous 2-propanol (180 grams, 3 mol) was used. This procedure recovered 673 grams containing 50.7% (by GC) of the desired ester. The desired product was confirmed by GC/MS.
Example 12 (EX-12): Preparation of 1-ethylpropyl 2,3,3,4,4,4-hexafluoro-2-(1,1,2,2,2-pentafluoroethyldibutanoate

\[
\begin{align*}
\text{CF}_3\text{CF}_2\text{F} & \quad \text{OCH(CH}_2\text{CH}_3)_2 \\
\text{CF}_2\text{CF}_3 &
\end{align*}
\]

A one liter poly-bottle was charged with 3-pentanol (96 grams, 3.0 mol), capped, cooled with a dry-ice acetone bath, charged with perfluoro-2-ethylbutyryl fluoride (PE-4; 658 grams, 1.0 mol), in about 150 gram increments, mixed by shaking, then cooled in the dry-ice acetone bath before adding the next increment. Once the final charge has been added and the heat removed, the contents was transferred to a clean, dry, 600 ml, stainless steel, Parr, pressure reactor. The reactor was sealed and heated to 65°C and held for 64 hours. The material was phase split and the lower product phase was washed three times with water (500 grams per wash) to afford 674 grams at 54.7 % desired ester. The material was fractionated using the same system as EX-1 to obtain a purity of 88.3% (by GC) of the desired ester. The desired ester was confirmed by GC/MS.

Preparative Example 5 (PE-5): Preparation of intermediate ECF cell feed methyl 2-methyl-3-morpholino-propanoate

Morpholine (1200 grams, 13.8 mol) and methanol (604 grams) were charged to a 3 neck, 5 liter round bottom flask equipped with an overhead stirrer, thermocouple, pressure equalizing addition funnel, and cold water condenser. Methyl methacrylate (1379.6 grams, 13.8 mol) was added over the course of 2.5 hours with stirring at 40°C. The reaction was held at 50 °C for 5 days. The methanol and unreacted materials were removed by single plating under reduced pressure at 50 °C to afford 233.2 grams of product with a purity of 91.7%. This material was feed to the ECF cell without further purification.
Preparative Example 6 (PE-6): 2-[difluoro-(2,2,3,3,5,5,6,6-octafluoromorpholin-4-yl)methyl]-2,3,3,3-tetrafluoro-propanoyl fluoride

The 2-[difluoro-(2,2,3,3,5,5,6,6-octafluoromorpholin-4-yl)methyl]-2,3,3,3-tetrafluoro-propanoyl fluoride was prepared by electrochemical fluorination of methyl 2-methyl-3-morpholino-propanoate (PE-5) in a Simons ECF cell as described in U.S. Pat. No. 2,713,593 (Brice et al.) and in R.E. Banks, Preparation, Properties, and Industrial Applications of Organofluorine Compounds 19-43 (1982). The gaseous products from the cell were further purified by fractional distillation to yield about 86.9% purity (by $^{19}$F-NMR) (2-[difluoro-(2,2,3,3,5,5,6,6-octafluoromorpholin-4-yl)methyl]-2,3,3,3-tetrafluoro-propanoyl fluoride with the remainder being mostly inert materials. This mixture was used in subsequent reactions without further purification. As used herein, the term "perfluoromorpholino methacrylate acyl fluoride" will refer to this mixture.

Example 13 (EX-13): Preparation of methyl 2-[difluoro-(2,2,3,3,5,5,6,6-octafluoromorpholin-4-yl)methyl]-2,3,3,3-tetrafluoro-propanoate.

A one liter poly-bottle was charged with anhydrous methanol (250 grams, 7.8 mol), capped, cooled with a dry-ice acetone bath, charged with perfluoromorpholino methacrylate acyl fluoride (PE-6; 400 grams, 0.81 mol), in about 150 gram increments, mixed by shaking, then cooled in the dry-ice acetone batch before adding the next increment. Once the final charge has been added and the heat removed, the sample is allowed to sit for two hours. The reaction mixture is washed three times with water (500 grams per wash) to afford 394 grams at 87.0 % purity (by GC) of the desired ester. Purify by fractionation using silver coated, vacuum jacketed, 20 perforated plate, internal...
bellow, distillation column, available from Ace Glass Incorporated. The desired product was confirmed by GC/MS.

Example 14 (EX-14): Preparation of ethyl 2-rdifluoro-(2,2,3,3,5,5,6,6-octafluoromorpholin-4-yl)methyl-2,3,3,3-tetrafluoro-propanoate

Using techniques similar to those described for EX-13, 200 proof ethanol (200 grams, 4.3 mol, dried over 3 Ang. molecular sieves for 3 days) was reacted with perfluoromorpholino methacrylate acyl fluoride (PE-6; 468 grams, 0.95 mol) to afford 462 grams at 86.4 % purity (by GC) of the desired material. The material was purified by fractional distillation using the same column described in EX-13. The desired product was confirmed by GC/MS.

