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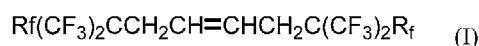
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(54) Title: HYDROFLUOROOLEFIN CONTAINING COMPOSITIONS AND METHODS FOR USING SAME



(57) Abstract: A composition includes a hydrofluoroolefin having Structural Formula (I): (I) R_f is a perfluoroalkyl group having 2 - 6 carbon atoms. The composition further includes a free radical scavenger.

HYDROFLUOROOLEFIN CONTAINING COMPOSITIONS AND METHODS FOR USING SAME

FIELD

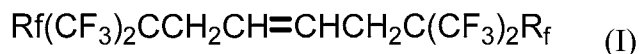
This disclosure relates to compositions, apparatuses, and methods that include hydrofluoroolefins.

BACKGROUND

Various hydrofluoroolefins are described in, for example, Paul L. Coe, et. al., J. Chem. Soc. Perkin Trans. 1, Organic and Bioorganic Chemistry, 1974, 1732-1736; A. E. Tipping, et. al., J. Chem. Soc. [Section] C: Organic (1971), (22), 3289; M. G. Barlow, Chem. Commun, (1966), (19), 703; A. E. Tipping et. al., J. Chem. Soc. Perkin Trans. 1: Organic and Bio-Organic Chemistry (1972), (15), 1877; and A. E. Tipping, et. al., J. Chem. Soc. [Section] C: Organic (1968), (4), 398.

SUMMARY

In some embodiments, a composition is provided. The composition comprises a hydrofluoroolefin having Structural Formula (I):



R_f is a perfluoroalkyl group having 2 - 6 carbon atoms. The composition further includes a free radical scavenger.

In some embodiments, an apparatus for heat transfer is provided. The apparatus includes a device and a mechanism for transferring heat to or from the device. The mechanism includes a heat transfer fluid that comprises the above-described composition.

The above summary of the present disclosure is not intended to describe each embodiment of the present disclosure. The details of one or more embodiments of the disclosure are also set forth in the description below. Other features, objects, and advantages of the disclosure will be apparent from the description and from the claims.

DETAILED DESCRIPTION

Certain hydrofluoroolefins (HFOs), such as those described in International Publication WO 2016/094113 have been demonstrated to have desirable physical, thermal, and electrical properties that render them particularly useful as working fluids in high temperature applications (e.g., heat transfer and vapor phase soldering). In addition, these HFOs have very good environmental and toxicological properties such as low global warming potential and low toxicity. However, it has been discovered that when these HFOs are used in high temperature environments (e.g., >150 degrees Celsius), dissolved oxygen reacts with the HFOs to form epoxides and other undesirable oxidation by-products. Regarding such epoxidation, generally, epoxidation by oxygen proceeds by nucleophilic mechanism where oxygen first performs a nucleophilic conjugate addition to alkene to give a stabilized carbon ion. This carbon ion then attacks the same oxygen atom to close epoxide ring and form epoxidation products. However, surprisingly, it has also been discovered that the epoxidation is occurring via a free radical mechanism. It has been further discovered that certain additives can significantly inhibit the reaction of oxygen with the HFOs and prevent formation of epoxides and other oxidation by-products.

Generally, the present disclosure is directed to the incorporation of additives into certain hydrofluoroolefin containing working fluids to improve the stability and useful working life time of such fluids. The additives may function to inhibit reactions of the hydrofluoroolefins with oxygen and prevent formation of epoxides and other oxidation by-products when the working fluids are used in high temperature environments.

In this disclosure:

“device” refers to an object or contrivance which is heated, cooled, or maintained at a predetermined temperature or temperature range;

“free radical scavenger” refers to a molecule or compound that functions to remove or de-activate free radical impurities such as those generated by oxidants;

“inert” refers to chemical compositions that are generally not chemically reactive under normal conditions of use;

“mechanism” refers to a system of parts or a mechanical appliance; and

“perfluoro—” (for example, in reference to a group or moiety, such as in the case of

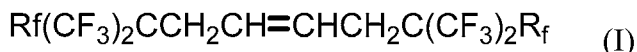
“perfluoroalkylene” or “perfluoroalkylcarbonyl” or “perfluorinated”) means completely fluorinated such that, except as may be otherwise indicated, there are no carbon-bonded hydrogen atoms replaceable with fluorine.