Example 15 (EX-15): Preparation of isopropyl 2-[difluoro-(2,2,3,5,5,6,6-octafluoromorpholin-4-yl)methyl]-2,3,3,3-tetrafluoro-propanoate

Using techniques similar to those described for EX-13, anhydrous 2-propanol (240 grams, 4.0 mol) was reacted with perfluoromorpholino methacrylate acyl fluoride (PE-6; 491 grams, 1.0 mol) to afford 515 grams at 87.6 % purity (by GC) of the desired material. The material was purified by fractional distillation using the same column described in EX-1.
Preparative Example 7 (PE-7): Preparation of intermediate ECF cell feed methyl 2-methyl-3-pyrrolidino-propanoate.

Pyrrolidine (871.3 grams, 12.25 mol) and methanol (332 grams) were charged to a 3 neck, 3 liter round bottom flask equipped with an overhead stirrer, thermocouple, pressure equalizing addition funnel, and cold water condenser. Methyl methacrylate (1226.8 grams, 12.25 mol) was added over the course of 2.5 hours and held at 50 °C for 24 hours. The methanol and unreacted materials were removed by single plating under reduced pressure at 45 °C to afford 2002.5 grams of product with a purity of 96.6%. This material was fed to the ECF cell without further purification.

Preparative Example 8 (PE-8): 2-rdifluoro-(2,2,3,3,4,4,5,5-octafluoropyrrolidin-l-y1)methyl1-2,3,3,3-tetrafluoro-propanoyl fluoride

The 2-[difluoro-(2,2,3,3,4,4,5,5-octafluoropyrrolidin-l-y1)methyl]-2,3,3,3-tetrafluoro-propanoyl fluoride was prepared by electrochemical fluorination of methyl 2-methyl-3-pyrrolidino-l-y1-propanoate (PE-7) in a Simons ECF cell as described in U.S. Pat. No. 2,713,593 (Brice et al.) and in R.E.Banks, Preparation, Properties, and Industrial Applications of Organofluorine Compounds 19-43 (1982). The gaseous products from the cell contained about 64% 2-[difluoro-(2,2,3,3,4,4,5,5-octafluoropyrrolidin-l-y1)methyl]-2,3,3,3-tetrafluoro-propanoyl fluoride with about another 16% of other acyl fluorides and the remaining 20% being mostly inert materials. This mixture was used in subsequent reactions without further purification. As used herein, the term "perfluoropyrrolidino methacrylate acyl fluoride" refers to this mixture.

Example 16 (EX-16): Preparation of methyl 2-[difluoro-(2,2,3,3,4,4,5,5-octafluoropyrrolidin-l-y1)methyl]-2,3,3,3-tetrafluoro-propanoate
A one liter poly-bottle was charged with anhydrous methanol (300 grams, 9.4 mol), capped, cooled with a dry-ice acetone bath, charged with perfluoromorpholino methacrylate acyl fluoride (PE-8; 1033 grams, 2.01 mol), in about 150 gram increments, mixed by shaking, then cooled in the dry-ice acetone batch before adding the next increment. Once the final charge has been added and the heat removed, the sample is allowed to sit for two hours. The reaction mixture is washed three times with water (500 grams per wash) to afford 1046 grams at 80.3% purity (by GC) of the desired esters. The material was purified by fractional distillation using the same column described in EX-13. The desired product was confirmed by GC/MS.

Example 17 (EX-17): Preparation of propyl 2,2,3,3,4,4,5,5-octafluoropyrrolidin-1-yl)methyl-2,3,3,3-tetrafluoro-propanoate

Using techniques similar to those described for EX-16, anhydrous 1-propanol (300 grams, 5.0 mol) was reacted with perfluoropyrrolidino methacrylate acyl fluoride (PE-8; 1019 grams, 1.98 mol) to afford 1100 grams at 80.7% purity (by GC) of desired material. The material was purified by fractional distillation using the same column described in EX-13. The desired product was confirmed by GC/MS.

Example 18 (EX-18V Preparation of allyl 2,2,3,3,4,4,5,5-octafluoropyrrolidin-1-yl)methyl-2,3,3,3-tetrafluoro-propanoate
Using techniques similar to those described for EX-16, allyl alcohol (300 grams, 5.17 mol, dried over 3A molecular sieves for 3 days) was reacted with perfluoropyrrolidino methacrylate acyl fluoride (PE-8; 978 grams, 1.90 mol) to afford 1034.7 grams at 79.4% purity (by GC) of desired material. The material was purified by vacuum distillation using the same column described in EX-1. The desired product was confirmed by GC/MS.