As used herein, the singular forms “a”, “an”, and “the” include plural referents unless the content clearly dictates otherwise. As used in this specification and the appended embodiments, the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

As used herein, the recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.8, 4, and 5).

Unless otherwise indicated, all numbers expressing quantities or ingredients, measurement of properties and so forth used in the specification and embodiments are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached listing of embodiments can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings of the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claimed embodiments, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

In some embodiments, the present disclosure is directed to a working fluid that includes a hydrofluoroolefin and a free radical scavenger. The hydrofluoroolefin may be represented by Structural Formula (I):



where each Rf is, independently, a perfluoroalkyl group having 1-6, 2-6, 3-5, 3-4, or 3 carbon atoms. In some embodiments, each Rf is the same perfluoroalkyl group. In some embodiments, the hydrofluoroolefin may be a liquid at 25, 22, or 20 degrees Celsius. In some embodiments, the hydrofluoroolefin may be represented by Structural Formula (II):



For purposes of the present disclosure, it is to be appreciated that the hydrofluoroolefin compounds may include the *E* isomer, the *Z* isomer, or any mixture of the *E* and *Z* isomers, irrespective of what is depicted in any of the general formulas or chemical structures.

The working fluids of the present disclosure may further include one or more free radical scavengers. The free radical scavengers may be present in the working fluids in an amount of between 1 and 10,000 ppm, 1 and 1000 ppm, or 10 and 100 ppm, based on the total weight of the hydrofluoroolefin and the free radical scavengers in the working in the fluid. In some embodiments, the free radical scavengers may include (individually or in any combination), hydroquinone, hydroquinone monomethyl ether, methylhydroquinone, p-benzoquinone, phenothiazine, TEMPO, 4-hydroxyl-TEMPO, 4-amino-TEMPO, or 4-oxo-TEMPO. Alternatively, any conventional free radical scavenger or combination of conventional free radical scavengers may be employed.

In some embodiments, the working fluids may include the above-described hydrofluoroolefins as a major component. For example, the working fluids may include at least 25%, at least 50%, at least 70%, at least 80%, at least 90%, at least 95%, or at least 99% by weight of the above-described hydrofluoroolefins based on the total weight of the working fluid. In addition to the above-described hydrofluoroolefins and the free radical scavengers, the working fluids may include a total of up to 75%, up to 50%, up to 30%, up to 20%, up to 10%, up to 5%, or up to 1% by weight of one or more of the following components (individually or in any combination): alcohols, ethers, alkanes, alkenes, perfluorocarbons, perfluorinated tertiary amines, perfluoroethers, cycloalkanes, esters, ketones, oxiranes, aromatics, siloxanes, hydrochlorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons, hydrofluoroolefins, hydrochlorofluoroolefins, hydrofluoroethers, perfluoroketones, or mixtures thereof, based on the total weight of the working fluid. Such additional components can be chosen to modify or enhance the properties of a composition for a particular use. Minor amounts of optional components can also be added to the working fluids to impart particular desired properties for particular uses. Useful components can include conventional additives such as, for example, surfactants, coloring agents, stabilizers, anti-oxidants, flame retardants, and the like, and mixtures thereof.

In some embodiments, the working fluids of the present disclosure may exhibit properties that render them particularly useful as heat transfer fluids. For example, the working fluids may be chemically inert (i.e., they do not easily react with base, acid, water, etc.), and may have high boiling points (up to 300°C), low freezing points (they may be liquid at -40°C or lower), low viscosity, high thermal stability over extended

periods, good thermal conductivity, adequate solvency in a range of potentially useful solvents, and low toxicity.