Example 19 (EX-19): Preparation of 2-methoxyethyl 2-difluoro-(2,2,3,3,4,4,5,5-octafluoropyrrolidin-l-yl)methyl-2,3,3,3-tetrafluoro-propanoate

Using techniques similar to those described for EX-16, 2-methoxy ethanol (300 grams, 3.95 mol, dried over 3A molecular sieves for 3 days) was reacted with perfluoropyrrolidino methacrylate acyl fluoride (1030 grams, 2.00 mol) to afford 1034.7 grams at 37.4% purity (by GC) of desired material. The material was purified by vacuum distillation using the same column described in EX-1. The desired product was confirmed by GC/MS.

Preparatory Example 9 (PE-9): Preparation of intermediate ECF cell feed methyl 2-methyl-3-(4-methyl-1-piperidyDpropanoate.

The 4-methylpiperidine (1608.6 grams, 16.2 mol) and methanol (868 grams) were charged to a 3 neck, 5 liter round bottom flask equipped with an overhead stirrer, thermocouple, pressure equalizing addition funnel, and cold water condenser. Methyl methacrylate (1624.0 grams, 16.2 mol) was added over the course of 2 hours and held at 50 °C for 16 hours. The methanol and unreacted materials were removed by single plating under reduced pressure at 50 °C to afford 3058.1 grams of product with a purity of 91.6%. This material was feed to the ECF cell without further purification.
Preparatory Example 10: 2-rdifluoro-2,2,3,3,4,5,5,6,6-nonafluoro-4-(trifluoromethyl)-1-piperidyllmethyl]-2,3,3-tetrafluoro-propanoyl fluoride

The 2-[difluoro-[2,2,3,3,4,5,5,6,6-nonafluoro-4-(trifluoromethyl)-1-piperidyl]methyl]-2,3,3-tetrafluoro-propanoyl fluoride was prepared by electrochemical fluorination of methyl 2-methyl-3-(4-methyl-l-piperidyl)propanoate in a Simons ECF cell as described in U.S. Pat. No. 2,713,593 (Brice et al.) and in R.E.Banks, Preparation, Properties, and Industrial Applications of Organofluorine Compounds, 19-43 (1982). The gaseous products from the cell were further purified by fractional distillation to yield about 86.9 % functional acyl fluoride material with the remaining being mostly inert materials. This mixture was used in subsequent reactions without further purification. As used herein, the term "perfluoromethylpiperdino methacrylate acyl fluoride" refers to this mixture.

Example 20: Preparation of methyl 2-[difluoro-[2,2,3,3,4,5,5,6,6-nonafluoro-4-(trifluoromethyl)-1-piperidyllmethyl]-2,3,3-tetrafluoro-propanoate

A one liter poly-bottle was charged with anhydrous methanol (102.1 grams, 3.2 mol), capped, cooled with a dry-ice acetone bath, charged with perfluoromethylpiperdino methacrylate acyl fluoride (PE-10; 813 grams, 1.38 mol), in about 150 gram increments, mixed by shaking, then cooled in the dry-ice acetone batch before adding the next increment. Once the final charge was added and the heat removed, the sample was allowed to sit for two hours. The reaction mixture was washed three times with water (500 grams per wash) to afford 803 grams with 80.6% of the material having a methyl
ester functionality. The material was purified by fractional distillation using the same column described in EX-13.

Example 21 (EX-21): Preparation of ethyl 2-rdifluoro-r2,2,3,3,4,5,5,6,6-nonafluoro-4-(trifluoromethyl)- 1-piperidyllmethyl]-2,3,3 ,3-tetrafluoro-propanoate

Using techniques similar to those described for EX-20, 200 proof ethanol (147.2 grams, 3.2 mol, dried over 3 Ang. molecular sieves for 3 days) was reacted with perfluoromethylpiperdino methacrylate acyl fluoride (PE-10; 813 grams, 1.38 mol) to afford 838 grams with 86.5% of the material having an ethyl ester functionality. The material was purified by fractional distillation using the same column described in EX-13.

Example 22 (EX-22): Preparation of propyl 2-[difluoro-[2,2, 3,3,4,5,5,6,6-nonafluoro-4-(trifluoromethyl)- 1-piperidyllmethyl]-2,3,3 ,3-tetrafluoro-propanoate

Using techniques similar to those described in EX-20, anhydrous 1-propanol (192.0 grams, 3.2 mol) was reacted with perfluoromethylpiperdino methacrylate acyl fluoride (PE-10; 808 grams, 1.37 mol) to afford 843 grams with 88.2% of the material having propyl ester functionality. The material was purified by vacuum distillation using the same column described in EX-1.
Example 23 (EX-23): Preparation of allyl 2-[difluoro-[2,2,3,3,4,5,5,6,6-nonafluoro-4-(trifluoromethyl)]-1-piperidyllmethyl]-2,3,3,3-tetrafluoro-propanoate

Using techniques similar to those described for EX-20, allyl alcohol (185.6 grams, 3.2 mol, dried over 3A molecular sieves for 3 days) was reacted with perfluoromethylpiperidine methacrylate acyl fluoride (PE-10; 813 grams, 1.38 mol) to afford 856.8 grams with 86.1% of the material having allyl ester functionality. The material was purified by vacuum distillation using the same column described in EX-1.