Hydrocarbon alkenes are known to react with hydroxyl radicals and ozone in the lower atmosphere at rates sufficient to lead to short atmospheric lifetimes (see Atkinson, R.; Arey, J., Chem Rev. 2003, 103 4605-4638). For example, ethene has an atmospheric lifetime by reaction with hydroxyl radicals and ozone of 1.4 days and 10 days, respectively. Propene has an atmospheric lifetime by reaction with hydroxyl radicals and ozone of 5.3 hours and 1.6 days, respectively. Both the *E* and *Z* isomers of the hydrofluoroolefins of the present disclosure were found to react at a very high rate with ozone in the gas phase. As a result, it is believed that these compounds have relatively short atmospheric lifetimes.

Furthermore, in some embodiments, the working fluids of the present disclosure may have a low environmental impact. In this regard, the working fluids may have a global warming potential (GWP) of less 300, 200, 100 or even less than 10. As used herein, 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).

$$GWP_i(t') = \frac{\int_0^{ITH} a_i[C(t)]dt}{\int_0^{ITH} a_{CO_2}[C_{CO_2}(t)]dt} = \frac{\int_0^{ITH} a_i C_{oi} e^{-t/\tau} dt}{\int_0^{ITH} a_{CO_2}[C_{CO_2}(t)]dt}$$

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, τ 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).

In some embodiments, the above-described hydrofluoroolefins may be prepared by using halogenated butenes such as, for example, 1,4-dibromo-2-butene, 1-chloro-4-bromo-2-butene, 1,4-dichloro-2-butene, 1,4-diiodo-2-butene, or the mixture of these butenes as an alkylating agent. Addition of fluoride ion, F⁻, to a perfluoroolefin can form a fluorocarbanion which can be alkylated to form the desired product. In some embodiments, the fluoride ion sources may be metal salts of fluoride such as LiF, NaF, KF, CsF, AgF, , individually, or as a mixture thereof. Other halogen salt such as KBr, CsBr, AgBr, CuBr, KI, CsI, AgI, CuI can be used to assist the alkylation reaction by halogen exchange with the 1,4-dihalo-2-butene. The perfluoroolefin can be one or a mixture of (*Z*)-1,1,1,2,3,4,5,5,5-nonafluoro-4-(trifluoromethyl)pent-2-ene, (*E*)-1,1,1,2,3,4,5,5,5-nonafluoro-4-(trifluoromethyl)pent-2-ene or 1,1,1,3,4,4,5,5,5-nonafluoro-2-(trifluoromethyl)pent-2-ene. The amount of fluoride ion may be at least a stoichiometric amount, i.e., one mole of perfluoroolefin requires one mole or more of fluoride ion. A polar organic solvent may be used to dissolve sufficient amount of fluorocarbanion and alkylating agent in order for the reaction to occur. Many polar solvents such as acetonitrile, benzonitrile, N,N-dimethylformamide (DMF), bis(2-methoxyethyl) ether (diglyme), tetraethylene glycol dimethyl ether (tetraglyme), tetrahydrothiophene-1,1-dioxide (sulfolane), N-methyl-2-pyrrolidinone (NMP), dimethyl sulfone, dimethylsulfoxide (DMSO) can be used individually or as a mixture. In some embodiments, one or more catalysts may be employed. Suitable catalysts may include quaternary ammonium salt, phosphonium salt, and crown ethers, such as 18-crown-6, dibenzo-18-crown-6, diaza-18-crown-6, 12-crown-4, 15-crown-5, or combinations thereof.

The working fluids of the present disclosure can be used in various applications. For example, the working fluids which may include the above-described hydrofluoroolefins and one or more free radical inhibitors are believed to possess the required stability as well as the necessary short atmospheric lifetime (or low global

warming potential) to make them commercially viable environmentally-friendly candidates for high temperature heat transfer applications.

In some embodiments, the present disclosure is further directed to an apparatus for heat transfer that includes a device and a mechanism for transferring heat to or from the device. The mechanism for transferring heat may include a heat transfer fluid that includes the working fluids of the present disclosure.

The provided apparatus for heat transfer may include a device. The device may be a component, work-piece, assembly, etc. to be cooled, heated or maintained at a predetermined temperature or temperature range. Such devices include electrical components, mechanical components and optical components. Examples of devices of the present disclosure include, but are not limited to microprocessors, wafers used to manufacture semiconductor devices, power control semiconductors, electrical distribution switch gear, power transformers, circuit boards, multi-chip modules, packaged and unpackaged semiconductor devices, lasers, chemical reactors, fuel cells, and electrochemical cells. In some embodiments, the device can include a chiller, a heater, or a combination thereof.

In yet other embodiments, the devices can include electronic devices, such as processors, including microprocessors. As these electronic devices become more powerful, the amount of heat generated per unit time increases. Therefore, the mechanism of heat transfer plays an important role in processor performance. The heat-transfer fluid typically has good heat transfer performance, good electrical compatibility (even if used in “indirect contact” applications such as those employing cold plates), as well as low toxicity, low (or non-) flammability and low environmental impact. Good electrical compatibility suggests that the heat-transfer fluid candidate exhibit high dielectric strength, high volume resistivity, and poor solvency for polar materials. Additionally, the heat-transfer fluid should exhibit good mechanical compatibility, that is, it should not affect typical materials of construction in an adverse manner.

The provided apparatus may include a mechanism for transferring heat. The mechanism may include a heat transfer fluid. The heat transfer fluid may include the working fluids of the present disclosure. Heat may be transferred by placing the heat transfer mechanism in thermal contact with the device. The heat transfer mechanism,

when placed in thermal contact with the device, removes heat from the device or provides heat to the device, or maintains the device at a selected temperature or temperature range.

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 may include facilities for managing the heat-transfer fluid, including, but not limited to 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, temperature controlled wafer chucks in plasma enhanced chemical vapor deposition (PECVD) tools, temperature-controlled test heads for die performance testing, temperature-controlled work zones within semiconductor process equipment, thermal shock test bath liquid reservoirs, and constant temperature baths. In some systems, such as etchers, ashers, PECVD chambers, vapor phase soldering devices, and thermal shock testers, the upper desired operating temperature may be as high as 170°C, as high as 200°C, or even as high as 240°C.

Heat can be transferred by placing the heat transfer mechanism in thermal contact with the device. The heat transfer mechanism, when placed in thermal contact with the device, may remove heat from the device or provide heat to the device, or maintain the device at a selected temperature or temperature range. 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 provided apparatus can also include refrigeration systems, cooling systems, testing equipment and machining equipment. In some embodiments, the provided apparatus can be a constant temperature bath or a thermal shock test bath. In some systems, such as etchers, ashers, PECVD chambers, vapor phase soldering devices, and thermal shock testers, the upper desired operating temperature may be as high as 170°C, as high as 200°C, or even higher.

In some embodiments, the working fluids of the present disclosure may be used as a heat transfer agent for use in vapor phase soldering. In using the working fluids of the present disclosure in vapor phase soldering, the process described in, for example, U.S. Pat. No. 5,104,034 (Hansen) can be used, which description is hereby incorporated by reference in its entirety. Briefly, such process includes immersing a component to be

soldered in a body of vapor comprising the working fluids of the present disclosure to melt the solder. In carrying out such a process, a liquid pool of the working fluid is heated to boiling in a tank to form a saturated vapor in the space between the boiling liquid and a condensing means.

A workpiece to be soldered is immersed in the vapor (at a temperature of greater than 170°C, greater than 200°C, greater than 230°C, or even greater), whereby the vapor is condensed on the surface of the workpiece so as to melt and reflow the solder. Finally, the soldered workpiece is then removed from the space containing the vapor.

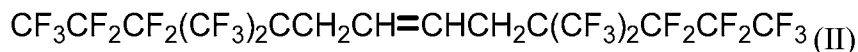
Listing of Embodiments

1. A composition comprising:
a hydrofluoroolefin having Structural Formula (I):

$$\text{Rf}(\text{CF}_3)_2\text{CCH}_2\text{CH}=\text{CHCH}_2\text{C}(\text{CF}_3)_2\text{Rf} \quad (\text{I})$$

wherein R_f is a perfluoroalkyl group having 2 - 6 carbon atoms; and
a free radical scavenger.
2. The composition according to embodiment 1, wherein the hydrofluoroolefin is present in the composition in an amount of at least 50% by weight, based on the total weight of the composition.
3. The composition according to any one of the previous embodiments, wherein the free radical scavenger is present in the composition in an amount of between 1 and 10,000 ppm, based on the total weight of the composition.
4. The composition according to any one of the previous embodiments, wherein the free radical scavenger comprises hydroquinone, hydroquinone monomethyl ether, methylhydroquinone, p-benzoquinone, phenothiazine, TEMPO, 4-hydroxyl-TEMPO, 4-amino-TEMPO, or 4-oxo-TEMPO.
5. The composition according to any one of the previous embodiments, wherein the hydrofluoroolefin is a liquid at 25 degrees Celsius.