Example 24 (EX-24): Preparation of isopropyl 2-difluoro-r2,2,3,3,4,5,5,6,6-nonafluoro-4-(trifluoromethyl)-1-piperidyllmethyl]-2,3,3,3-tetrafluoro-propanoate

Using techniques similar to those described for EX-20, anhydrous 2-propanol (192.0 grams, 3.2 mol) was reacted with perfluoromethylpiperidine methacrylate acyl fluoride (PE-10; 813 grams, 1.38 mol) to afford 856.8 grams with 83.1% of the material having isopropyl ester functionality. The material was purified by vacuum distillation using the same column described in EX-1.
Preparatory Example 1 (PE-1): Preparation of intermediate ECF cell feed methyl 3-
(3,5-dimethyL-1-piperidyl)-2-methyl-propanoate

The 3,5-dimethylpiperidine (617.6 grams, 5.4 mol) and methanol (479 grams) were
charged to a 3 neck, 3 liter round bottom flask equipped with an overhead stirrer,
thermocouple, pressure equalizing addition funnel, and cold water condenser. Methyl
methacrylate (596.4 grams, 5.96 mol) was added over the course of 30 minutes and held at
50 °C for 24 hours. The methanol and unreacted materials were removed by single plating
under reduced pressure at 50 °C to afford 1065.3 grams of product with a purity of 95.1%
This material was feed to the ECF cell without further purification.

Preparatory Example 12 (PE-12): 2-[difluoro-[2,2,3,4,4,5,6,6-octafluoro-3,5-
bis(trifluoromethyl)-1-piperidyl)methyl]-2,3,3,3-tetrafluoro-propanoyl fluoride

The 2-[difluoro-[2,2,3,4,4,5,6,6-octafluoro-3,5-bis(trifluoromethyl)-1-
piperidyl)methyl]-2,3,3,3-tetrafluoro-propanoyl fluoride was prepared by electrochemical
fluorination of methyl 2-methyl-3-(4-methyl-1-piperidyl)propanoate (PE-11) in a Simons
ECF cell as described in U.S. Pat. No. 2,713,593 (Brice et al.) and in R.E.Banks,
Preparation, Properties, and Industrial Applications of Organofluorine Compounds 19-43
(1982). The gaseous products from the cell consisted of about 75.3 % functional acyl
fluoride material with the remaining being mostly inert materials. This mixture was used
in subsequent reactions without further purification. As used herein, the term
"perfluorodimethylpiperidino methacrylate acyl fluoride" will refer to this mixture.

Example 25 (EX-25): Preparation of methyl 2-[difluoro-[2,2,3,4,4,5,6-octafluoro-3,5-
bis(trifluoromethyl)-1-piperidyl]-1-methyl]-2,3,3,3-tetrafluoro-propanoate
A one liter poly-bottle was charged with anhydrous methanol (105.6 grams, 3.3 mol), capped, cooled with a dry-ice acetone bath, charged with perfluorodimethylpiperdino methacrylate acyl fluoride (PE-12; 1059 grams, 1.42 mol), in about 150 gram increments, mixed by shaking, then cooled in the dry-ice acetone bath before adding the next increment. Once the final charge has been added and the heat removed, the sample is allowed to sit for two hours. The reaction mixture is washed three times with water (500 grams per wash) to afford 1009 grams with 79.2% of the material having a methyl ester functionality. The material was purified by fractional distillation using the same column described in EX-13.

Example 26 (EX-26): Preparation of propyl 2-[difluoro-[2,2, 3,4,4,5,6,6-octafluoro-3, 5-bis(trifluoromethyl)-l-piperidyl1methyl1-2,3,3,3-tetrafluoro-propanoate

![Chemical structure image]

Using techniques similar to those described for EX-26, anhydrous 1-propanol (600 grams, 10.0 mol) was reacted with perfluorodimethylpiperdino methacrylate acyl fluoride (PE-12; 1394 grams, 1.87 mol) to afford 1394 grams with 76.3% of the material having propyl ester functionality. The material was purified by vacuum distillation using the same column described in EX-1.

Test data for the compounds of EX-1 to EX-27 and CE-1 was obtained according to Test Methods described above, with results as summarized in Table 1.
<table>
<thead>
<tr>
<th>Example No.</th>
<th>Boiling point, °C</th>
<th>Melting point, °C</th>
<th>Pour point, °C</th>
<th>Dielectric Strength, 0.1” (2.5 mm), KV</th>
<th>GC purity</th>
<th>Hydrolytic Stability, 100°C for 24 hours</th>
<th>Thermal Stability at atmospheric pressure reflux</th>
<th>Closed cup flammability</th>
</tr>
</thead>
<tbody>
<tr>
<td>EX-1</td>
<td>200</td>
<td>10.4</td>
<td>9.7, 14.7</td>
<td>100.0%</td>
<td>0.033% decomposed</td>
<td>Turned orange in 2 days</td>
<td>No flash at 200°F (93°C)</td>
<td></td>
</tr>
<tr>
<td>EX-2</td>
<td>184</td>
<td>0.5</td>
<td>40, 41.6</td>
<td>99.7%</td>
<td>0.13% decomposed</td>
<td>0.88</td>
<td>15 day study; GC purity improved; material did yellow</td>
<td>No flash at 200°F (93°C)</td>
</tr>
<tr>
<td>EX-3</td>
<td>219</td>
<td>-3.3</td>
<td></td>
<td>99.3%</td>
<td>0.17% decomposed</td>
<td>Not stable at boiling point</td>
<td>No flash at 200°F (93°C)</td>
<td></td>
</tr>
<tr>
<td>EX-4</td>
<td>201</td>
<td>-59</td>
<td>40, 39.9</td>
<td>99.5%</td>
<td>Stable (Detection limit: 0.0018%)</td>
<td>Not stable at boiling point</td>
<td>No flash at 200°F (93°C)</td>
<td></td>
</tr>
<tr>
<td>EX-5</td>
<td>197</td>
<td>37.7</td>
<td></td>
<td>99.9%</td>
<td>33% decomposed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EX-6</td>
<td>260</td>
<td>-26</td>
<td>53.6, 53.9</td>
<td>99.4%</td>
<td></td>
<td></td>
<td>Not stable during fractionation</td>
<td>No flash at 200°F (93°C)</td>
</tr>
<tr>
<td>EX-7</td>
<td>109 @ 2mmHg (266 Pa)</td>
<td>-12.3</td>
<td>53.6, 53.9</td>
<td>99.4%</td>
<td>97.6%</td>
<td>Poor stability</td>
<td>No flash at 200°F (93°C)</td>
<td></td>
</tr>
<tr>
<td>EX-8</td>
<td>144 @ 2mmHg (266 Pa)</td>
<td>&gt;22</td>
<td></td>
<td>95.1%</td>
<td>3.6% decomposed</td>
<td></td>
<td>Not stable during fractionation</td>
<td>No flash at 200°F (93°C)</td>
</tr>
<tr>
<td>Example No.</td>
<td>Boiling point, °C</td>
<td>Melting point, °C</td>
<td>Pour point, °C</td>
<td>Dielectric Strength, 0.1” (2.5 mm), KV</td>
<td>GC purity</td>
<td>Hydrolytic Stability, 100°C for 24 hours</td>
<td>Fluoride release, ppm F g/hr</td>
<td>Thermal Stability at atmospheric pressure reflux</td>
</tr>
<tr>
<td>------------</td>
<td>-------------------</td>
<td>------------------</td>
<td>----------------</td>
<td>--------------------------------------</td>
<td>----------</td>
<td>------------------------------------------</td>
<td>-----------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>CE-1</td>
<td>160 @ 2mmHg (266 Pa)</td>
<td></td>
<td></td>
<td>Not stable during GC analysis</td>
<td>9.0%</td>
<td>decomposed by $^{19}$F-NMR</td>
<td></td>
<td>Not stable during fractionation</td>
</tr>
<tr>
<td>EX-9</td>
<td>109</td>
<td></td>
<td></td>
<td>88.0%</td>
<td>0.11%</td>
<td>decomposed over 16 hours</td>
<td></td>
<td>Stable during atmospheric pressure distillation</td>
</tr>
<tr>
<td>EX-10</td>
<td>123</td>
<td></td>
<td></td>
<td>90.6%</td>
<td>0.28%</td>
<td>decomposed over 16 hours</td>
<td></td>
<td>Stable during atmospheric pressure distillation</td>
</tr>
<tr>
<td>EX-11</td>
<td>131 - 60</td>
<td>29.8</td>
<td>95%</td>
<td></td>
<td></td>
<td>0.40</td>
<td></td>
<td>Turned very slightly yellow and did not darken over 3 days</td>
</tr>
<tr>
<td>EX-12</td>
<td>200</td>
<td></td>
<td></td>
<td>88.3%</td>
<td></td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EX-13</td>
<td>161</td>
<td></td>
<td></td>
<td>83.5%</td>
<td>0.0343%</td>
<td>decomposed</td>
<td></td>
<td>Not stable during fractionation</td>
</tr>
<tr>
<td>EX-14</td>
<td>172 -85</td>
<td>42.6</td>
<td>97.3%</td>
<td></td>
<td></td>
<td>0.08</td>
<td></td>
<td>Very slightly yellow - 2</td>
</tr>
<tr>
<td>Example No.</td>
<td>Boiling point, °C</td>
<td>Melting point, °C</td>
<td>Pour point, °C</td>
<td>Dielectric Strength, 0.1” (2.5 mm), KV</td>
<td>GC purity</td>
<td>Hydrolytic Stability, 100°C for 24 hours</td>
<td>Fluoride release, ppm F g/hr</td>
<td>Thermal Stability at atmospheric pressure reflux</td>
</tr>
<tr>
<td>------------</td>
<td>-------------------</td>
<td>-------------------</td>
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<td>-------------------------------------</td>
<td>-----------</td>
<td>-------------------------------------</td>
<td>-----------------------------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>EX-15</td>
<td>178</td>
<td>-22</td>
<td>41.3</td>
<td>97.9%</td>
<td>0.03%</td>
<td>0.03% decomposed</td>
<td></td>
<td>Not stable - very little color change but Bp dropped 10°C Bp over 2-days</td>
</tr>
<tr>
<td>EX-16</td>
<td>151</td>
<td>-87</td>
<td>44.7</td>
<td>88%</td>
<td>0.25%</td>
<td>0.25% decomposed</td>
<td></td>
<td>Stable over 4 days, clear and colorless</td>
</tr>
<tr>
<td>EX-17</td>
<td>172</td>
<td>-91</td>
<td>44.7</td>
<td>88.9%</td>
<td></td>
<td></td>
<td></td>
<td>Turned yellow in 2 days</td>
</tr>
<tr>
<td>EX-18</td>
<td>183.2</td>
<td>-96</td>
<td>44.7</td>
<td>92.2%</td>
<td></td>
<td></td>
<td></td>
<td>Not stable during fractionation</td>
</tr>
<tr>
<td>EX-19</td>
<td>70@ 2mmHg (266 Pa)</td>
<td>-53</td>
<td>17.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Not stable during fractionation</td>
</tr>
<tr>
<td>EX-20</td>
<td>186</td>
<td>-58</td>
<td>44 % (2 peaks)</td>
<td>Stable over 3 days, clear and colorless</td>
<td></td>
<td></td>
<td></td>
<td>Turned brown over 4 days</td>
</tr>
<tr>
<td>EX-21</td>
<td>196</td>
<td>-66</td>
<td>65% (2 peaks)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Turned brown over 4 days</td>
</tr>
<tr>
<td>Example No.</td>
<td>Boiling point, °C</td>
<td>Melting point, °C</td>
<td>Pour point, °C</td>
<td>Dielectric Strength, 0.1” (2.5 mm), KV</td>
<td>GC purity</td>
<td>Hydrolytic Stability, 100°C for 24 hours</td>
<td>Thermal Stability at atmospheric pressure reflux</td>
<td>Closed cup flammability</td>
</tr>
<tr>
<td>------------</td>
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<td>------------------</td>
<td>----------------</td>
<td>-------------------------------------</td>
<td>-----------</td>
<td>-----------------------------------------</td>
<td>-------------------------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>EX-22</td>
<td>59 @ 2mmHg (266 Pa)</td>
<td>-72</td>
<td>41.5</td>
<td>% decomposed, by $^{19}$F-NMR</td>
<td></td>
<td>Fluoride release, ppm F/g/hr</td>
<td>Turned brown over 3 days</td>
<td></td>
</tr>
<tr>
<td>EX-23</td>
<td>55 @ 2mmHg (266 Pa)</td>
<td></td>
<td>44.4</td>
<td></td>
<td></td>
<td></td>
<td>Not stable during fractionation</td>
<td></td>
</tr>
<tr>
<td>EX-24</td>
<td>58 @ 2mmHg (266 Pa)</td>
<td>-65</td>
<td>38.0</td>
<td></td>
<td></td>
<td></td>
<td>Turned black 1 day</td>
<td></td>
</tr>
<tr>
<td>EX-25</td>
<td>199</td>
<td>-58</td>
<td>45.9</td>
<td>8°C boiling range (many peaks)</td>
<td>0.0215% decomposed</td>
<td>Stable over 3 days, clear and colorless</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EX-26</td>
<td>228.5</td>
<td></td>
<td>43.6</td>
<td>5°C boiling range (many peaks)</td>
<td>0.14</td>
<td></td>
<td>Not stable, turned black after 4 days</td>
<td></td>
</tr>
</tbody>
</table>
Kinematic viscosity was determined for select samples, according to the method described in the Test Methods section above, with results as summarized in Table 2.