6. The composition according to any one of the previous embodiments, wherein the hydrofluoroolefin has Structural Formula (II):



7. The composition according to any one of the previous embodiments, wherein the hydrofluoroolefin comprises the *E* isomer.

8. A composition according to any one of the previous embodiments, wherein the hydrofluoroolefin comprises the *Z* isomer.

9. 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 that comprises the composition according to any one of the previous embodiments.

10. An apparatus for heat transfer according to embodiment 9, wherein the device is selected from a microprocessor, a semiconductor wafer used to manufacture a semiconductor device, a power control semiconductor, an electrochemical cell, an 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.

11. An apparatus according to any one of embodiments 9-10, wherein the mechanism for transferring heat is a component in a system for maintaining a temperature or temperature range of an electronic device.

12. An apparatus according to any one of embodiments 9-10, wherein the device comprises an electronic component to be soldered.

13. An apparatus according to any one of embodiments 6 and 9, wherein the mechanism comprises vapor phase soldering.

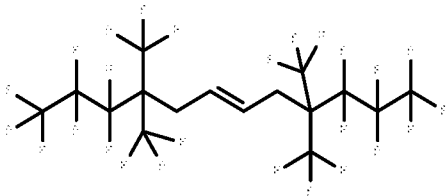
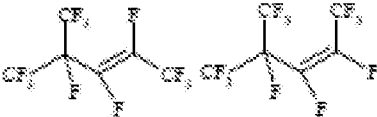
14. A method of transferring heat comprising:
providing a device; and
transferring heat to or from the device using the composition according to any one of embodiments 1-8.

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

Objects and advantages of this disclosure are further illustrated by the following comparative and illustrative examples.

Materials Used

Chemical	Description	Source
(E)-1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-4,4,9,9-tetrakis(trifluoromethyl) dodec-6-ene		Synthesis procedures provided below
N,N-dimethylformamide	$(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$	EMD Chemicals, Inc. Gribbstown, NJ, USA
Methyltrialkyl(C8-C10) ammonium chloride	$\text{CH}_3(\text{C}_8\text{H}_{17})_3\text{N}^+\text{Cl}^-$	Sigma Aldrich, Milwaukee, WI, USA
Potassium fluoride	KF	Sigma Aldrich, Milwaukee, WI, USA
1,1,1,2,3,4,5,5,5-nonafluoro-4-trifluoromethyl-pent-2-ene	HFP Dimer, 2 Isomers: 	Foam Additive FA-188, 3M Company, St. Paul, MN, USA
trans-1,4-dibromo-2-butene	Trans $\text{BrCH}_2\text{CH}=\text{CHCH}_2\text{Br}$	AK Scientific Inc, Union City, CA, USA
MEHQ	Hydroquinone monomethyl ether	VWR International, Radnor, PA, USA
PTZ	Phenothiazine	VWR International, Radnor, PA, USA

(E)-1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-4,4,9,9-tetrakis(trifluoromethyl)dodec-6-ene was synthesized as follows. A 600 ml stainless steel reactor was fitted with a mixer and charged with 185g N,N-dimethylformamide, 34g methyltrialkyl(C8-C10) ammonium chloride, 43g potassium fluoride, 185g 1,1,1,2,3,4,5,5,5-nonafluoro-4-trifluoromethyl-pent-2-ene, and 60g trans-1,4-dibromo-2-butene. The reactor was heated to 40°C, with stirring (500 rpm), and allowed to react at this temperature for 72 hours. At the end of reaction, the reactor contents were vacuum distilled at 20 torr and 150°C. The distillate was condensed by dry ice and collected in a flask. 180g FC phase in the distillate was collected. The FC phase was then washed by

180g water and allowed to phase split. 161g bottom phase was collected. Analysis of the bottom phase by Gas Chromatography indicated 89% purity of trans-
 $\text{CF}_3\text{CF}_2\text{CF}_2\text{C}(\text{CF}_3)_2\text{-CH}_2\text{CH=CHCH}_2\text{-C}(\text{CF}_3)_2\text{CF}_2\text{CF}_2\text{CF}_3$. This material was then further purified by vacuum fractionation to yield a 99% pure fluid.