**TABLE 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kinematic Viscosity, in centistokes, at indicated temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>EX-1</td>
<td>4.48</td>
</tr>
<tr>
<td>EX-2</td>
<td>4.38</td>
</tr>
<tr>
<td>EX-4</td>
<td>4.65</td>
</tr>
<tr>
<td>EX-5</td>
<td>3.86</td>
</tr>
<tr>
<td>EX-6</td>
<td>59.3</td>
</tr>
<tr>
<td>EX-11</td>
<td>0.91</td>
</tr>
<tr>
<td>EX-14</td>
<td>2.00</td>
</tr>
<tr>
<td>EX-15</td>
<td>2.2</td>
</tr>
<tr>
<td>EX-16</td>
<td>2.05</td>
</tr>
<tr>
<td>EX-17</td>
<td>2.00</td>
</tr>
<tr>
<td>EX-18</td>
<td>2.6</td>
</tr>
<tr>
<td>EX-19</td>
<td>4.2</td>
</tr>
<tr>
<td>EX-20</td>
<td>3.8</td>
</tr>
<tr>
<td>EX-21</td>
<td>3.1</td>
</tr>
<tr>
<td>EX-22</td>
<td>3.5</td>
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<td>EX-23</td>
<td>3.0</td>
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<tr>
<td>EX-24</td>
<td>3.4</td>
</tr>
<tr>
<td>EX-25</td>
<td>5.24</td>
</tr>
<tr>
<td>EX-26</td>
<td>4.69</td>
</tr>
</tbody>
</table>
What is claimed is:

1. A fluorinated ester of the formula:

\[
\begin{array}{c}
\text{R}_1^1 \text{O} \\
\text{F} \\
\text{R}_f^2 \\
\text{R}_1^1 \\
x \\
\end{array}
\]

wherein,

- each of \( \text{R}_1^1 \) and \( \text{R}_f^2 \) are independently a perfluorinated group;
- wherein the number of total perfluorinated carbon atoms is \( \geq 4 \) when \( x = 1 \), and the number of total perfluorinated carbon atoms is \( \geq 3 \) when \( x \) is 2-4,
- \( \text{R}_1^1 \) is a (hetero)hydrocarbyl group of valence \( x \); and
- \( x \) is 1 to 4.

2. The fluorinated ester of claim 1, where \( x = 1 \).

3. The fluorinated ester of claim 2, where \( x = 1 \) and \( \text{R}_1 \) is a C1-C8 alkyl.

4. The fluorinated ester of claim 1, where \( x = 2-4 \) and \( \text{R}_1 \) is a C2-C8 alkyl.

5. The fluorinated ester of claim 1 wherein \( \text{R}_1^1 \) and \( \text{R}_f^2 \) are taken together to form a perfluorinated ring.

6. The fluorinated ester of claim 1 wherein \( \text{R}_1^1 \) and \( \text{R}_f^2 \) are taken together to form a cyclobutyl, cyclopentyl, cyclohexyl or tetrahydrofuran rings.

7. The fluorinated ester of claim 1, wherein each of \( \text{R}_1^1 \) and \( \text{R}_f^2 \) are perfluoroalkyl groups having from 1 to about 12 perfluorinated carbon atoms.

8. The fluorinated ester of claim 1 of the formula:
wherein each of R\textsubscript{f3}, R\textsubscript{f4} and R\textsubscript{f5} are independently a perfluorinated group, y is 1-4; and R\textsubscript{1} is a (hetero)hydrocarbyl group of valence y.

9. The fluorinated ester of claim 8 where y is 1 and R\textsubscript{1} is Ci-Cs alkyl.

10. The fluorinated ester of claim 8, where y is 2-4 and R\textsubscript{1} is a C\textsubscript{2}-C\textsubscript{8} alkylene.

11. The fluorinated ester of claim 8 wherein R\textsubscript{f3} and R\textsubscript{f5} are taken together to form a perfluorinated piperazine, piperidine, morpholine or pyrrolidine ring.

12. The fluorinated ester of claim 8 wherein at least one of R\textsubscript{f3} and R\textsubscript{f5} are cyclobutyl, cyclopentyl, cyclohexyl or tetrahydrofuran rings.

13. The fluorinated ester of any of the previous claims wherein x is 2-4 and R\textsubscript{1} is an C\textsubscript{2}-C\textsubscript{8} alkylene.

14. The fluorinated ester of claim 1 of the formula:

\[
\begin{array}{c}
\text{R}_1^4 \\
\text{R}_1^3 \\
\text{R}_1^5
\end{array}
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{O}
\end{array}
\begin{array}{c}
\text{F}_2 \\
\text{C}_\text{I} \\
\text{O}
\end{array}
\begin{array}{c}
\text{O} \\
\text{R}_1^1
\end{array}
\text{y}
\]

wherein each of R\textsubscript{f3}, R\textsubscript{f4} and R\textsubscript{f5} are independently a perfluorinated group, y is 1-4; and R\textsubscript{1} is a (hetero)hydrocarbyl group of valence y.

15. The fluorinated ester of claim 14 where y is 1 and R\textsubscript{1} is Ci-Cs alkyl.
16. The fluorinated ester of claim 14, where y is 2-4 and R^1 is a C_2-C_8 alkyl.

17. The fluorinated ester of claim 14 wherein Rf4 and Rf5 are taken together to form a perfluorinated piperazine, piperidine, morpholine or pyrrolidine ring.