Example 1: (E)-1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-4,4,9,9-tetrakis(trifluoromethyl)dodec-6-ene and MEHQ

To a 600 mL Parr reaction vessel (stainless steel) was added (E)-1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-4,4,9,9-tetrakis(trifluoromethyl)dodec-6-ene (108.5 g, 156.7 mmol) and MEHQ (5.4 g, 43 mmol). The reactor was then sealed and pressurized by air to 50 psi. The internal mixture was heated to 248 °C with stirring at which point the internal pressure reached 71 psi. The resultant mixture was allowed to stir for 16 h before cooling to room temperature at which point the pressure dropped back to 51 psi. GC-FID analysis of the resultant mixture revealed less than 0.1% conversion of the hydrofluoroolefin to oxidation product (i.e., hydrofluoroepoxide).

Comparative Example 1: (E)-1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-4,4,9,9-tetrakis(trifluoromethyl)dodec-6-ene without MEHQ

To a 600 mL Parr reaction vessel (stainless steel) was added (E)-1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-4,4,9,9-tetrakis(trifluoromethyl)dodec-6-ene (100.5 g, 145.2 mmol). The reactor was then sealed and pressurized by air to 50 psi. The internal mixture was heated to 248 °C with stirring at which point the internal pressure reached 71 psi. After a 16 hour stir at the same temperature, the internal pressure had reached 74 psi. The mixture was allowed to cool to room temperature at which point the pressure dropped back to 40 psi. GC-FID analysis of the resultant mixture revealed approximately 6.8% conversion of the hydrofluoroolefin starting material to the oxidized product (i.e., hydrofluoroepoxide).

Example 2: (E)-1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-4,4,9,9-tetrakis(trifluoromethyl)dodec-6-ene with PTZ

To a 250 mL 3-neck glass flask was added (E)-1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-4,4,9,9-tetrakis(trifluoromethyl)dodec-6-ene (210 g). The flask was fitted

with a water condenser and a thermometer. 2 grams of phenothiazine (PTZ) was placed in the 0.5 micron filter through which the HFO liquid was circulated for 48 hours before a sample was taken from the flask. NMR analysis of the sample indicated that the liquid in the flask contained about 100 ppm of PTZ. The flask was then heated to reflux (approximately at 230 °C) for 2 hours. At the end of the 2-hour reflux, the flask was cooled to ambient temperature to take a second sample. GC-MS analysis of the sample revealed that less than 10 ppm of the epoxide of the starting hydrofluoroolefin had been formed.

Comparative Example 2: (E)-1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-4,4,9,9-tetrakis(trifluoromethyl)dodec-6-ene without PTZ

To a 250 mL 3-neck glass flask was added (E)-1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-4,4,9,9-tetrakis(trifluoromethyl)dodec-6-ene (150 g). The flask was fitted with a water condenser and a thermometer before it was heated to reflux (approximately 230 C) for 2 hours. At the end of the 2-hour reflux, the flask was cooled to room temperature to take a sample. GC-MS analysis of the sample revealed that 440 ppm of the epoxide of the starting hydrofluoroolefin had been formed.

Example 3 and Comparative Example 3:

For CE3, 200 g of (E)-1,1,1,2,2,3,3,10,10,11,11,12,12,12-tetradecafluoro-4,4,9,9-tetrakis(trifluoromethyl)dodec-6-ene was added to a 250 mL 3-neck glass flask. The flask was fitted with a water condenser and a thermometer. The flask was then heated to reflux (at approximately 230 °C) for 2 hours. At the end of the 2-hour reflux, the flask was cooled to ambient temperature, a sample of the contents of the flask was taken for GC-MS analysis. After sampling another heating/cooling cycle was started. The cooling step was intended to allow more oxygen to enter the fluid in the flask. For Example 3, 100 ppm of PTZ was added to the fluid, and heating and cooling proceeded as described for CE3. Results of the GC-MS analysis are provided in Table 1. Analysis of the samples taken at the end of each cycle by GC-MS indicated that the amount of epoxide increased dramatically as a function of the number of cycles for CE3, whereas Example 3 exhibited much lower increases in the amount of epoxide present.

Table 1. Amount of Epoxide (ppm) after Heating/Cooling Cycling

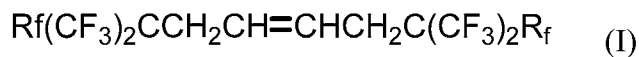
Cycle Number	CE3	Example 3
1	471.4	63
2	1278.3	59
3		65
4		67
5		71
6		74
7		80
8		79
9		87
10		90
11		91
12		92

Various modifications and alterations to this disclosure will become apparent to those skilled in the art without departing from the scope and spirit of this disclosure. It should be understood that this disclosure is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the disclosure intended to be limited only by the claims set forth herein as follows. All references cited in this disclosure are herein incorporated by reference in their entirety.

What is claimed is:

1. A composition comprising:

a hydrofluoroolefin having Structural Formula (I):



wherein R_f is a perfluoroalkyl group having 2 - 6 carbon atoms; and
a free radical scavenger.

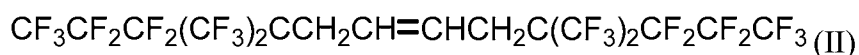
2. The composition according to claim 1, wherein the hydrofluoroolefin is present in the composition in an amount of at least 50% by weight, based on the total weight of the composition.

3. The composition according to claim 2, wherein the free radical scavenger is present in the composition in an amount of between 1 and 10,000 ppm, based on the total weight of the composition.

4. The composition according to claim 2, wherein the free radical scavenger comprises hydroquinone, hydroquinone monomethyl ether, methylhydroquinone, p-benzoquinone, phenothiazine, TEMPO, 4-hydroxyl-TEMPO, 4-amino-TEMPO, or 4-oxo-TEMPO.

5. The composition according to claim 2, wherein the hydrofluoroolefin is a liquid at 25 degrees Celsius.

6. The composition according to claim 2, wherein the hydrofluoroolefin has Structural Formula (II):



7. The composition according to claim 2, wherein the hydrofluoroolefin comprises the *E* isomer.

8. The composition according to claim 2, wherein the hydrofluoroolefin comprises the Z isomer.
9. 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 that comprises the composition according to claim 2.
10. An apparatus for heat transfer according to claim 9, wherein the device is selected from a microprocessor, a semiconductor wafer used to manufacture a semiconductor device, a power control semiconductor, an electrochemical cell, an 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.
11. An apparatus according to claim 9, wherein the mechanism for transferring heat is a component in a system for maintaining a temperature or temperature range of an electronic device.
12. An apparatus according to claim 9, wherein the device comprises an electronic component to be soldered.
13. An apparatus according to claim 9, wherein the mechanism comprises vapor phase soldering.
14. A method of transferring heat comprising:
providing a device; and
transferring heat to or from the device using the composition according to claim 2.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2018/051674

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C09K 5/10; B23K 1/015; C07C 21/18; H01L 23/373 (2018.01)

CPC - C07C 21/18; B23K 1/015; C09K 5/10; H01L 23/373 (2018.05)

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)

See Search History document

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/094113 A1 (3M INNOVATIVE PROPERTIES COMPANY) 16 June 2016 (16.06.2016) entire document	1-5, 7, 9-14
A	US 2015/0135745 A1 (E I DU PONT DE NEMOURS AND COMPANY) 21 May 2015 (21.05.2015) entire document	1-5, 7, 9-14
A	US 4,173,654 A (SCHERER) 06 November 1979 (06.11.1979) entire document	1-5, 7, 9-14
A	US 2011/0215273 A1 (UENVEREN et al) 08 September 2011 (08.09.2011) entire document	1-5, 7, 9-14

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* 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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