18. The fluorinated ester of claim 14 wherein at least one of Rf4 and Rf5 are cyclobutyl, cyclopentyl, cyclohexyl or tetrahydrofuran rings.

19. The fluorinated ester of claim 1 wherein at least one of Rf1 and Rf2 is a perfluoroether group.

20. The fluorinated ester of claim 19 wherein at least one of Rf1 and Rf2 is a perfluoropolyether group.

21. The fluorinated ester of any of the previous claims wherein

\( \frac{(# \text{C-F bonds} + # \text{S-F bonds})}{(\# \text{C-F bonds} + \# \text{C-H bonds} + \# \text{C-C bonds} + \# \text{C-N bonds} + \# \text{C-S bonds})} \times 100 \) is >40.

22. The fluorinated ester of any of the previous claims having a boiling point of ≥ 100°C.

23. The fluorinated ester of any of the previous claims having a dielectric strength of ≥ 30 kV at 0.1 inches.

24. The fluorinated ester of any of the previous claims being fluid at ≤ 50°C.

25. The fluorinated ester of any of the previous claims being non-flammable when tested according to ASTM D 7236-06.

26. An electrical device containing as a component a dielectric liquid comprising the fluorinated ester of any of the previous claims.
27. The electrical device according to claim 26, wherein the electrical device is an electrical capacitor comprising metal electrodes spaced from each other, and such that the dielectric fluid fills the space between the electrodes.

28. The electrical device according to claim 27 further comprising a capacitor comprising dielectric solid sheets impregnated with the dielectric liquid.

29. An apparatus for heat transfer comprising: a device; and a mechanism for transferring heat to or from the device, the mechanism comprising a heat transfer fluid, wherein the device is selected from a microprocessor, a semiconductor wafer used to manufacture a semiconductor device, a power control semiconductor, an electrochemical cell, electrical distribution switch gear, a power transformer, a circuit board, a multi-chip module, a packaged or unpackaged semiconductor device, a fuel cell, and a laser, and wherein the heat transfer fluid comprises a fluorinated ester of any of claims 1 to 25.

30. The apparatus according to claim 29 wherein the heat transfer fluid has a specific heat capacity of greater than 1.200 J/gK at 20°C.

31. The apparatus according to claim 29 wherein the heat transfer fluid has a specific heat capacity of greater than 1.250 J/gK at 20°C.

32. The apparatus according to claim 29, wherein the mechanism transfers heat to the device.

33. The apparatus according to claim 29, wherein the mechanism transfers heat from the device.

34. The apparatus according to claim 29, wherein the mechanism maintains the device at a selected temperature.
35. The apparatus according to claim 29, wherein the mechanism for transferring heat is a component in a system for cooling the device, wherein the system is selected from a system for cooling wafer chucks in PECVD tools, a system for controlling temperature in test heads for die performance testing, a system for controlling temperatures within semiconductor process equipment, a thermal shock testing of an electronic device, and a system for maintaining a constant temperature of an electronic device.

36. A method for transferring heat comprising: providing a device; and providing a mechanism for transferring heat to or from the device, the mechanism comprising a heat transfer fluid, wherein the device is selected from a microprocessor, a semiconductor wafer used to manufacture a semiconductor device, a power control semiconductor, an electrochemical cell, electrical distribution switch gear, a power transformer, a circuit board, a multi-chip module, a packaged or unpackaged semiconductor device, a fuel cell, and a laser, and wherein the heat transfer fluid comprises a fluorinated ester of any of claims 1 to 25.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

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**ADD.**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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**See patent family annex.**

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:
  * A*: document defining the general state of the art which is not considered to be of particular relevance
  * E*: earlier application or patent but published on or after the international filing date
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*"T"* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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*"A"* document member of the same patent family

**Date of the actual completion of the international search**

11 January 2016

**Date of mailing of the international search report**

25/01/2016

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
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Fax.: (+31-70) 340-3016

**Authorized officer**

Dunet, Guillaume

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<td>DAVID C. ENGLAND ET AL: &quot;Fluoroketenes 1-3, 5-7, VII. Synthesis and reactivity of trifluoromethyl trifluoroketene, perfluoroacryloyl fluoride, perfluoromethacryloyl fluoride, methyl perfluoromethacrylate and methyl perfluoromethacrylate &quot;.</td>
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<td>JOURNAL OF FLUORINE CHEMISTRY, vol. 3, no. 1, July 1973 (1973-07), pages 63-89, XP55234379, NL ISSN: 0022-1139, DOI: 10.1016/50022-1139(00)82862-6 page 67; compound XVII * penultimate paragraph *; page 80</td>
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<td>EP 1 300 386 Al (ASAHI GLASS CO LTD [JP]) 9 April 2003 (2003-04-09) page 5; compounds 3-15, 4-15 paragraphs [0068], [0092] paragraph [0114] examples 2-2, 3-3 claims 1-9</td>
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## INTERNATIONAL SEARCH REPORT

Information on patent family members

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