20 July 2018

Date of mailing of the international search report

03 AUG 2018

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, VA 22313-1450

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PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2018/051674

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Extra Sheet

Claims 1-5, 7, and 9-14 have been analyzed subject to the restriction that the claims read on the Formula (I) as described in the Lack of Unity of Invention (See Extra Sheet). The claims are restricted to a composition comprising: a hydrofluoroolefin having Structural Formula (I); wherein RF is a perfluoroalkyl group having 2 carbon atoms, wherein the hydrofluoroolefin is the E isomer; and a free radical scavenger, wherein the free radical scavenger comprises hydroquinone; apparatuses for heat transfer thereof; and methods of transferring heat thereof.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-5, 7, 9-14

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Continued from Box No. III Observations where unity of invention is lacking

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I+: claims 1-14 are drawn to compositions, apparatuses for heat transfer thereof, and methods of transferring heat thereof.

The first invention of Group I+ is restricted to a composition comprising: a hydrofluoroolefin having Structural Formula (I); wherein RF is a perfluoroalkyl group having 2 carbon atoms, wherein the hydrofluoroolefin is the E isomer; and a free radical scavenger, wherein the free radical scavenger comprises hydroquinone; apparatuses for heat transfer thereof; and methods of transferring heat thereof. It is believed that claims 1-5, 7, and 9-14 read on this first named invention and thus these claims will be searched without fee to the extent that they read on the above embodiment.

Applicant is invited to elect additional formula(e) for each additional compound to be searched in a specific combination by paying an additional fee for each set of election. Each additional elected formula(e) requires the selection of a single definition for each compound variable. An exemplary election would be a composition comprising: a hydrofluoroolefin having Structural Formula (I); wherein RF is a perfluoroalkyl group having 6 carbon atoms, wherein the hydrofluoroolefin is the E isomer; and a free radical scavenger, wherein the free radical scavenger comprises hydroquinone; apparatuses for heat transfer thereof; and methods of transferring heat thereof. Additional formula(e) will be searched upon the payment of additional fees. Applicants must specify the claims that read on any additional elected inventions. Applicants must further indicate, if applicable, the claims which read on the first named invention if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched/examined.

The inventions listed in Groups I+ do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The Groups I+ formulae do not share a significant structural element requiring the selection of alternatives for the compound variable Rf and accordingly these groups lack unity a priori.

Additionally, even if Groups I+ were considered to share the technical features of a composition comprising: a hydrofluoroolefin having the core of Structural Formula (I); and a free radical scavenger; wherein the hydrofluoroolefin is present in the composition in an amount of at least 50% by weight, based on the total weight of the composition; 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 that comprises the composition; and a method of transferring heat comprising: providing a device; and transferring heat to or from the device using the composition, these shared technical features do not represent a contribution over the prior art as disclosed by US 2015/0135745 A1 to E I Du Pont De Nemours and Company and US 4,173,654 A to Scherer.

US 2015/0135745 A1 to E I Du Pont De Nemours and Company teaches a composition (Claim 49; Para. [0016]) comprising: a hydrofluoroolefin (Para. [0025], Table 1, F33iE); and a free radical scavenger (Claim 51; Para. [0123],...free radical scavengers...); wherein the hydrofluoroolefin is present in the composition in an amount of at least 50% by weight, based on the total weight of the composition (Para. [0110],... the compositions of the present invention may contain about 10 weight percent to about 80 weight percent fluoroolefin...); an apparatus for heat transfer (Para. [0016],...heat pump apparatus...) comprising: a device (Para. [0195] through [0200]); and a mechanism for transferring heat to or from the device (Para. [0195] through [0200]), the mechanism comprising a heat transfer fluid that comprises the composition (Para. [0195] through [0200]); and a method of transferring heat (Para. [0195] through [0200]) comprising: providing a device (Para. [0195] through [0200]); and transferring heat to or from the device using the composition (Para. [0195] through [0200]).

US 4,173,654 A to Scherer teaches a hydrofluoroolefin having the core of Structural Formula (I) (Col. 5, Lns. 50-55, Example 3,...see shown product...).

The inventions listed in Groups I+ therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.